Half-Sandwich Silane Complexes of Ruthenium and Iron; Synthesis, Structure, and Application to Catalysis

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Dedicated to my parents

Abstract

The present thesis describes syntheses, structural studies, and catalytic reactivity of new non-classical silane complexes of ruthenium and iron. The ruthenium complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_3)$ (**1**) (SiR_3 = $SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), $SiMe_2Ph$ (**e**)) were prepared by reactions of the new unsaturated complex $CpRu(PPr^i_3)Cl$ with silanes. According to NMR studies and X-ray analyses, the complexes **1a-c** exhibit unusual simultaneous Si···H and Si···Cl-Ru interactions. The complex $CpRu(PPr^i_3)Cl$ was also used for the preparation of the first examples of late transition metal agostic silylamido complexes $CpRu(PPr^i_3)(N(\eta^2\text{-}HSiMe_2)R)$ (**2**) (R= Ar or Bu^t), which were characterized by NMR spectroscopy. The iron complexes $CpFe(PMePr^i_2)H_2(SiR_3)$ (**3**) (SiR_3 = $SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), $SiMe_2Ph$ (**e**)) were synthesized by the reaction of the new borohydride iron complex $CpFe(PMePr^i_2)(BH_4)$ with silanes in the presence NEt_3. The complexes **3** exhibit unprecedented two simultaneous and equivalent Si···H interactions, which was confirmed by X-ray analyses and DFT calculations. A series of cationic ruthenium complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ (PR_3 = PPr^i_3 (**4**), PPh_3 (**5**); SiR'_3 = $SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), $SiMe_2Ph$ (**e**)) was obtained by substitution of one of the labile acetonitrile ligands in $[CpRu(PR_3)(CH_3CN)_2]BAF$ with silanes. Analogous complexes $[TpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ (**5**) were obtained by the reaction of $TpRu(PR_3)(CH_3CN)Cl$ with LiBAF in the presence of silanes. The complexes **4-5** were characterized by NMR spectroscopy, and the observed coupling constants *J*(Si-H) allowed us to estimate the extent of Si-H bond activation in these compounds.

The catalytic activity in hydrosilylation reactions of all of the above complexes was examined. The most promising results were achieved with the cationic ruthenium

precatalyst $[CpRu(PPr^{i}_{3})(CH_3CN)_2]^+$ (**6**). Complex **6** shows good to excellent catalytic activity in the hydrosilylation of carbonyls, dehydrogenative coupling of silanes with alcohols, amines, acids, and reduction of acid chlorides. We also discovered very selective reduction of nitriles and pyridines into the corresponding N-silyl imines and 1,4-dihydropyridines, respectively, at room temperature with the possibility of catalyst recycling. These chemoselective catalytic methods have no analogues in the literature. The reactions were proposed to proceed *via* an ionic mechanism with intermediate formation of the silane σ-complexes **4**.

Manuscripts based on this work

1. Gutsulyak, D. V.; Kuzmina, L. G.; Howard, J. A. K.; Vyboishchikov, S. F.; Nikonov, G. I., $Cp(i\text{-}Pr_2MeP)FeH_2SiR_3$: Nonclassical iron silyl dihydride. *J. Am. Chem. Soc.* **2008,** *130* (12), 3732.
2. Gutsulyak, D. V.; Churakov, A. V.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I., Steric and Electronic Effects in Half-Sandwich Ruthenium Silane σ-Complexes with Si-H and Si-Cl Interligand Interactions. *Organometallics* **2009,** *28* (9), 2655.
3. Gutsulyak, D. V.; Vyboishchikov, S. F.; Nikonov, G. I., Cationic Silane sigma-Complexes of Ruthenium with Relevance to Catalysis. *J. Am. Chem. Soc.* **2010,** *132* (17), 5950.
4. Gutsulyak, D. V.; Nikonov G.I., Chemoselective catalytic hydrosilylation of nitriles. *Angew. Chem. Int. Ed.* **2010**, *49*, 7553; *Angew. Chem.* **2010**, *122*, 7715.
5. Gutsulyak, D. V.; van der Est Art; Nikonov G.I., Facile catalytic hydrosilylation of pyridines. *Angew. Chem. Int. Ed.* **2011**, 50, 1384; *Angew. Chem.* **2011**, *123*, 1420 (featured as a VIP paper and highlighted in *Angew. Chem. Int. Ed.* **2011**, *50*, DOI:10.1002/anie.201008199).

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Finally, I am most grateful to my family for their everlasting love and support during all these years.

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Abbreviations

Å	Angstrom
acac	Acetylacetonate
ACHN	1,1'-azobis(cyclohexanecarbonitrile)
Ar	Aryl
atm	Atmosphere (1atm = 101.3 kPa)
b	Broad (in NMR)
BAF	$B(C_6F_5)_4^-$
Bu	Butyl
t-Bu	Tert-butyl
Calc.	Calculated
cat	Catalyst
Conv.	Conversion
°C	Degrees Celcius
3c-2e	Three centre – two electron
Cp	η^5-C_5H_5
Cp*	η^5-C_5Me_5
Cp'	η^5-C_5H_5 or η^5-C_5Me_5, unless specified
d	Doublet (in NMR)
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
DPPE	1,2-Bis(diphenylphosphino)ethane
Et	Ethyl
Equiv.	Equivalents
Exc.	Excess
h	Hour
Hz	Hertz
IHI	Interligand Hypervalent Interaction
J	Coupling constant (in NMR)
IR	Infrared
L_n	Ligands

M	Metal
m	Meta
m	Multiplet (in NMR)
Me	Methyl
Mes	Mesityl
MO	Molecular orbital
NMR	Nuclear magnetic resonance
o	Ortho
OTf	Triflate
p	Para
Ph	Phenyl
Pr^i	Isopropyl
Py	Pyridine
q	Quartet (in NMR)
RT	Room temperature
s	Singlet (in NMR)
sat	Satellite (in NMR)
Sept	Septet (in NMR)
t	Triplet (in NMR)
t	Tertiary
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy radical
TMDS	Tetramethyldisiloxane
TMP	2,2,6,6-tetramethylpiperidine
TBAF	Tetrabutylammonium fluoride
TOF	Turnover frequency
TON	Turnover number
THF	Tetrahydrofuran
VT	Variable temperature
UV	Ultraviolet
δ	Chemical shift, ppm (in NMR)

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I. Introduction

Catalytic hydrosilylation is one of the major methods for reduction of unsaturated organic compounds.[1] Since the discovery of Pt-catalyzed hydrosilylation of olefins by Speier et al. in 1957,[2] the hydrosilylation reactions have been extensively studied and have become a well-established method for not only reduction of organic molecules[1] but also for preparation of a wide range of valuable silicon containing compounds, which find many important applications such as silicon rubbers, paper coatings, adhesives, etc.[3]

The catalytic hydrosilylation of alkenes, alkynes, carbonyls, and imines are the most investigated reactions of this type,[1] whereas reduction of other unsaturated compounds, such as nitriles, pyridines, esters etc., has received much less attention and requires further studies for the development of practical applications.[1] Hydrosilanes can be also used for the reduction/deoxygenation/dehalogenation of many different organic substrates, such as nitro compounds,[4] phosphine oxides, sulfoxides and amine N-oxides,[5] amides,[6] alkyl and aryl halides,[7] which are also of great interest for potential synthetic applications.

In order to make further improvements in these reduction methods, significant efforts were devoted to establishing the mechanisms of hydrosilylation. In their classical paper of 1965, Chalk and Harrod[8] proposed the mechanism of hydrosilylation of alkenes mediated by Group 9 and 10 catalysts (Figure 1, left), which involves the oxidative addition of silane $HSiR_3$ to metal followed by coordination of alkene and its insertion into the M-H bond. The final product is then released *via* the reductive elimination of the Si-C bond.[8] There are several modifications of this mechanism,[1] which depend on the type of substrate and the metal complex, but many similar mechanistic pathways were also proposed for the hydrosilylation of other organic substrates, e. g. the Ojima mechanism[9] for the hydrosilylation of carbonyls (Figure 1, right). Recently, a few very different mechanisms of hydrosilylation have been reported, such as Glaser-Tilley hydrosilylation of alkenes *via* intermediate formation of silylene complexes,[10] which has been recently extended to carbonyl substrates as well,[11a,b] and Toste mechanism of hydrosilylation by rhenium dioxo complexes.[11c]

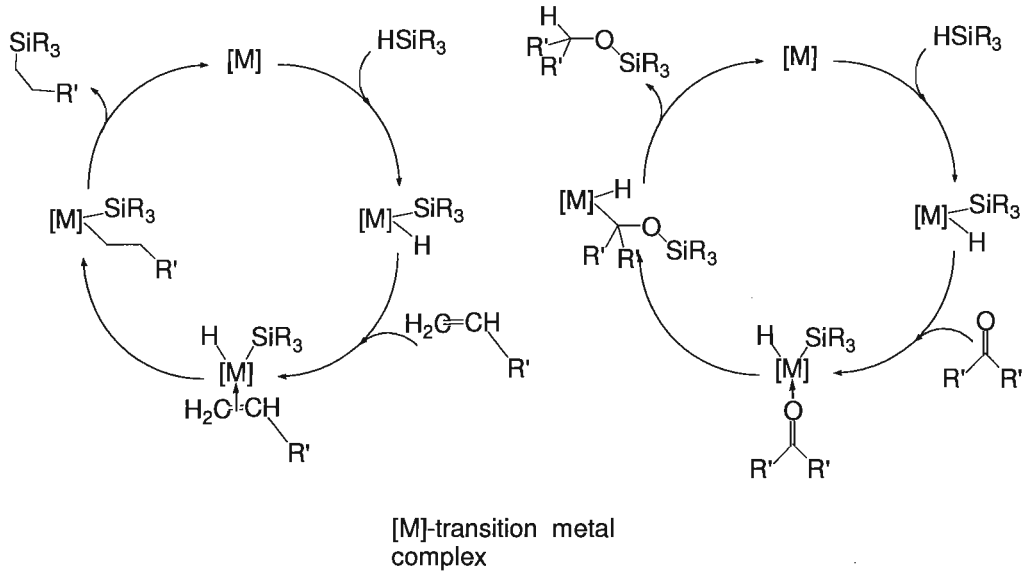
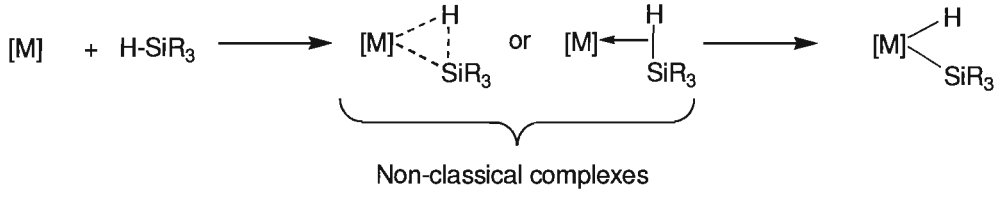


Figure 1. Chalk-Harrod mechanism for hydrosilylation of alkenes (left) and Ojima mechamism for hydrosilylation of carbonyls (right).

However, most of the proposed mechanisms involve the activation of the Si-H bond of hydrosilanes by a metal centre as one of the key steps and the formation of hydrosilyl complexes as the key intermediates. Therefore, investigation of Si-H activation also received substantial attention.[12]



Scheme 1. Oxidative addition of silane to a metal centre

The oxidative addition of silanes to a metal can be schematically depicted as a multistep process (Scheme 1), which involves the coordination of silane to a metal centre followed by oxidative addition of the Si-H bond with the formation of a hydridosilyl complex, which does not exhibit any significant direct Si-H interaction.[12b] However, many transition metal complexes are not capable of the full activation of the Si-H bond and exist in intermediate ("frozen") state of Si-H oxidative addition, so called non-classical silane complexes.[12b] The presence of a residual Si-H

bond can significantly alter the properties of these compounds, which could also influence the catalytic activity.

Nikonov et al. reported several new classes of non-classical silane complexes with unusual structural features.[12c, 13] Thus, the complexes with Interligand Hypervalent Interactions (IHI) exhibit significant interaction between the metal bound hydrides and the Si-Cl bond of the silyl ligands (Figure 2, left).[13a] Also, the first examples of non-classical complexes with unusual simultaneous Si···Cl and Si···H interactions have been discovered (Figure 2, right).[13b]

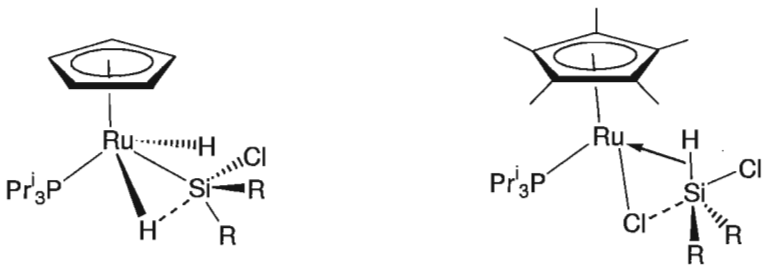


Figure 2. Examples of ruthenium complexes with IHI (left) and simultaneous Si···Cl and Si···H interactions (right)

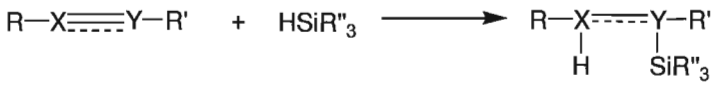
As a continuation of Nikonov's research in this field, the present study is partially devoted to investigation of similar non-classical silane complexes of ruthenium $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$ and iron $CpFe(PR_3)H_2(SiR'_3)$ focusing on the extent of Si-H bond activation in these compounds as well as their application to catalytic hydrosilylation reactions.

A significant part of the present work is devoted to investigation of cationic silane complexes, which are barely studied due to their high reactivity and instability. Thus, we investigated the influence of ancillary ligands on the extent of Si-H activation in the ruthenium silane σ-complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$. Also, we examined the catalytic activity of the cationic ruthenium complexes $[CpRu(PR_3)(CH_3CN)_2]^+$ in a variety of reactions with hydrosilanes, such as hydrosilylation of carbonyls, nitriles, pyridines, dehydrogenative coupling reactions with alcohols, acids, amines, and reduction of acyl chlorides.

II. Historical

II.1 *Reduction of organic substrates with silanes*

Reduction is one of most fundamental transformations in organic chemistry. There is a wide range of different reducing procedures available for almost all possible unsaturated organic substrates.[14] Depending on the substrate, different reductants can be used to perform this transformation. Hydrosilanes are universal reducing agents, which are commonly used for reduction of a large number of different organic substrates. There are several features that make hydrosilanes so attractive to synthetic chemists. First of all, most of commonly used hydrosilanes are very stable compounds and can be safely handled and stored under air without any additional precautious. Second, use of hydrosilanes usually does not generate a large amount of waste, which is often produced in the reductions with other reducing agents, such as alumohydrides. Third, reduction with hydrosilanes usually does not require special equipment, as opposed to high pressure hydrogenation reactions, because most of the silanes are liquids at room temperature and can be used under atmospheric pressure.



X≡Y : C=C, C=O, C=N, N=N, C≡C, C≡N

Scheme 2. Hydrosilylation of unsaturated organic substrates

In most cases, reduction with hydrosilanes proceeds *via* addition of the Si-H bond across the multiple bond of unsaturated organic substrate, which is commonly referred to as hydrosilylation (hydrosilation) reaction (Scheme 2).[1] One of the advantages of this method is that reduction by hydrosilylation leads to silylated organic products (alcohols, amines, etc.), which are widely used in organic synthesis due to the valuable properties of the protecting silyl group.[1] Most of hydrosilylation reactions are exothermic. However, due to the high activation barrier, these reactions usually require activation by high temperature, UV-irradiation or the presence of a catalyst.[1] Among all these conditions, the transition metal catalyzed hydrosilylation is

the most convenient and most widely used method. The requirement of a catalyst might seem as a drawback of hydrosilylation reactions. On the other hand, the proper choice of a transition metal complex from a vast library of readily available catalysts can offer a very high level of selectivity towards functional groups, which becomes a crucial factor for the preparation of complex organic substrates.

Catalytic hydrosilylation can be used for reduction of a large number of different unsaturated organic compounds, containing C=O, C=N, C=C, C≡C, C≡N, N=N etc. bonds.[1] It has become a universal method of reduction not only in the laboratory but also on the industrial scale with tons of applications.[15] Due to the high affinity of silicon to oxygen and halogen, hydrosilanes can be also used for deoxygenation or dehalogenation with the formation of siloxanes or halosilanes as by-products of these reactions.[7, 16]

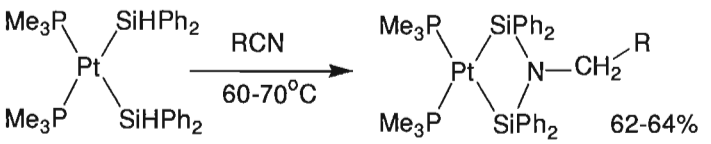
Overall, hydrosilanes have proven to be very convenient and effective reducing agents for the reduction of different common organic compounds. Notably, most of the work in this field was devoted to hydrosilylation of alkenes, alkynes, carbonyls, and imines, which has been extensively reviewed in literature.[1, 17] On the other hand, reduction of other organic substrates with silanes received much less attention. Therefore, the following chapters of this historical will be devoted to the reduction of challenging and/or less common substrates.

II.1.1 Reactions of nitriles with hydrosilanes

Nitriles are very common organic compounds that can be easily prepared by a number of standard procedures, such as nucleophilic substitution of alkyl halides with cyanides, dehydration of amides, hydrocyanation of alkenes and alkynes.[18] As a result, the use of nitriles as starting materials has achieved considerable attention in organic synthesis. Reduction of nitriles allows for the preparation of amines and aldimines, which are very abundant classes of organic compounds with endless applications in almost all fields of chemistry. One of the most common methods of reduction is the hydrogenation of nitriles into the corresponding amines in the presence of transition metal catalysts.[19] In contrast, there are only few examples of the reduction of nitriles with silanes. One of the possible products of this reaction, silylimines $R_3SiN{=}CHR'$, are valuable building blocks in both organic and medicinal chemistry.[20] Silylimines are usually prepared in several steps, starting from the corresponding aldehydes or amines. These compounds are also often prepared by reductions of nitriles with DIBALH, followed by the reaction with chlorosilanes.[20] However, the hydrosilylation of nitriles would be the most direct and 100% atom efficient method for the preparation silylimines. Unfortunately, the cyano group is very inert and can be usually hydrosilylated only in stoichiometric reactions with transition metal complexes or catalytically under harsh conditions.

Stoichiometric reactions with silanes

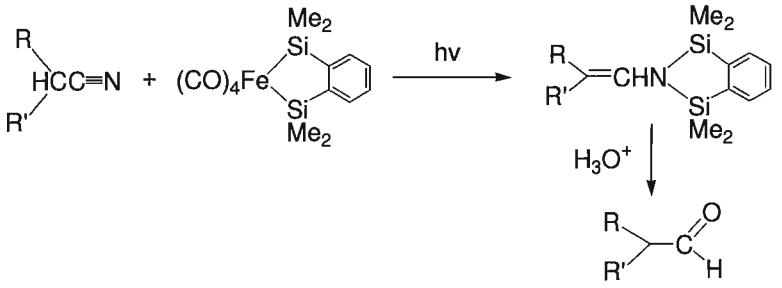
Stoichiometric insertion of nitriles into Si-H bonds at 60-70°C was reported for the (bis)silyl platinum complex $Pt(PMe_3)_2(SiHPh_2)_2$ (Scheme 3).[21] The reactions proceed with moderate yields (62-64%) but with high selectivity, e.g. no insertion of nitriles into the Pt-Si bond was observed.



Scheme 3. Stoichiometric reduction of nitriles with (bis)silyl platinum complex

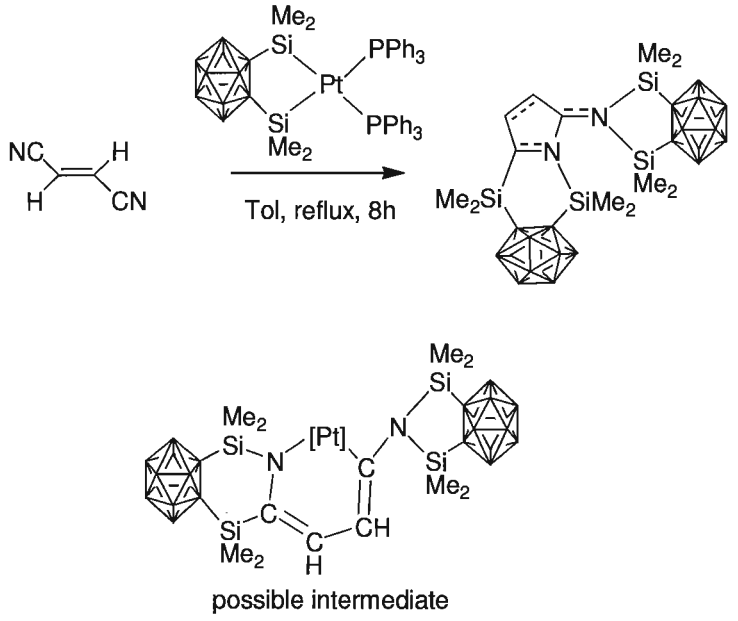
(Bis)silyl enamines can be prepared in good yields by the reaction of nitriles with (bis)silyl iron complex $Fe(CO)_4((SiMe_2)_2(C_6H_4))$ under UV irradiation (Scheme

4).[22] The resulting enamines are surprisingly inert towards $LiAlH_4$ as well as towards Grignard and lithium reagents, but can be hydrolysed into corresponding aldehydes under acidic conditions (Scheme 4).



Scheme 4. The reaction of nitriles with (bis)silyl iron carbonyl complex

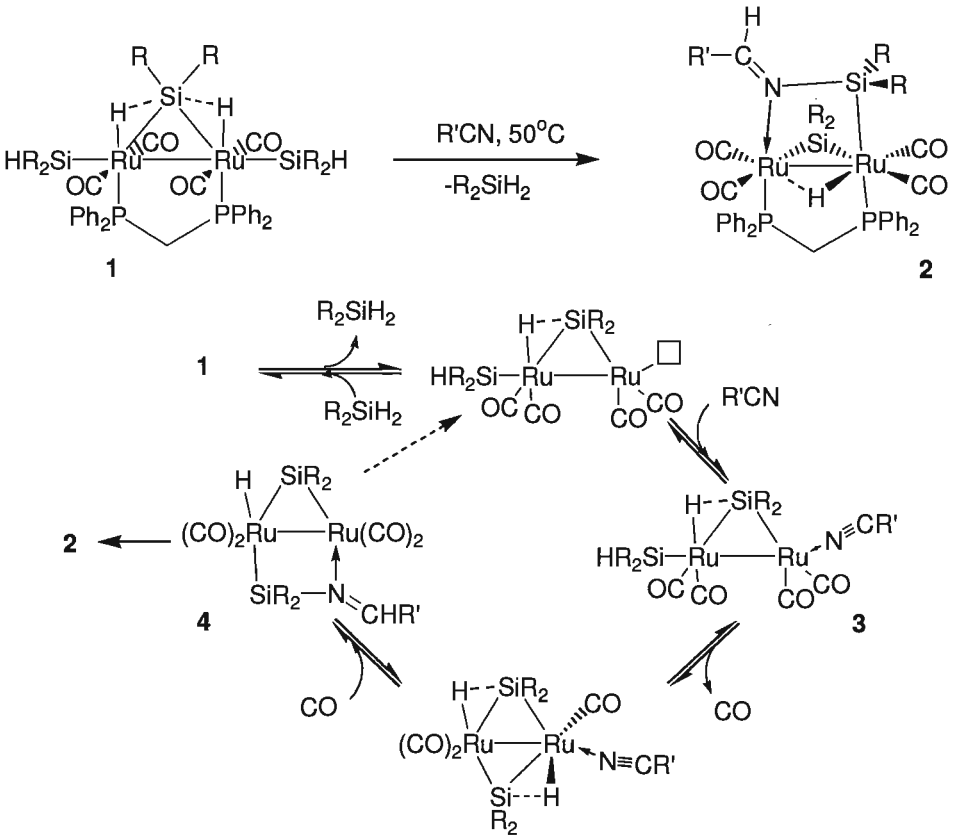
A very unusual product was observed by Ko et al.[23] in the reaction of (bis)silyl platinum complex $Pt(PPh_3)_2((SiMe_2)_2R)$ (R – carborane) with fumaronitrile after 8 h in refluxing toluene (Scheme 5). The suggested mechanism of this reaction involves a multistep silylation of both ends of the fumaronitrile with formation of cyclic platinum intermediate depicted in Scheme 5, which can be converted into the final product after reductive elimination of the C-N bond.



Scheme 5. The reaction of (bis)silyl carborane platinum complex with fumaronitrile

Several stoichiometric monohydrosilylation reactions of nitriles with a binuclear ruthenium complex were reported by Kira et al..[24] These reactions resulted

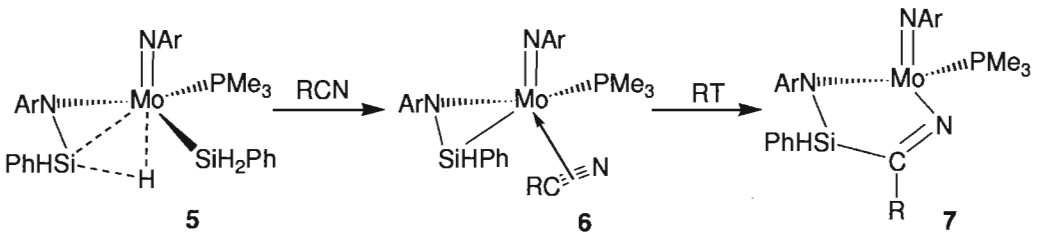
in preparation of new μ-iminosilyl-bridged diruthenium complexes (Scheme 6). The proposed mechanism includes the reductive elimination of R_2SiH_2 from the starting complex **1**, followed by coordination of nitrile to give the intermediate **3** (Scheme 6). Release of CO from **3** allows for the Si-H bond activation of the silyl group. The activated Si-H bond could then insert into the C≡N bond of the coordinated nitrile, affording the intermediate **4**, the precursor of complex **2**. Unfortunately, the very strong interaction of the iminosilyl ligand with ruthenium in **4** prevents the catalytic hydrosilylation of nitriles even at 80°C. At the same time, imines can be successfully hydrosilylated catalytically at 50°C in the presence of 5% mol of **1**.[24]



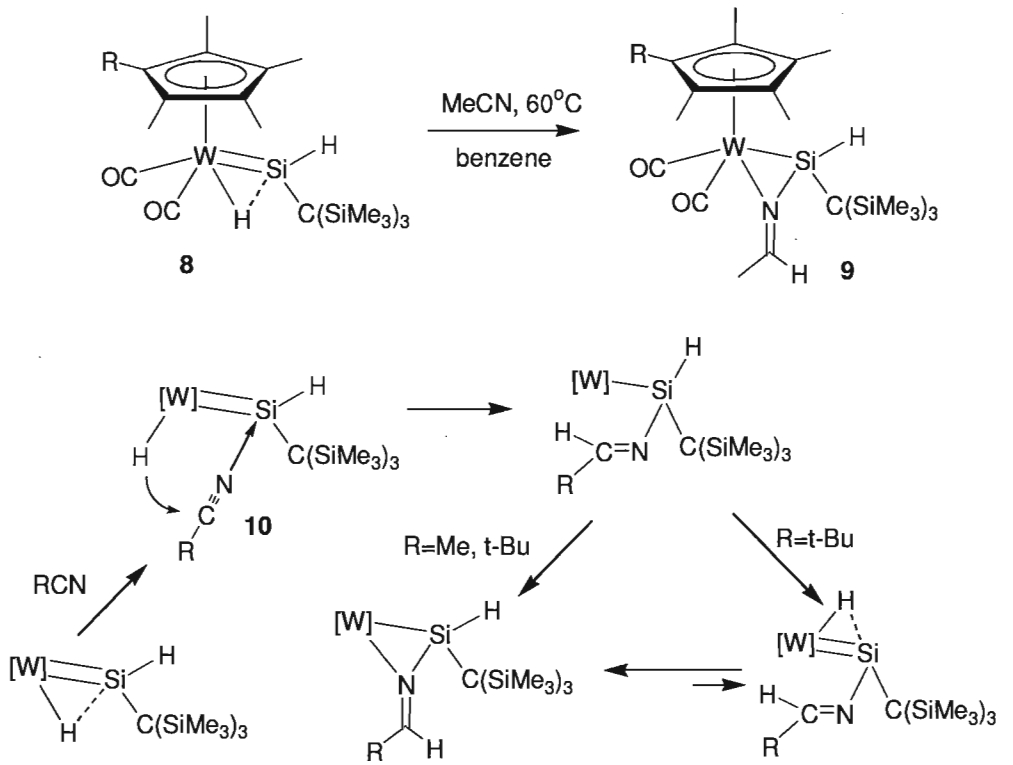
Scheme 6. The reactions of binuclear ruthenium complex with nitriles and the proposed mechanism

Stoichiometric addition of nitriles to the molybdenum silylamido complex $(ArN)Mo(SiH_2Ph)(\eta^3\text{-}NAr\text{-}SiHPh\text{-}H)(PMe_3)$ was studied by Nikonov et al. (Scheme 7).[25] The reaction gives initially the η^2-NCR adduct with molybdenum, which rearranges into the final product *via* insertion of nitrile into the Mo-Si bond (Scheme

7). Interestingly, the final molybdenum complex **7** contains silicon attached to the iminium carbon instead of nitrogen, which is very uncommon for this type of reaction.



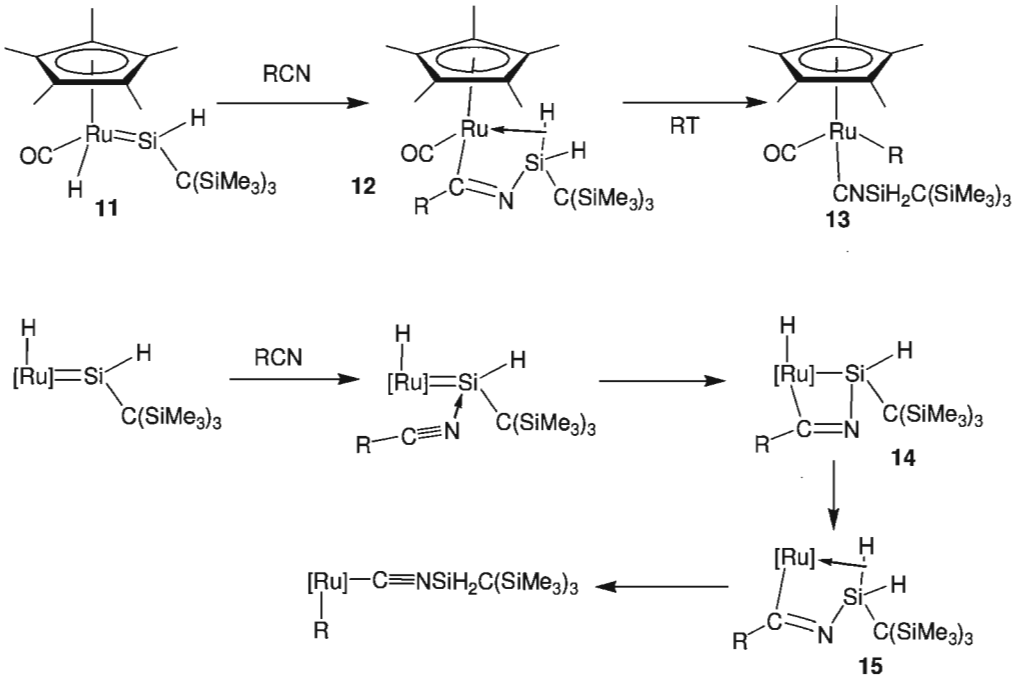
Scheme 7. The reactions of silylamido molybdenum complex with nitriles



Scheme 8. The reactions of silylene tungsten complexes with nitriles and the proposed mechanism

Another example of stoichiometric monohydrosilylation of nitriles was reported for the tungsten silylene complexes $W(CO)_2(H)(=SiH(CSiMe_3)_3)(Cp')$ by Tobita et al. (Scheme 8).[26] Treatment of **8** with acetonitrile at 60°C in benzene results in insertion of the Si-H bond into the C≡N bond of the nitrile and formation of the first example of a mononuclear iminosilyl complex **9** (Scheme 8). The X-ray structure of complex **9** revealed a W-Si-N three-membered ring structure. The possible

mechanism of the reaction starts with coordination of the nitrile to the electrophilic Si-centre of the silylene ligand with the formation of intermediate **10**, followed by migration of the hydride from metal to the coordinated nitrile, which gives the final product of the reaction (Scheme 8). Interestingly, the reaction of **8** with bulky t-BuCN resulted in the formation of an equilibrium mixture of iminosilyl and iminosilylene complexes.

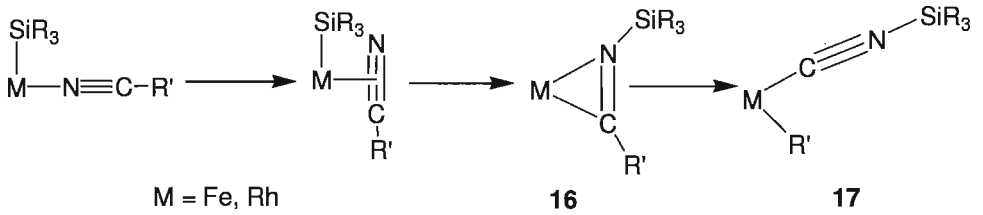


Scheme 9. The reactions of ruthenium silylene complexes with nitriles and the proposed mechanism

Later, Tobita et al.[27] reported analogous reactions with the ruthenium silylene complex Ru(H)(CO)(=SiH(C(SiMe$_3$)$_3$)(Cp*) (Scheme 9). Surprisingly, the final products of these reactions were cyanosilyl complexes Ru(R)(CO)(NCSiH$_2$(C(SiMe$_3$)$_3$)(Cp*), which were obtained as a result of the C-C bond cleavage in the nitrile molecule (Scheme 9). Presumably, this reaction proceeds through the formation of iminoacyl complexes **12**, which were isolated and characterized by NMR and X-ray crystal structure analysis. The reasons for such a big difference in reactivity in comparison with analogous tungsten complexes remain unclear. One of the suggested mechanisms for this reaction includes coordination of nitrile to the silylene ligand, followed by [2+2] cycloaddition with the formation of the ruthenium species **14** (Scheme 9). The reductive elimination of the Si-H bond in

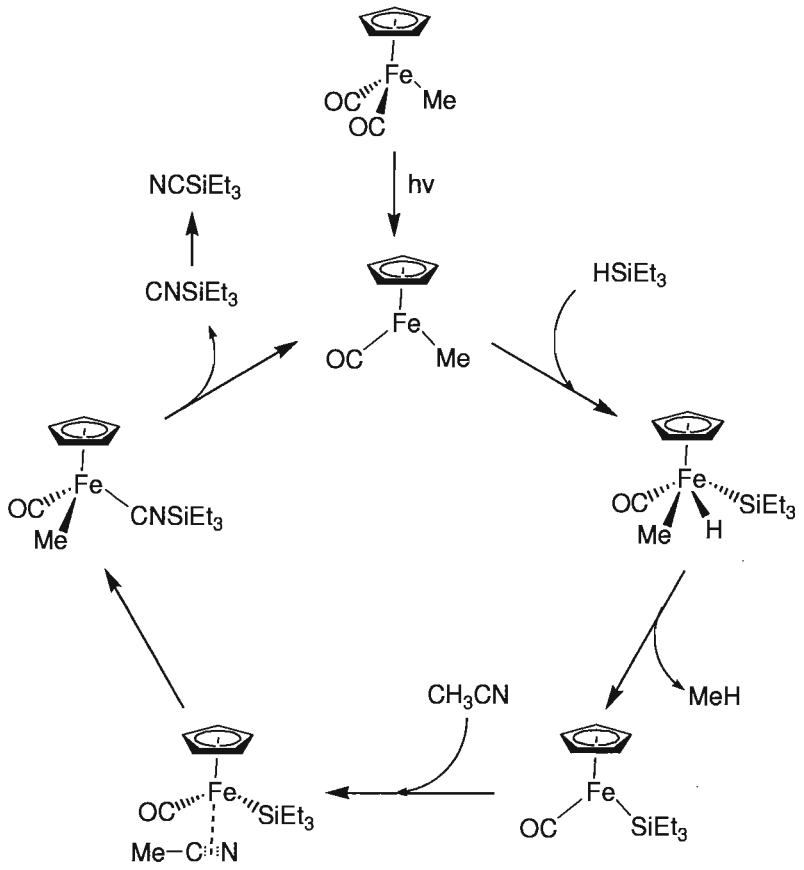
14 could then give complex **15**, which converts slowly into the final product *via* the intramolecular C-C bond oxidative addition.[27]

Analogous C-C bond activation in nitriles by half-sandwich rhodium complexes $[RhCp^*(PMe_3)(CH_2Cl_2)(SiPh_3)]BAr'_4$ and iron compounds $Cp(CO)_2FeSiR_3$ were also reported by Brookhart et al.[28] and Nakazawa et al. (Scheme 10).[29] In both systems the reactions proceed through the formation of η^2-iminoacyl compounds **16**, which can be then converted into silylisocyanide complexes **17** (Scheme 10). The intermediate iminoacyl rhodium complex $[Cp^*(PMe_3)Rh(\eta^2\text{-}C(4\text{-}(OMe)C_6H_4)=N(SiPh_3))]BAr'_4$ was isolated and characterized by NMR spectroscopy and X-Ray analysis.[28a]



Scheme 10. Cleavage of the C-C bond in nitriles by silyl rhodium and iron complexes

The cleavage of the C-C bond in nitriles can be also performed catalytically in the presence of iron complex $Cp(CO)_2FeSiR_3$.[29a] Both aromatic and aliphatic nitriles can be used in the reaction, which requires 5% mol of the iron catalyst and photolysis. The initial products are thermodynamically unstable silylisocyanide compounds R_3SiNC, which convert easily into more stable silylcyanide R_3SiCN. The proposed catalytic cycle for the reaction with acetonitrile is illustrated in Scheme 11. The reaction starts with dissociation of CO, followed by coordination of silane and release of methane. Subsequent coordination of nitrile, N-Si coupling, C-C bond activation and release of silylisocyanide regenerates the alkyl complex. The catalytic reaction was found to proceed faster in the presence of excess acetonitrile due to a by-process of dehydrogenative coupling of silanes.

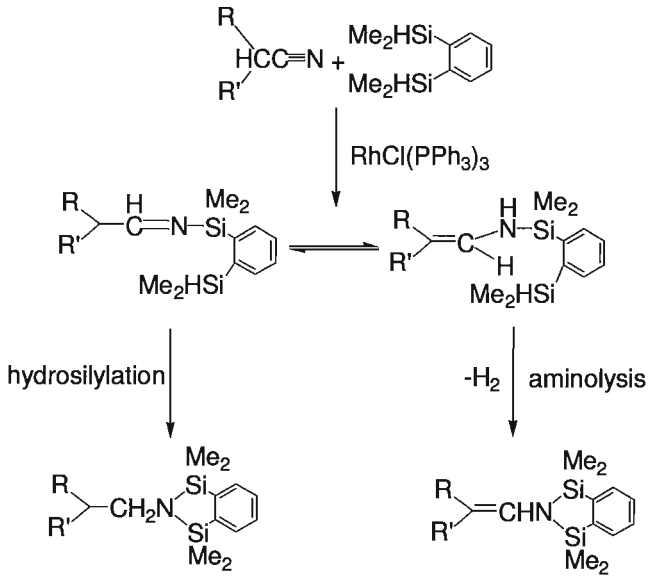


Scheme 11. The proposed catalytic cycle for the iron-catalyzed aryl-CN bond cleavage reaction

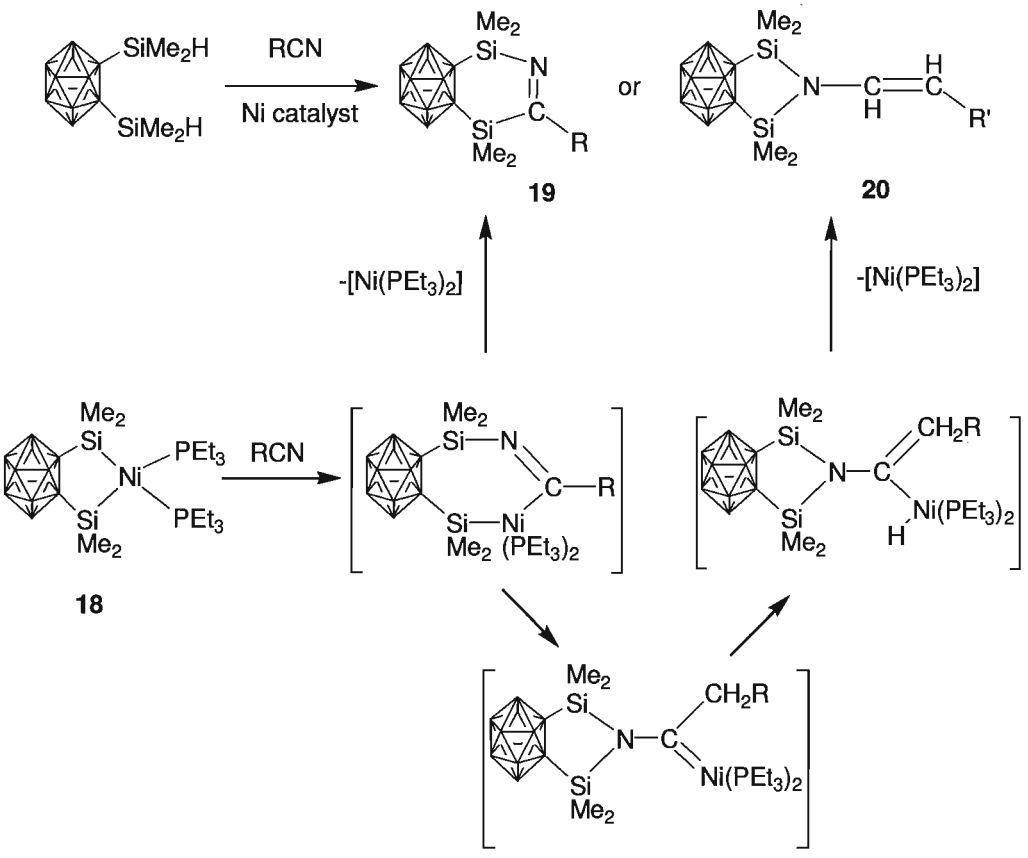
Catalytic reactions with silanes

Most of the procedures for catalytic hydrosilylation of nitriles require harsh reaction conditions and usually result in the formation of (bis)silylated amines or enamines. In 1970, Chalk reported hydrosilylation of $CH_2=C(CH_3)CN$ in the presence cobalt catalyst, which gave (bis)silylated enamine $(CH_3)_2C=CHN(SiMe_2Cl)_2$ in 20% yield.[30] Later, in 1982, Corriu et al. described catalytic hydrosilylation of nitriles with *ortho*-bis(dimethylsilyl)benzene in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$ at 110°C (Scheme 12).[30] The silylated enamines can be obtained in moderate yields in a mixture with (bis)silylamines by this method. The formation of a mixture can be explained by the presence of an equilibrium between the monosilylated imine, which is initially formed in the reaction, and the corresponding isomeric enamine (Scheme 12). Therefore, hydrosilylation of silylimine results in the formation of (bis)silylated

amine. On the other hand, dehydrodenative aminolysis of enamine gives the corresponding silylated enamine.[30]



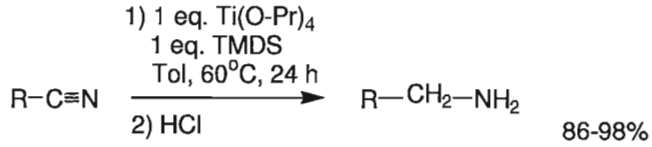
Scheme 12. The catalytic hydrosilylation of nitriles in the presence of Wilkinson's catalyst



Scheme 13. Catalytic silylation of nitriles in the presence of nickel catalyst

Another example of utilization of 1,2-(bis)silanes for a closely related process of silylation of nitriles was reported by Ko et al. (Scheme 13).[31] Cyclic (bis)silyl nickel complex **18** was found to catalyze the silylation of nitriles with 1,2-bis(dimethylsilyl)carborane in refluxing toluene. The usual products of this reaction are silylated cyclic imines **19** or silylated enamines **20** depending on the presence of α-hydrogen in starting nitriles. A possible mechanism involves insertion of nitrile into Ni-Si bond followed by reductive elimination with the formation of cyclic imines or by migration of silicon to nitrogen with subsequent izomerization of the carbene intermediate and reductive elimination of silylated enamine (Scheme 13).[31]

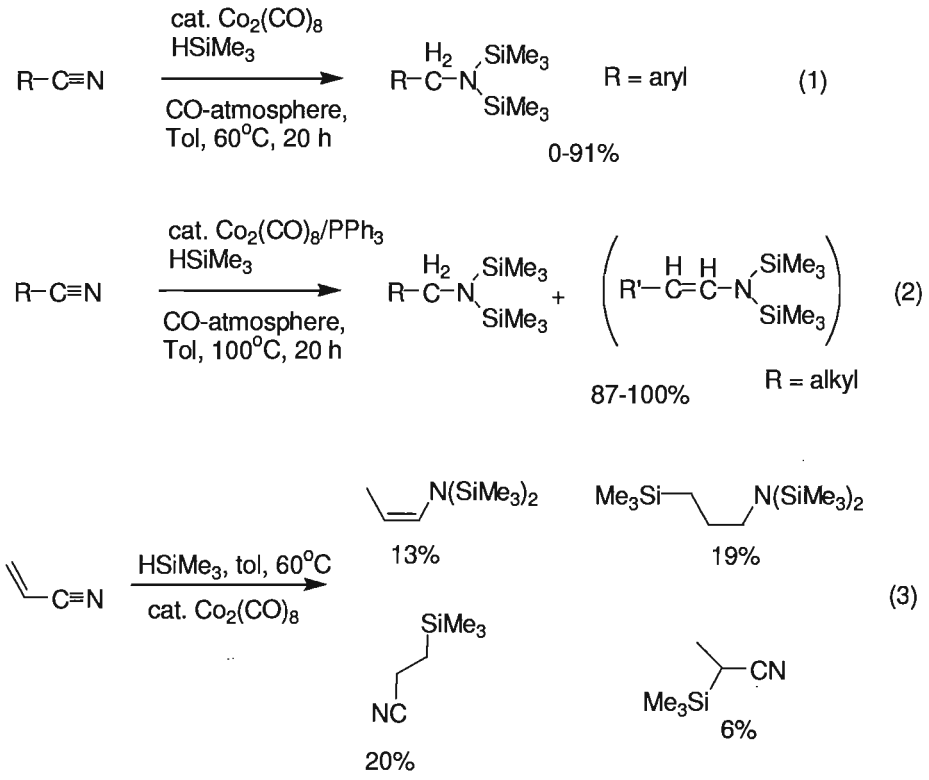
A convenient procedure for the reduction of nitriles into corresponding amines was reported by Lemaire et al.[32] Both aromatic and aliphatic nitriles can be converted directly into amines in the presence of stoichiometric amounts of $Ti(OPr^i)_4$ and tetramethyldisiloxane at 60°C in toluene (Scheme 14). Importantly, α,β-unsatuturated nitriles can be also used in this reaction with a very selective formation of amines in high yield.[32]



Scheme 14. Hydrosilylation of nitriles in the presence of stoichiometric amount of $Ti(OPr^i)_4$

Murai et al. reported detailed investigation of hydrosilylation of both aromatic and aliphatic nitriles in the presence of $Co_2(CO)_8$ (Scheme 15).[33] In this case hydrosilylation of aromatic nitriles can be performed at 60°C under the atmosphere of CO with selective formation of (bis)silylated amines in moderate yields (Scheme 15, eq. 1). Importantly, the reaction tolerates several functional groups, such as dimethylamino, chloro and methoxy substituents in the aromatic ring. The best results can be achieved with $HSiMe_3$, and utilization of other silanes usually gave complex mixtures or very small conversion of starting nitriles. Hydrosilylation of aliphatic nitriles requires more severe conditions and proceeds at higher temperature (100°C) in the presence of free phosphine and CO for stabilization of the catalyst (Scheme 15, eq. 2). Hydrosilylation of α,β-unsatuturated nitriles in toluene at 60°C in the presence of

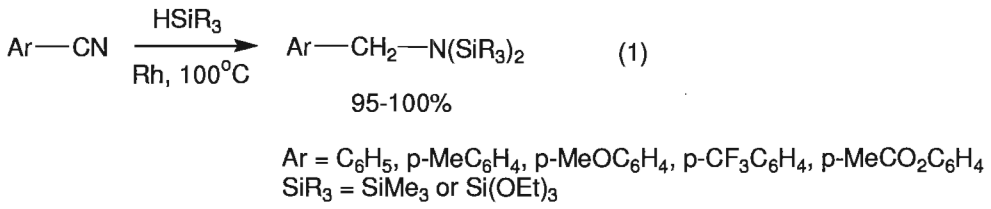
$Co_2(CO)_8$ results in the formation of a mixture of products, which usually contains silylated enamines as one of the major components (Scheme 15, eq. 3).[33]

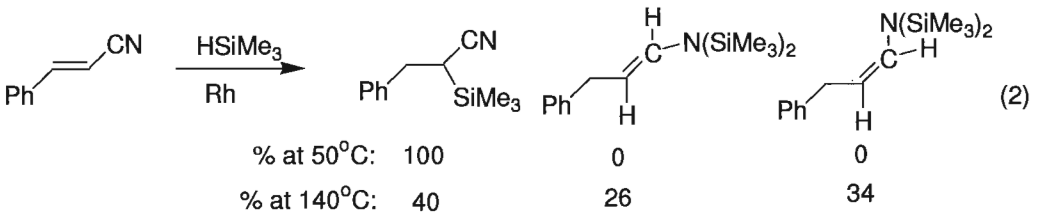


Scheme 15. Catalytic hydrosilylation of nitriles in the presence of $Co_2(CO)_8$

Heterogeneously catalyzed hydrosilylation of nitriles by rhodium powder at 100°C was reported by Pertici et al. (Scheme 16).[34] Importantly, the reactions in this case can be performed without solvent, which could be considered as a more environmentally friendly method, and at the same time it simplifies the isolation of the products. Moreover, aromatic solvents, such as mesitylene or toluene, usually significantly diminish the yield of the reaction due to competitive coordination to the metal centre. This method allows for hydrosilylation of aromatic nitriles containing different functional groups, such as -OMe, $-CF_3$, -COOMe, with high yields under solvent-free conditions (Scheme 15, eq. 1). Interestingly, the rate of the reaction increases in the presence of electron-withdrawing groups in nitriles, such as CF_3 or COOMe groups, which could activate the CN triple bond and facilitate the silane addition. In contrast to the previously described Co-catalyzed hydrosilylation, the reaction in the presence of Rh powder can be also performed with different silanes, such as $HSiMe_3$ or $HSi(OEt)_3$. Hydrosilylation of α,β-unsatuturated nitriles by this

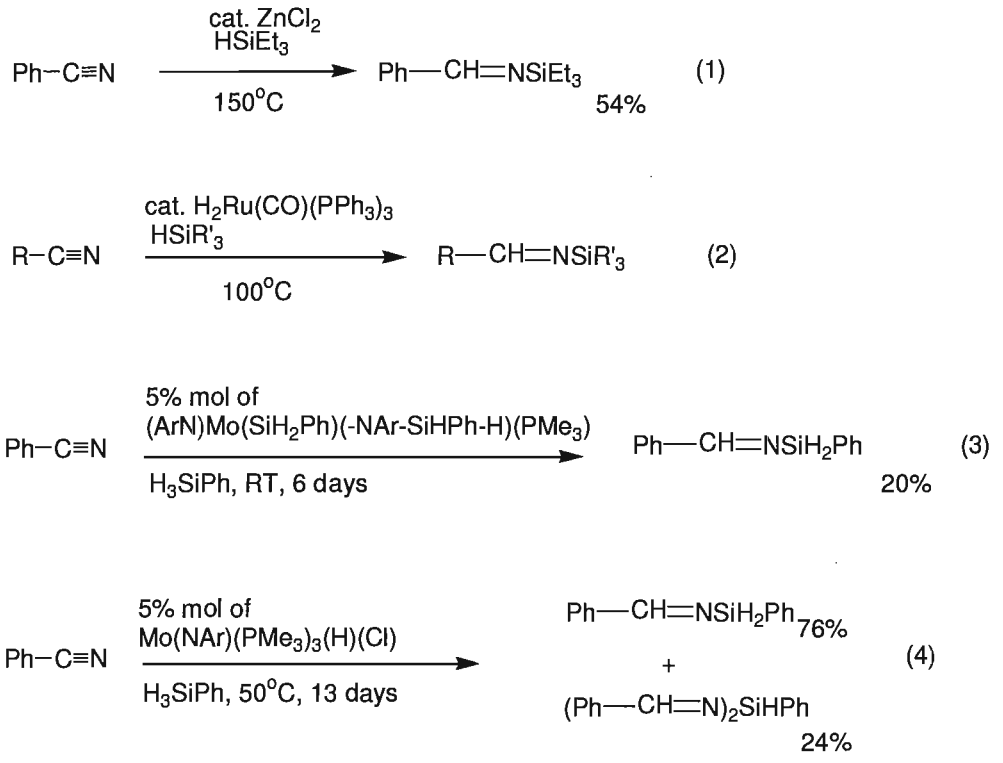
method is highly dependent on temperature. Selective addition of silane across the C=C bond was observed at 50°C, but increasing the temperature to 140°C leads to predominant formation of a mixture of *cis* and *trans* silylated enamines (Scheme 15, eq. 2).[34]





Scheme 16. Catalytic hydrosilylation of nitriles in the presence of Rh-powder

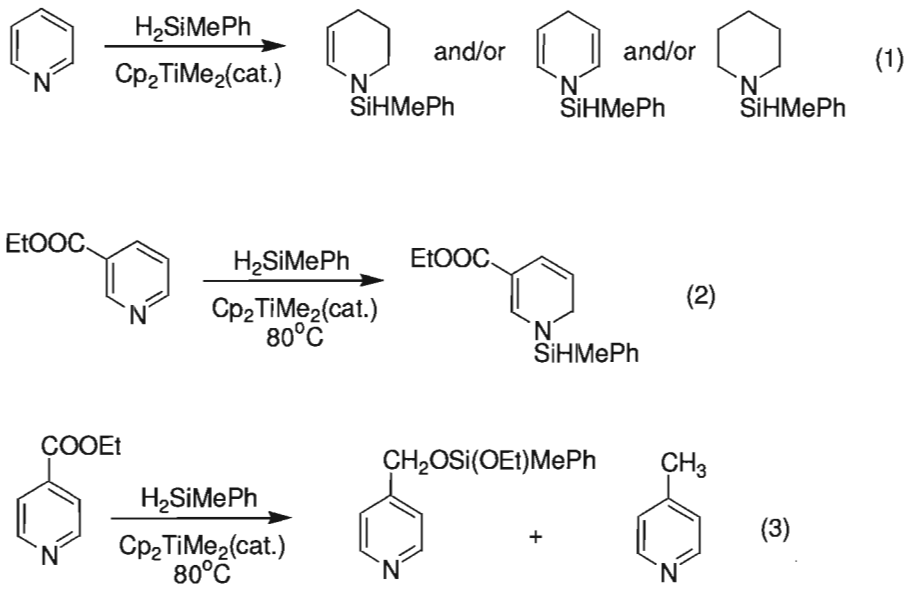
Only few catalytic monohydrosilylations of nitriles have been published since the original report by Calas et al. in 1961 on the $ZnCl_2$–catalyzed mono-addition of $HSiEt_3$ to PhCN at 150°C with only 54% yield (Scheme 17, eq. 1).[35] A more general approach to the catalytic monohydrosilylation of nitriles was reported by Fuchigama and Igarashi in the patent literature.[36] According to the scarce patent information, both aromatic and aliphatic nitriles can be hydrosilylated in the presence of $H_2Ru(CO)(PPh_3)_3$ at 100°C (Scheme 17, eq. 2). Catalytic mono-addition of H_3SiPh to PhCN catalyzed by molybdenum imido complexes has been recently reported by Nikonov et al., but the reactions were very slow or gave poor yields (Scheme 17, eq. 3, 4).[25, 37]



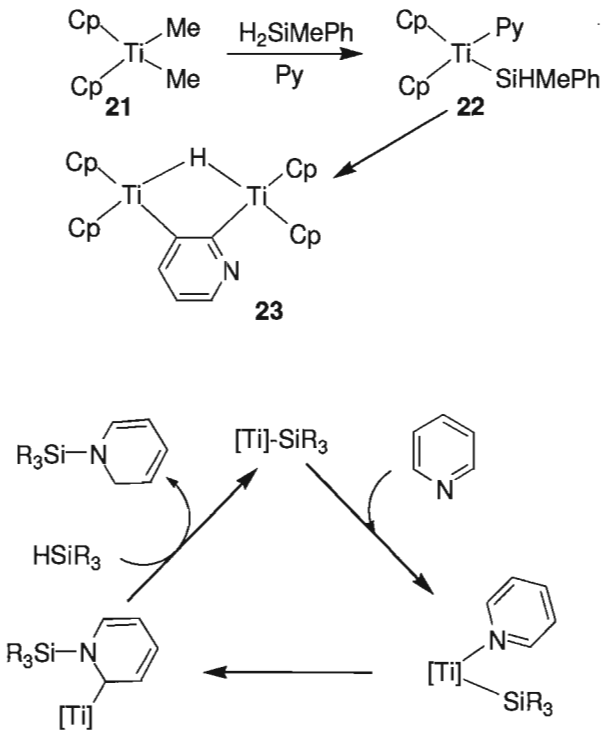
Scheme 17. Catalytic (mono)hydrosilylation of nitriles

II.1.2 Hydrosilylation of pyridines

Catalytic and stoichiometric additions of silanes to pyridines are very rare. However, the possible products of these reactions, dihydropyridines, are very abundant and widely used class of compounds with many applications in organic and medicinal chemistry.[38] The catalytic selective addition of silanes to pyridines represents a challenging task of selective reduction of a stable aromatic compound. The feasibility of this process was for the first time demonstrated by Cook and Lyons in 1966.[39] They found that a heterogeneous Pd-catalyzed reaction of pyridine with trimethylsilane $HSiMe_3$ gave a complex mixture of partially reduced hydrosilylated pyridines. Since then, only a few examples of hydrosilylation of pyridines have been reported. The first catalytic homogeneous reaction was reported by Harrod et al. (Scheme 18).[40] The hydrosilylation of pyridines in this case was performed with $H_2SiMePh$ or H_3SiPh in the presence of titanium catalyst $CpCp^*TiMe_2$. The reactions usually result in the formation of N-silylated tetrahydropyridines due to concomitant hydrogenation of the initially produced silylated dihydropyridines (Scheme 18, eq. 1). However, dihydropyridines or piperidines could be also prepared as the major products under certain reaction conditions. The scope of substrates for this method is mostly limited to lutidines and picolines, but interesting chemoselectivity was observed in the hydrosilylation of nicotinic and isonicotinic esters. The position of the ester group plays a crucial role, and partial reduction of the ring was only observed in the case of nicotinic ester (Scheme 18, eq. 2). In contrast, the reaction with a pyridine containing the ester group in the 4-position resulted in exclusive hydrosilylation of the ester group (Scheme 18, eq. 3).[40]



Scheme 18. Catalytic hydrosilylation of pyridine in the presence of Cp_2TiMe_2

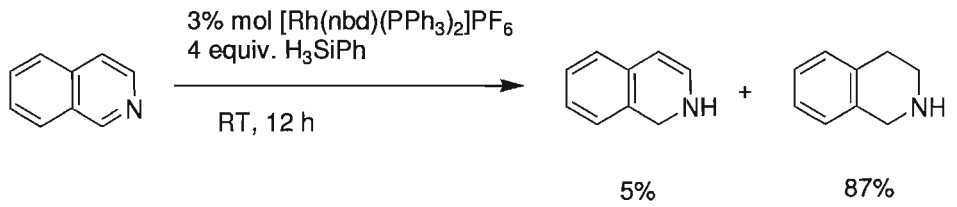


Scheme 19. The proposed mechanism of hydrosilylation in the presence of Cp_2TiMe_2

The reaction of Cp_2TiMe_2 with $H_2SiMePh$ in the presence of pyridine results in the formation of the titanium complex $Cp_2Ti(SiMePh)Py$, which then slowly

converts into the hydride bridged bimetallic titanium complex **23** (Scheme 19, top).[40] Formation of the titanium silyl complex **22** at the early stage of the reaction supports the proposed catalytic cycle. The latter involves the insertion of pyridine into the Ti-Si bond followed by the reaction with silane, which regenerates the catalyst and gives the hydrosilylated product (Scheme 19, bottom). The (mono)hydrosilylated 1,2-dihydropyridine could then isomerize into the 1,4-dihydropyridine or could be hydrogenated into the tetrahydropyridine or piperidine. Another possible catalytic cycle starts with the insertion of pyridine into the Ti-H bond of the possible intermediate [$Cp_2Ti(H)$], followed by the reaction with silane to give the hydrosilylated pyridine and regenerated titanium hydride species [Cp_2TiH].[40]

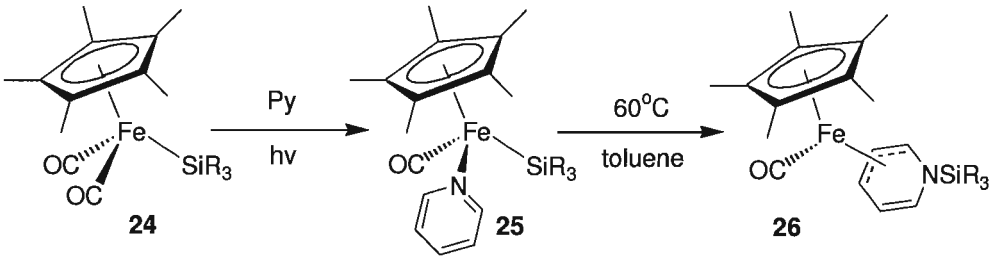
Crabtree et al. discovered the reduction of N-heterocyclic compounds by phenylsilane H_3SiPh mediated by [$Rh(nbd)(PPh_3)_2$]PF_6.[41] This reaction could result in dihydro or tetrahydro derivatives of the starting N-heterocyclic compounds depending on the nature of the substrates and the reaction conditions (Scheme 20). Interestingly, a specially designed set of experiments revealed, that the active reducing agent of the reaction was not $PhSiH_3$, but SiH_4, which evolves in the Rh-catalyzed redistribution reaction of $PhSiH_3$.[41]



Scheme 20. Reduction of isoquinoline with H_3SiPh in the presence of [$Rh(nbd)(PPh_3)_2$]PF_6

Stoichiometric silylation of pyridines is also of great interest, because it contributes to better understanding of this process and stimulates the development of new catalysts. The insertion of pyridine into the Fe-Si bond was reported by Tobita et. al.[42] The reaction of the iron silyl complex $Fe(CO)_2(SiMe_2NPh_2)Cp^*$ with pyridine under ultraviolet irradiation initially results in substitution of one of the CO ligands with pyridine (Scheme 21). Intramolecular insertion of pyridine into the Fe-Si bond of complex **25** happens at 60°C with the formation of complex **26**, which was characterized by NMR and X-ray analysis (Scheme 21). The structural parameters of **26** strongly suggested the η^3-allylic fashion of coordination of the N-silylated pyridine to the iron centre. Interestingly, analogous silyl pyridine ruthenium complex

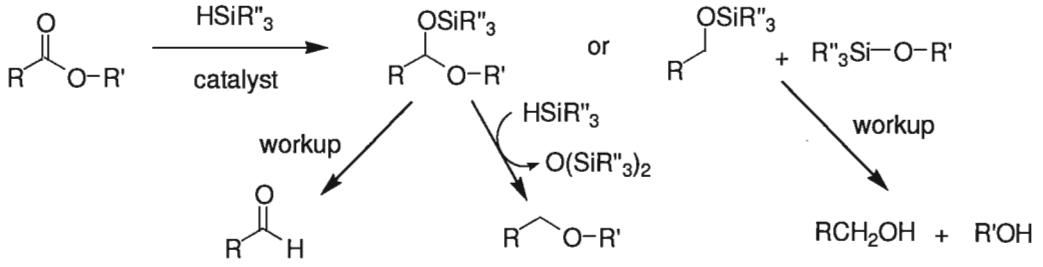
$Ru(CO)(Py)(SiMe_2NPh_2)Cp^*$ did not undergo insertion of pyridine into Ru-Si bond even at 80°C.[42b]



Scheme 21. The reaction of iron silyl complex $Fe(CO)_2(SiMe_2NPh_2)Cp^*$ with pyridine

II.1.3 Hydrosilylation of esters

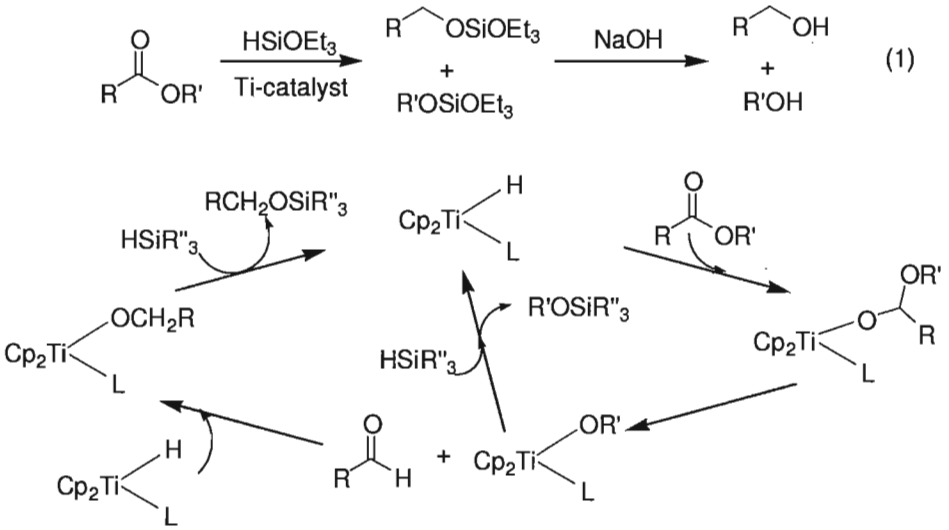
Esters are generally very robust substrates for reduction. Therefore, standard organic procedures for reduction of these compounds are based on the use of strong reducing agents, such as aluminium hydrides, which are air sensitive and pyrophoric. Thus, catalytic reduction of esters with air stable and easy-to-handle silanes could be a valuable alternative to the existing methods. However, esters are very challenging substrates and remain inert under many standard hydrosilylation conditions.[9, 43] In general, hydrosilylation of esters could be a very useful tool for the synthesis of different common organic compounds, such as alcohols, ethers, aldehydes, lactols and cyclic ethers (Scheme 22). Using different reaction conditions and catalytic systems, each of these compounds can be prepared selectively in high yield.



Scheme 22. Reduction of esters with hydrosilanes

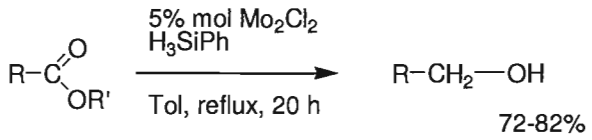
First reactions between silanes and esters were performed in the presence of metal halides, such as ScF, KF, $ZnCl_2$, $NiCl_2$ etc.,[44] to give the corresponding alcohols in relatively high yields, but harsh reaction conditions and/or stoichiometric amounts of the metal halides are required for these methods. Buchwald et. al. developed a very convenient and more general procedure for the reduction of esters under mild conditions using titanium catalyst.[45] It is believed that an active titanium hydride species can be generated priory to catalysis by the reaction of Cp_2TiCl_2 with n-BuLi. Most of the hydrosilylation reactions then proceed at ambient temperature within several hours and give corresponding silyl ethers, which can be easily converted into alcohols after basic or acidic workup (Scheme 23, eq. 1). Importantly, the reaction is tolerant to the presence of many functional groups, such as halogens, double bonds, oxiranes etc. However, both carbonyl and ester functionalities are easily reduced under these conditions. Later, a second generation catalyst was developed, which can

be used even under air atmosphere.[45a] Titanium alkoxide effectively catalyses hydrosilylation at slightly elevated temperature (50°C), but no activation of the catalyst is required. There were no detailed mechanistic studies taken, but the possible catalytic cycle starts with insertion of ester into the Ti-H bond of an active titanium hydride species, followed by liberation of aldehyde (Scheme 23). The latter could then react with another titanium hydride complex with the formation of a second titanium alkoxide complex. Both titanium alkoxide species could react with silane and give silyl ethers *via* heterolytic splitting of the Si-H bond. In addition to the Buchwald's titanium catalytic systems, Homma et. al. also reported hydrosilylation of esters with $HSiEt_3$ in the presence of equimolar amounts of $TiCl_4$/TMSOTf.[46]



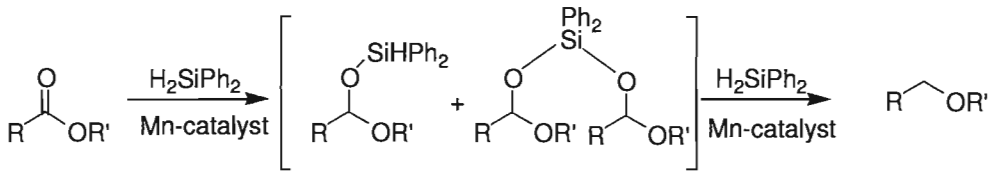
Scheme 23. Catalytic reduction of ester with silanes in the presence of titanium catalysts

The first example of molybdenum catalyzed hydrosilylation of esters was found by Fernandes and Romao.[47] The authors revealed a new catalytic system, based on the molybdenum oxo complex MoO_2Cl_2, which catalyses hydrosilylation of esters with different silanes, including the cheap PMHS, in refluxing toluene (Scheme 24). The molybdenum complex is insoluble in toluene and the reaction, therefore, was proposed to be heterogeneous. A wide range of alcohols can be obtained by this method in high yields (72-82%). The reaction is tolerant to several functional groups, such as $-CF_3$, -Br and -Cl, but nitro and sulfinyl functionalities are also reduced into the corresponding amines or sulfides under these conditions.



Scheme 24. Reduction of esters with H_3SiPh in the presence of MoO_2Cl_2

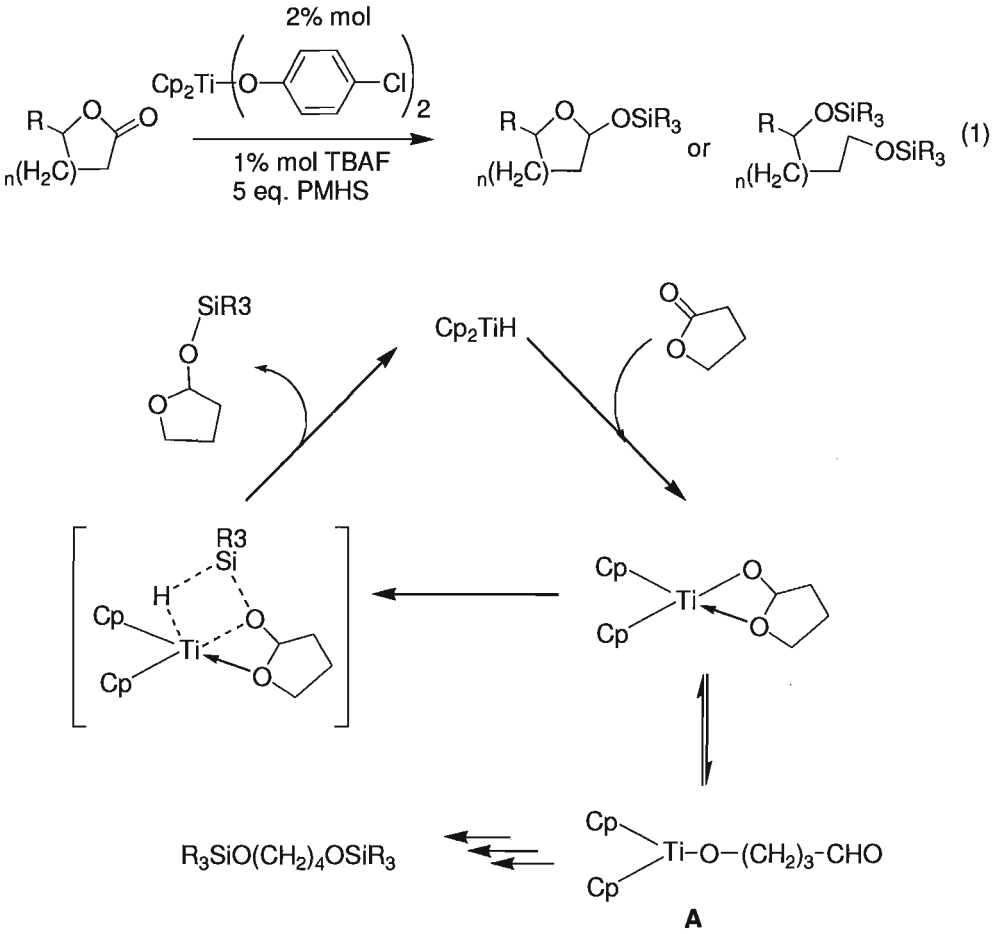
Cutler et. al. disclosed a new type of reduction of esters with silanes mediated by manganese complexes.[48] In contrast to the previously described catalytic systems, hydrosilylation of ester with H_3SiPh or $H_2SiMePh$ in the presence of $(PPh_3)(CO)_4MnC(O)CH_3$ resulted in deoxygenation of the C=O bond in the ester group with the formation of corresponding dialkyl ethers (Scheme 25). The reactions proceed at ambient temperature and usually give ethers in high yields within 1 h. In the proposed mechanism, the reaction starts with the addition of silane across the C=O bond with the formation of silyl acetal intermediates, which can be converted into ethers and siloxanes by the reaction with a second equivalent of silane (Scheme 25). Importantly, some cyclic esters, lactones, can be also reduced under these conditions into cyclic ethers with moderate yields.



Scheme 25. Catalytic reduction of esters with H_2SiPh_2 mediated by manganese complexes

A more general approach to the reduction of lactones by cheap polymethylhydrosiloxane PMHS was found at the same time by Buchwald et al.[49] The titanium-catalyzed reactions of lactones with PMHS proceed at ambient temperature and the resulting silyl lactols can be converted into unprotected lactols by a simple workup with aqueous NaOH (Scheme 26, eq. 1). This procedure is very effective for the reduction of 5- and 6-membered lactones, which could contain aromatic halides or be substituted in the α-position. Importantly, no epimerization was observed in the reaction of lactone, containing a stereocentre in the α-position. Notably, hydrosilylation of larger or sterically hindered lactones resulted in preparation of corresponding diols instead of lactols. There were no detailed mechanistic studies conducted, but the titanium hydride complex Cp_2TiH was suggested as the actual

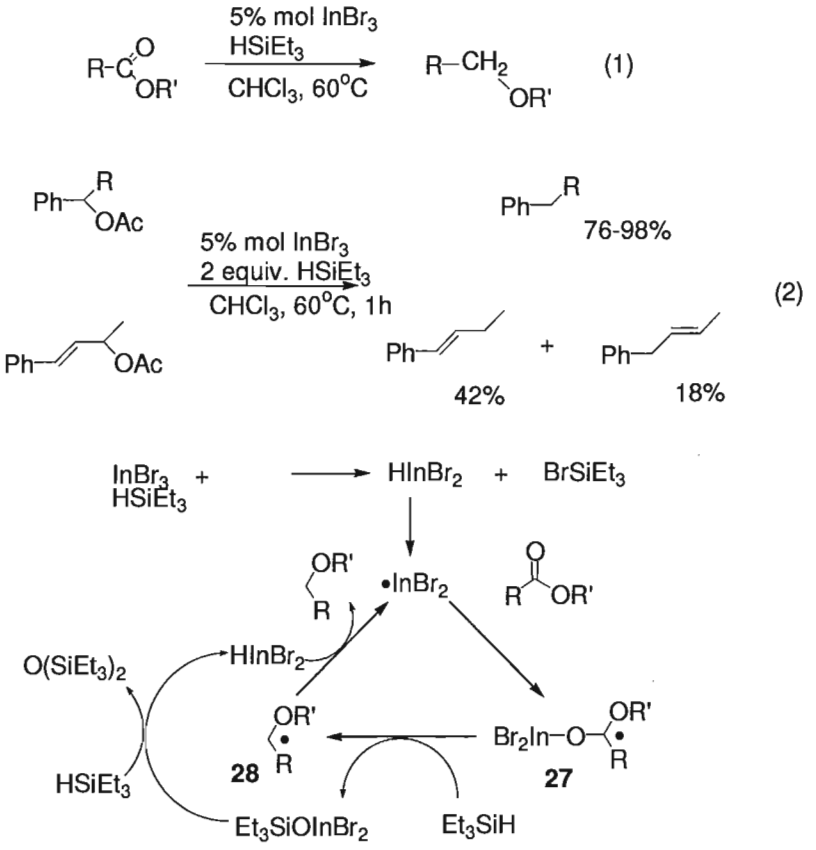
catalyst of the reaction, which was proposed to proceed *via* the reaction of titanium alkoxide and silane (Scheme 26, bottom).[49]



Scheme 26. The titanium-catalyzed reduction of lactones with PMHS

The formation of diols in the reactions with sterically hindered lactones can be explained by the presence in the reaction mixture of complex **A**, which could give the corresponding diols after a sequence of reactions with silanes (Scheme 26, bottom). Addition of catalytic amounts of TBAF is required for the conversion of the titanium complex $Cp_2Ti(O\text{-}p\text{-}ClC_6H_4)_2$ into the catalytically active Cp_2TiH, which proceeds *via* reaction of the generated Cp_2TiF species with silane. The use of TBAF in this reaction raised the question about the actual mechanism, because TBAF itself is known to catalyze a variety of hydrosilylation reactions. Later, Buchwald et. al. conducted additional experiments and found that the reaction could be indeed catalyzed by TBAF, but it was much slower than in the presence of titanium complex.[49a] In

addition, the hydrosilylation of lactones could be also performed without TBAF when titanium bisfluoride Cp_2TiF_2 was used as a catalyst.[49a]

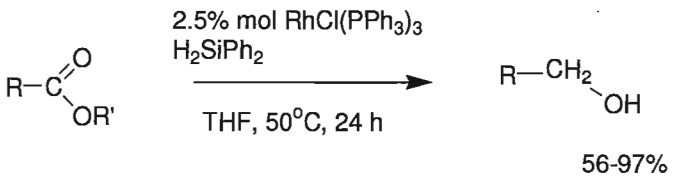


Scheme 27. Reduction of esters with $HSiEt_3$ in the presence of $InBr_3$

Sakai et al.[50] revealed a very effective catalytic system, based on the indium bromide catalyst. Good yields of ethers can be obtained by the reduction of esters with $HSiEt_3$ in the presence of $InBr_3$ (5% mol) at 60°C (Scheme 27, eq. 1). The reactions proceed smoothly within 1-6 h with no significant dependence on the length of alkyl chains in esters. Selective reduction of the ester functionality was observed in the presence of alkyl and aryl halides as well as thiophene ring. Also, simple lactones can be reduced into cyclic ethers under these conditions. However, several limitations of this catalytic system were reported. Thus, the reduction of α-phenyl substituted or olefin conjugated esters resulted in deacetoxylation of these substrates (Scheme 27, eq. 2). In order to establish the possible mechanism, 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), a radical scavenger, was added to the reaction mixture, which completely suppressed the reaction. This observation indicates the key role of indium radicals in the catalytic reaction. Therefore, the proposed mechanism of indium-

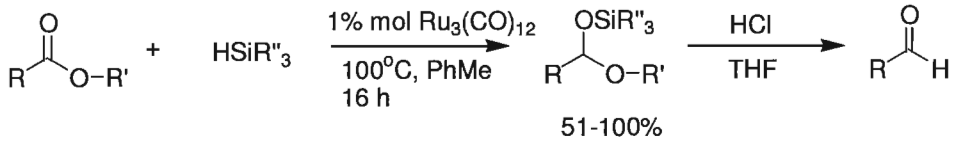
catalyzed reaction includes formation of highly active indium radicals, which could react with ester substrate and give carbon based radical species **27** (Scheme 27, bottom). The reaction of the latter with silane could result in the formation of free organic radicals **28**, which could be converted into ether by the reaction with indium hydride.[50]

Late transition metal catalysts were also successfully applied for the reduction of esters with silanes. Ohta et al. introduced an efficient catalytic system, based on Wilkinson's complex.[51] Reduction of both aromatic and aliphatic esters with 3 equivalents of H_2SiPh_2 proceeds smoothly in the presence of 2.5% mol of $Rh(PPh_3)_3Cl$ in THF (Scheme 28). In addition to Wilkinson's catalyst, other Rh-based catalytic systems, such as $[RhCl(cod)]_2$-BINAP, $[RhCl(cod)]_2$-1,10-phenanthroline or $RhCl(CO)(PPh_3)_3$, were also found to be active. Unfortunately, only H_2SiPh_2 can be effectively used as a reducing agent in this method. Also, the hydrosilylation of ester functionality cannot be performed effectively in the presence of the C=C bond due to competitive reduction of the alkene group.[51]



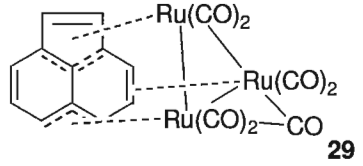
Scheme 28. Reduction of esters with H_2SiPh_2 in the presence of $Rh(PPh_3)_3Cl$

Cataytic hydrosilylation of esters in the presence of $Ru_3(CO)_{12}$ was reported by Fuchikami et al.[52] An unusual and unique feature of this catalytic system is that esters can be converted into silyl acetals and then into the corresponding aldehydes with very high selectivity (Scheme 29). This method requires high temperature, but both alkyl and aryl esters can be reduced efficiently with different silanes, such as $HSiEt_3$, $HSiMe_2Ph$ or $HSiMe_2Bu^t$. Instead of $Ru_3(CO)_{12}$, a combination of $[RuCl_2(CO)_3]_2$ with Et_2NH and EtI can be used with the same efficiency. Interestingly, other transition metal carbonyls, such as $Cr(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, were not active or showed insignificant catalytic activity.[52]



Scheme 29. Catalytic reduction of esters with silanes in the presence of $Ru_3(CO)_{12}$

Later, Nagashima et al.[53] reported a triruthenium carbonyl cluster **29** (Scheme 30), which catalyses hydrosilylation of esters at room temperature, but mixtures of alcohols and ethers were usually obtained after acidic workup.



29

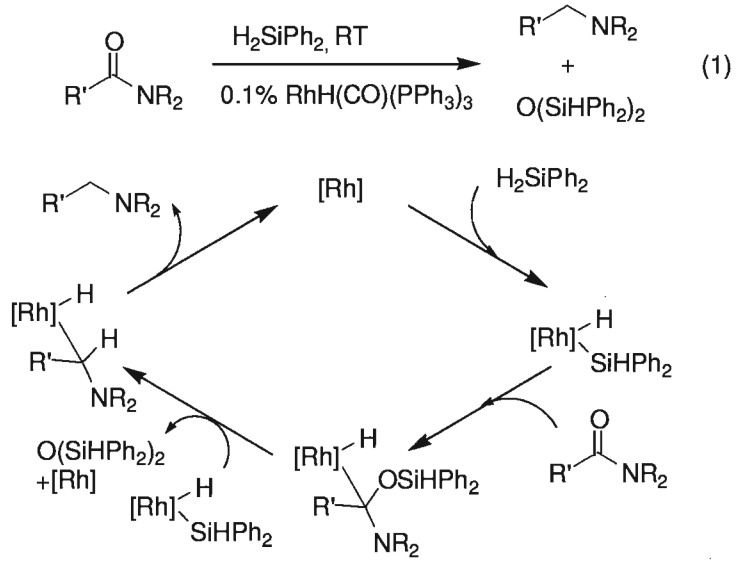
Scheme 30. Ruthenium catalyst for the reduction of esters

II.1.4 Reduction and dehydration of amides

Aromatic and aliphatic amines find numerous applications in almost all fields of chemistry. Therefore, the development of efficient synthetic routes to these compounds has received considerable attention.[54] One of the common methods for preparation of amines is reduction of amides. Catalytic hydrogenation of amides is extremely challenging[55] and usually stoichiometric amounts of aluminium hydrides or boranes are used as reducing agents.[56] However, primary and tertiary amides are quite challenging substrates, and even with these fairly strong reducing agents the reactions are slow and often do not go to completion.[56] Therefore, hydrosilylation of amides could be a very attractive alternative to the existing procedures for preparation of amines.

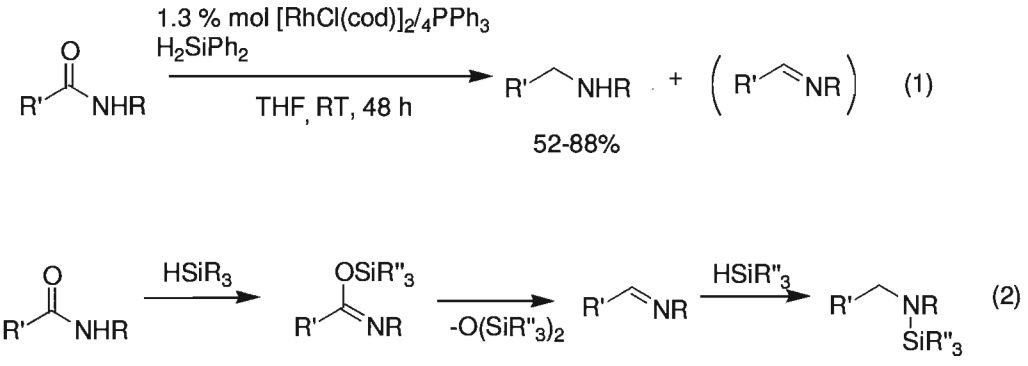
The first application of silanes for the reduction of amides was reported in 1979 by Mozdzen et al.[57] It was shown, that N,N-dimethylbenzamide could be reduced into amine (after basic workup) with $HSiCl_3$ in the presence of n-Pr_3N. However, secondary and primary amides as well as alkyl amides were found to be much less reactive or non-reactive.

Due to high inertness of amides, the first article on transition metal catalyzed hydrosilylation of these substrates appeared only in 1998. Ito et al. reported reduction of amides into amines with H_2SiPh_2 in the presence of different rhodium catalysts.[58] The best results were achieved in the catalytic reactions mediated by $RhH(CO)(PPh_3)_3$ and $RhH(PPh_3)_4$. Both aromatic and aliphatic tertiary amides can be easily reduced by this method within 0.5-48 h at ambient temperature with only 0.1% mol of $RhH(CO)(PPh_3)_3$ (Scheme 31, eq. 1). The reaction is tolerant to several functional groups, such as esters, aryl halides, epoxides. However, the catalyst was found to be totally inactive in the reduction of primary and secondary amides. The reaction was postulated to proceed *via* oxidative addition of silane to rhodium, followed by insertion of amide into the Rh-Si bond (Scheme 31, bottom). The reaction of the hydrido silyl rhodium complex with the resulting compound was assumed to give silyl ether and hydrido alkyl rhodium complex, which could undergo reductive elimination of the C-H bond with the formation of free amine and regenerated catalyst.[58]



Scheme 31. Reduction of tertiary amides with H_2SiPh_2 in the presence of $RhH(CO)(PPh_3)_3$

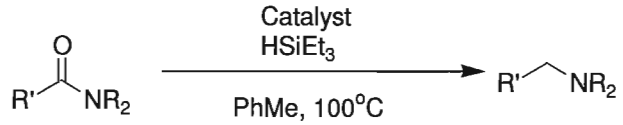
Later, Ohta et. al. discovered several other Rh-based catalytic systems, which were able to reduce secondary amides into amines at ambient temperature within 48 h.[51a] Interestingly, bulky amides were reduced into a mixture of amines and imines in the presence of $[RhCl(cod)]_2/4PPh_3$ or $RhCl(PPh_3)_3$ (Scheme 32, eq. 1). This indicates that the reduction of secondary amides could proceed through the intermediate formation of imines, which can be further reduced into amines (Scheme 32, eq. 2). Primary amides gave complex mixtures under these reaction conditions.[51a]



Scheme 32. Reduction of secondary amides in the presence of rhodium catalysts

A wide range of groups 7-10 transition metal (Mn, Re, Ru, Os, Rh, Ir, Pd and Pt) complexes were tested by Fuchikami and Igarashi[59] in the reduction of primary, secondary and tertiary amides with different monohydrosilanes, which are much

cheaper than dihydrosilanes used in previous examples. Surprisingly, all the tested complexes were active in hydrosilylation of tertiary amide (*N*-acetylpiperidine was used as a standard substrate) with $HSiEt_3$ at 100°C (Scheme 33). The authors also found the beneficial addition of EtI and Et_2NH into the reaction mixture as co-catalysts. This seems to be a very universal method for the reduction of amides with a variety of different catalysts and silanes. However, the selectivity of the reaction towards different functional groups was not established, and the reduction of primary amides gave amines with only poor yields (50% for p-TolC(O)NH_2 and 56% for n-$C_7H_{15}C(O)NH_2$).[59]

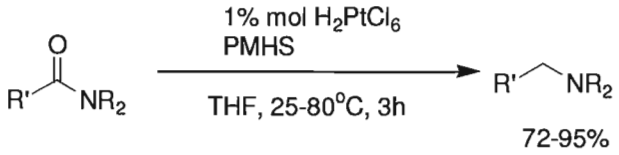


Catalysts: $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Ru_3(CO)_{12}$, $RuCl_2(CO)_2(PPh_3)_2$, $RuH_2(CO)(PPh_3)_3$, $Ru(acac)_3$, $Os_3(CO)_{12}$, $RhH(PPh_3)_4$, $IrCl_3$, K_2IrCl_6, $Pd(OH)_2/C$

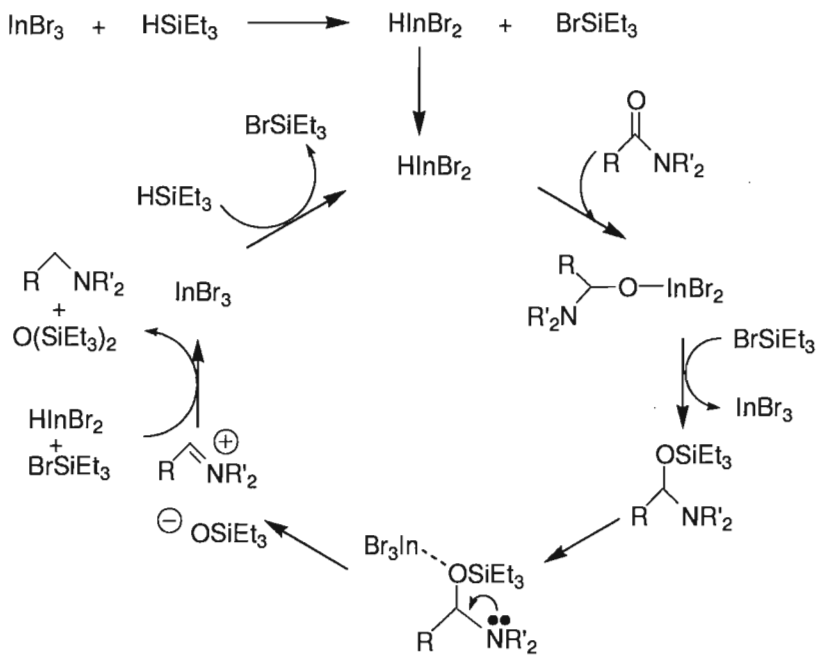
Scheme 33. Catalytic reduction of amides in the presence of groups 7-10 metal complexes

A very convenient method for the reduction of amides was reported by Nagashima et al.[60] Siloxanes with more than two Si-H groups were found to be very effective hydrosilylation agents in the presence of commercially available platinum catalysts, such as $H_2PtCl_6*6H_2O$, $PtCl_2(COD)$ and $Pt[((CH_2=CH)Me_2Si)_2O]_n$. Interestingly, no reduction of *N,N*-dimethyl dihydrocinnamamide was observed with silanes containing only one Si-H group under these conditions. In contrast, the reaction proceeds smoothly with $HSiMe_2OSiMe_2H$ or Me_3Si-$(OSiHMe)_2OSiMe_3$ and gives corresponding amines in 90% and 63% yields, respectively. This "dual Si-H" effect, which significantly enhances the reactivity, could be explained by coordination of both Si-H groups to the metal centre with the formation of highly active platinum complexes. The reduction of amides can be also performed with the cheap PMHS, which makes it very attractive for practical applications (Scheme 34). In this case the reactions proceed at 50°C within 3 h and are tolerant to aryl halide, alkene and methoxy groups. Moreover, at the end of the reaction the catalyst is encapsulated in insoluble silicon resins, which are always produced as a by-product in the reduction with PMHS, and can be easily separated from the product. This method is very

attractive for the reduction of tertiary amides, but all the attempts to extend this methodology to primary and secondary amides were unsuccessful so far.[60]



Scheme 34. Reduction of tertiary amides in the presence of platinum catalysts



Scheme 35. The proposed mechanism of $InBr_3$-catalyzed reduction of amides

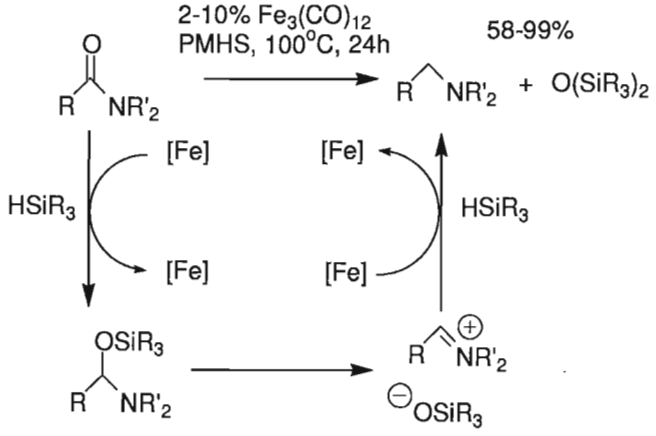
The indium based reducing system, $InBr_3/HSiEt_3$, which was previously described for the reduction of esters, can be used for amides as well. Sakai et al.[61] showed that a wide range of tertiary amides can be reduced into amines in the presence of 5% mol $InBr_3$ at 60°C. Moderate to good yields of amines can be obtained at this temperature within 12-72 h. Importantly, the cyano group, aryl halides and cyclopropane fragments in the amide substrate did not influence the course of the reaction. Reduction of the amide group can be also performed in the presence of C=C bond, but poor yield (27%) was achieved. Some of secondary amides, such as acetanilide or benzanilide, were also converted into corresponding amines in 45% and 72% yields, respectively. On the other hand, reduction of *N*-alkylacetamides did not occur. The best results can be obtained with the use of $HSiEt_3$ as a reducing agent, and

all the other tested silanes, such as $HSiMe_2Ph$, H_2SiPh_2 and $(HSiMe_2)_2O$, gave reduced yields of amines. Due to the fact that there was no ring opening of the cyclopropane fragment in one of the amide substrates, the reaction was assumed to proceed via an ionic mechanism (in contrast to the radical reduction of esters) (Scheme 35). Hydroindation of amide with $HInBr_2$ followed by the reaction with $BrSiEt_3$ could result in the formation of silylacetal, which could undergo the $InBr_3$ mediated transformation into an iminium intermediate. Finally, the reduction of the iminium species with $HInBr_2$ could lead to the formation of amine product.[61]

Analogously to hydrosilylation of esters, molybdenum oxo catalyst MoO_2Cl_2 can be also applied for the reduction of amides. Fernandes and Romao[62] reported reduction of tertiary and secondary amides with H_3SiPh in refluxing toluene. Moderate to good yields of the corresponding amines can be achieved within 20 h in the presence of 10% mol of MoO_2Cl_2. However, the reactivity of primary amides was very low. Thus, the reduction of 4-(trifluoromethyl)benzamide resulted in preparation of amine in only 20% yield and no reaction was observed with 4-chlorobenzamide. One of the advantages of this catalytic system is that it can be used efficiently with different silanes, including PMHS. Also, sterically hindered tertiary amides can be reduced with good yields by this method.[62]

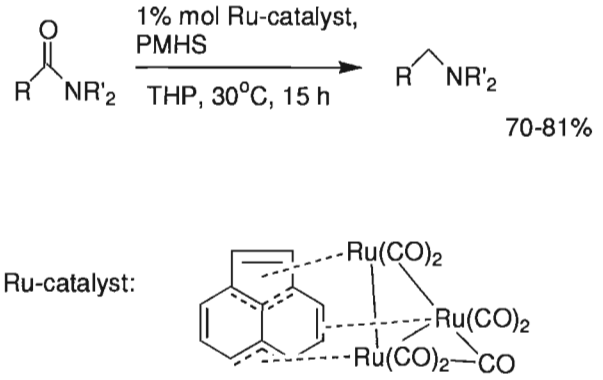
The first iron-catalyzed reaction of amides with silanes was simultaneously discovered by the groups of Beller and Nagashima in 2009.[6b, c] The use of iron catalysts is always beneficial in comparison with other late transition complexes due to environmental and cost-efficient issues. Nagashima et al.[6b] found that iron carbonyl complexes $Fe_n(CO)_m$ catalyzed reduction of tertiary amides with hydrosilanes that have proximal Si-H groups, including PMHS, under thermal conditions (24 h at 100°C) or under photoassisted conditions (9 h at ambient temperature). Interestingly, very small conversions of amides were observed in the presence of other iron complexes, such as $FeCl_2$, $FeCl_3$, $[FeCl_2(PPh_3)_2]$, and $[Fe(acac)_2]$. Almost no reaction was observed with other monohydrosilanes, such as $PhMe_2SiH$, $(EtO)_3SiH$, and $SiMe_3OSiMe_2H$. One of the drawbacks of this method is that nitro- and keto-groups as well as alkyl halides were also reduced under the thermal conditions, and the reaction with *N,N*-dimethyl-p-cyanobenzamide gave the corresponding amine in very low yield. However, the reaction is tolerant to aryl halides, methoxy, and ester groups. Beller et al.[6c] reported reduction of a wide range of aromatic, aliphatic, heteroaromatic, and heterocyclic amides (28 substrates in total) with PMHS mediated by $Fe_3(CO)_{12}$ at

100°C. The reaction is tolerant to the trifluoromethyl and methoxy groups, aryl halides, alkene and cyclopropyl fragments. Icreased catalyst load (10% mol) and excess silane (8 eq.) are required for the reduction of bulky amides. Secondary amides can be also reduced into secondary amines if H_3SiPh is used as the reducing agent. Ketoamides, however, gave a mixture of products. The reduction of amides was proposed to proceed via addition of silane across the C=O bond (Scheme 36), followed by the formation of iminium species, which can be further reduced into corresponding amines. The nature of the active iron complexes remains unknown.

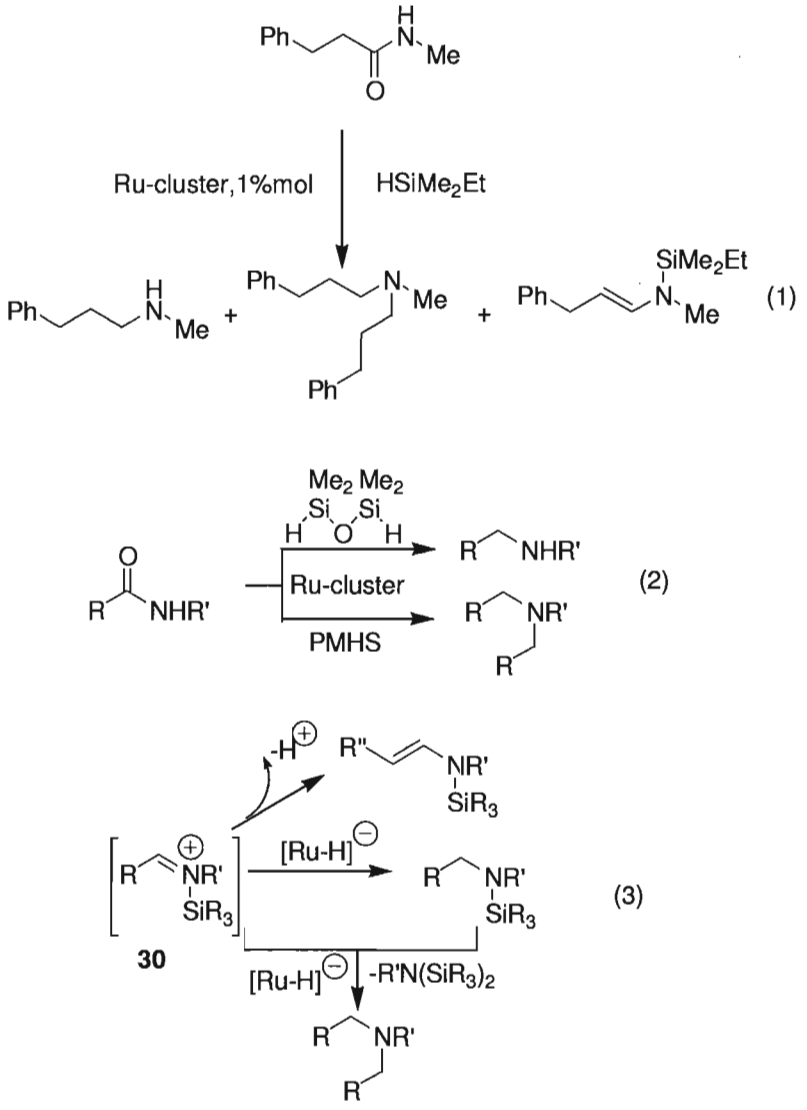


Scheme 36. The proposed mechanism for the iron-catalyzed reduction of amides

A series of reports on ruthenium catalyzed reduction of amides was published by Nagashima et al.[53, 63] A triruthenium carbonyl cluster bearing a bridging acenaphthylene ligand catalyzes reduction of tertiary amides with silanes at room temperature (Scheme 37). The catalyst has to be activated priory to catalysis, which consists of stirring the ruthenium complex with silane at room temperature. Sterically small monohydrosilanes, such as $HSiMe_2Et$, $HMe_2Si(CH_2)_2SiMe_2H$, and $HSiMeEt_2$, were found to be the most effective as the reducing agents in this method. In contrast, bulky monohydrosilanes, dihydro- and trihydrosilanes were much less effective in catalysis. Later, the same catalyst was successfully applied for the reduction of amides with the cheap PMHS. One of the advantages of PMHS is that it forms silicon resins at the end of the reaction, and most of the catalyst (> 99.8%) is trapped inside of this resin, which is not soluble in non-polar solvents. This significantly simplifies the isolation of amine product. Moreover, the catalyst can be also easily recovered and used again in the reaction.



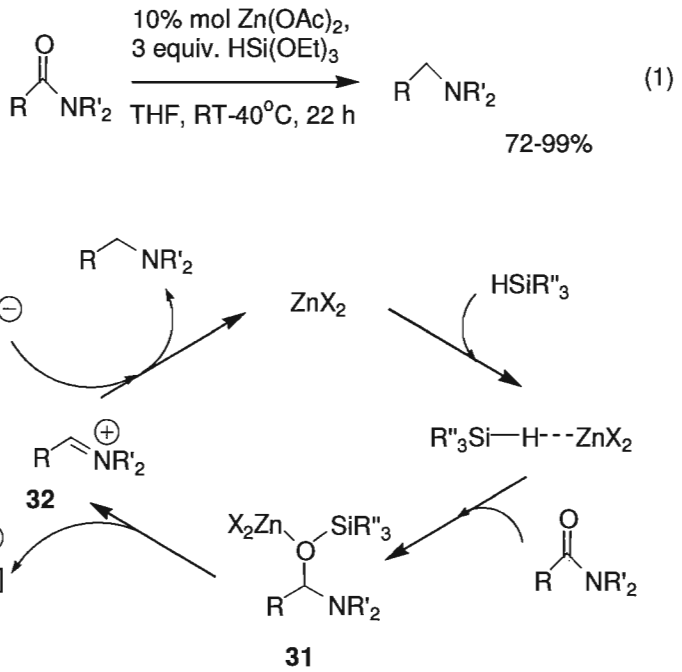
Scheme 37. Reduction of tertiary amides in the presence of ruthenium catalyst



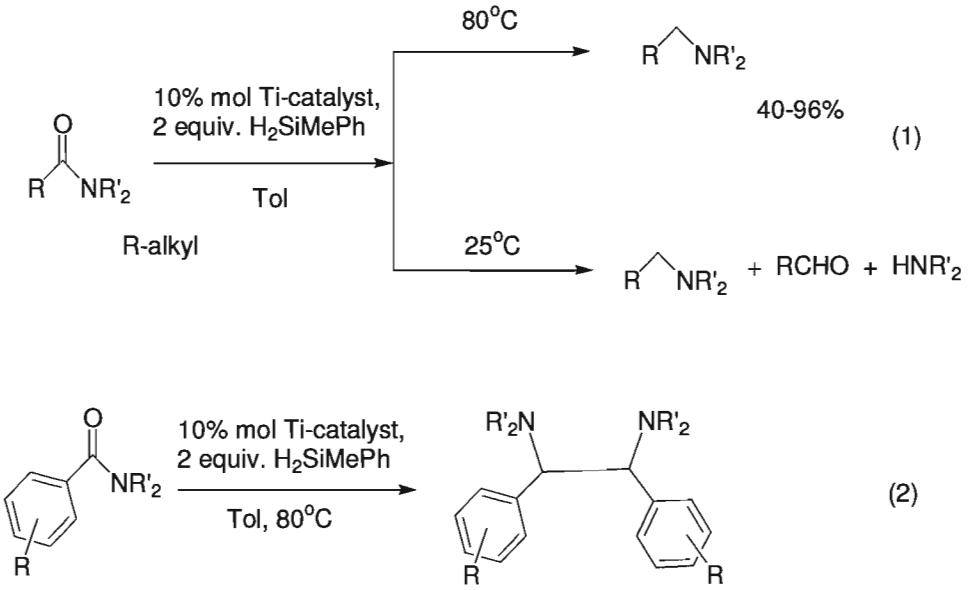
Scheme 38. Reduction of secodary amides in the presence of ruthenium catalyst

The triruthenium carbonyl cluster also catalyzes reduction of secondary amides, but a mixture of products is usually obtained with $HSiMe_2Et$ as a reducing agent (Scheme 38, eq. 1). Interestingly, the ratio of the products depends on the nature of silane (Scheme 38, eq. 2). Thus, the reduction of secondary amides with $[HSiMe_2]_2O$ gave predominately secondary amines at 40-60°C within 6-12 h. On the other hand, tertiary amines were obtained as major products when PMHS was used as a hydride source. The plausible mechanism of this reaction involves formation of intermediate silyl iminium species **30** (Scheme 38, eq. 3), which can be converted into silyl enamine after abstraction of one proton or into silyl amine *via* reduction with ruthenium hydride intermediate. On the other hand, the silyl amine can react with the iminium species **30** in the presence of the ruthenium hydride with the formation of tertiary amines. Notably, this is the first catalytic system, which allows for rather selective preparation of tertiary amines by the reduction of secondary amides. Due to high catalytic activity of the triruthenium carbonyl cluster, other fuctional groups, such as ester and carbonyl, are usually also reduced under these reaction conditions. In this case, addition of NEt_3 to the reaction mixture suppresses the reduction of carbonyls, and the amides could be reduced more selectively.[63]

A highly selective method for reduction of tertiary amides under very mild conditions was revealed by Beller et al.[6a] A wide range of aromatic, aliphatic, heteroaromatic, and heterocyclic amides can be converted into amines in the presence of cheap $Zn(OAc)_2$ at 40°C within 22 h (Scheme 39, eq. 1). The reactions showed remarkable tolerance to the presence of C=C bonds, aryl halides, methoxy-, keto-, nitro-, cyano- and ester groups in the amide substrates. Preliminary mechanistic studies of this reaction showed that $Zn(OAc)_2$ does not activate the amide substrate (no reaction between $Zn(OAc)_2$ and amide was observed by IR spectroscopy). At the same time, the reaction of $Zn(OAc)_2$ with $HSi(OEt)_3$ resulted in the appearance of a new single peak at 82.2 ppm in the ^{29}Si NMR spectra (for comparison, the chemical shift of $HSi(OEt)_3$ is 59.2 ppm). Based on these data, a catalytic cycle of the reaction was proposed (Scheme 39, bottom), which starts with coordination of silane to zinc acetate followed by reaction with amide with the formation of silyl acetal species **31**. The release of an anionic zinc siloxy complex from the latter results in preparation of the iminium species **32**, which can be further converted into the final amine product by the reaction with anionic zinc hydride complex.



Scheme 39. Reduction of tertiary amides in the presence of $Zn(OAc)_2$

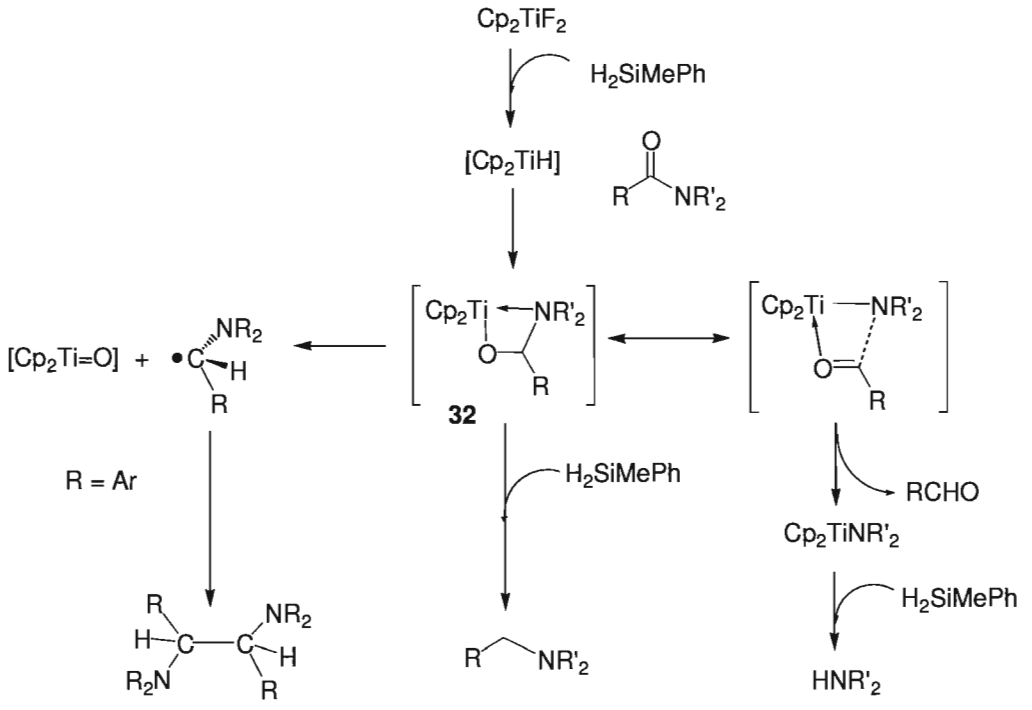


Scheme 40. Reduction of tertiary amides in the presence of Cp_2TiX_2 (X = Me, F).

Tertiary amines can be also prepared in high yields by the reduction of amides in the presence of titanium catalysts. Harrod et al. reported the reactions of $H_2SiMePh$ with a variety of tertiary acetamides catalyzed by Cp_2TiX_2 (X = Me, F).[64] Interestingly, the selective formation of tertiary amines was observed only at 80°C (Scheme 40, eq. 1 top). In contrast, hydrogenolysis of the C(O)-N bond takes place at

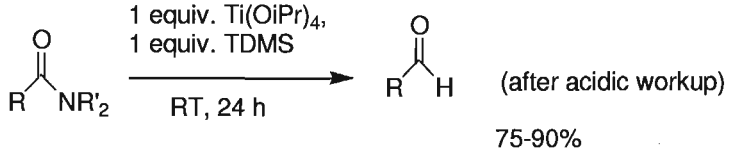
room temperature as a concomitant reaction, which results in the formation of a mixture of products, containing aldehydes, tertiary and primary amines (Scheme 40, eq. 1 bottom). Surprisingly, the reduction of aromatic amides $ArC(O)NR_2$ at 80°C gave an unexpected coupling of amides with a rather selective formation of vicinal diamines (Scheme 40, eq. 2). This unusual reaction proceeds smoothly even in the presence of several functional group in the aromatic ring of the amide substrates, such as 4-chloro-, 4-methoxy-, and 4-trifluoromethyl groups.[64]

The mechanisms of all these reactions remain unknown, but the following reaction sequence was proposed to explain the above results (Scheme 41). The reaction starts with the formation of an active Ti(III) hydride species Cp_2TiH, followed by the insertion of amide into the Ti-H bond. The resulting aminoalkoxy complex **32** could undergo several different transformations: 1) the homolysis of the C-O bond, followed by coupling of two radicals to form the 1,2-diaminoethane; 2) the metathesis between the C-O and Si-H bonds with the formation of a tertiary amine; 3) the intramolecular metathesis with the formation of an aldehyde and titanium amide, which can further react with silane to give a secondary amine. All the titanium derivatives, which can be produced in these reactions, could be transformed back into the titanium(III) hydride species *via* an appropriate reaction with $H_2SiMePh$.[64]

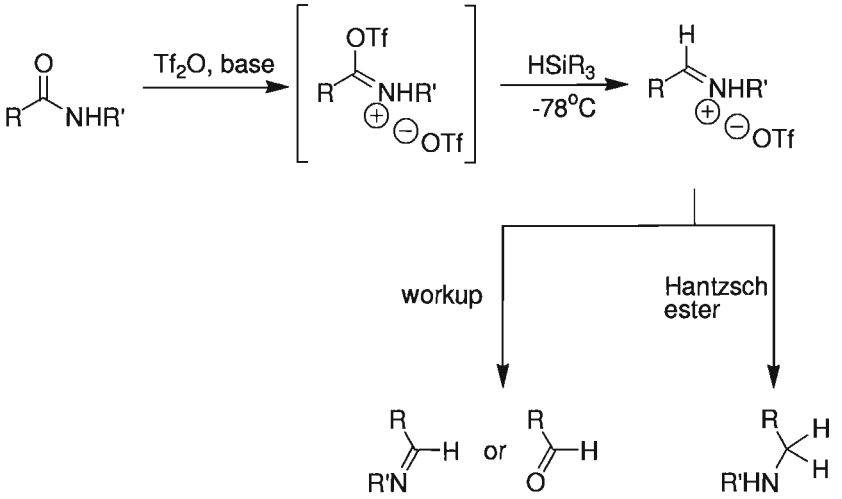


Scheme 41. The proposed reaction pathways for reduction of amides in the presence of Cp_2TiF_2

Buchwald and co-workers[65] reported the preparation of aldehydes from the reaction of amides with H_2SiPh_2 in the presence of stoichiometric amounts of Ti(Oi-Pr)$_4$. A wide range of amides can be converted into the corresponding aldehydes by this method after a mild acidic workup (Scheme 42). Importantly, the reactions proceed at room temperature and are tolerant to many functional groups in the amide substrates. Both tertiary and secondary amides can be used in this reaction. However, primary amides are much less reactive (only 3% conv. for the 2-(trifluoromethyl)-benzamide).[65]



Scheme 42. Preparation of aldehydes from amides in the presence of Ti(Oi-Pr)$_4$

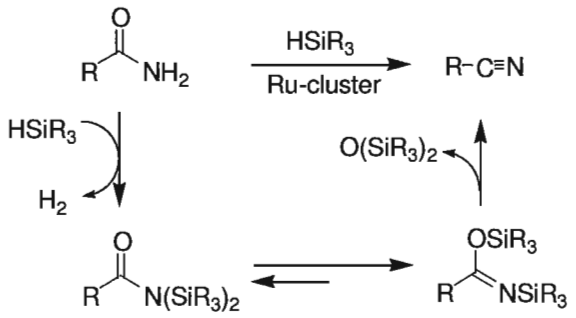


Scheme 43. Reduction of secondary amides activated by Tf_2O

Very recently, another non-catalytic method for the reduction of amides with silanes has been reported by Charette et al.[66] The key feature of this method is that secondary amides can be selectively converted into imines and aldehydes or into secondary amines under different reaction conditions (Scheme 43). Initially, activated by the triflic anhydride (Tf_2O) amides react with $HSiEt_3$ with the formation of iminium salt. The corresponding imines or aldehydes can be then obtained by the workup using $NaHCO_3$ or aqueous citric acid, respectively. Alternatively, secondary amines can be obtained by the reaction of the iminium salt with the Hantzsch ester.

Importantly, all of the above reactions proceed with very high chemoselectivity. Reduction of secondary amides can be performed in the presence of nitro-, azido-, ester- and α,β-unsaturated ester-, cyano-, and even aldehyde groups. In addition, reactions are tolerant to double and triple carbon bonds as well as tertiary amides.[66]

Catalytic reduction of amides with silanes is usually expected to give the corresponding amines. However, Nagashima et al.[67] found, that the reaction of primary amides with silane could also give nitriles in high yield. Treatment of both alkyl and aryl primary amides with $HSiMe_2(CH_2)_2SiMe_2H$ in the presence of triruthenium cluster **29** at 70-80°C resulted in the unexpected dehydration of amides with the formation nitriles after 12-24 h. Importantly, this reaction is tolerant to aryl and alkyl halides, C=C bonds, methoxy- and Me_2N-groups. Other ruthenium carbonyl complexes, such as $Ru_3(CO)_{12}$ and $[RuCl_2(CO)_3]_2$, were also found to be active catalysts. In contrast, most of the other common transition metal catalysts, such as $(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2$, $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$, and $[(\eta^6\text{-}C_6Me_6)RuCl(MeCN)_2](PF_6)$, $Co_2(CO)_8$, $RhH(CO)(PPh_3)_3$, and $IrCl(CO)(PPh_3)_2$, did not show any catalytic activity. The plausible mechanism of this reaction (Scheme 44) starts with a dehydrogenative coupling reaction with the formation of the *N,N*-bissilyl amide, which exists in equilibrium with the *N,O*-bis(silyl) amidate. The latter could undergo siloxane elimination with the formation of the final nitrile product. It is also known, that *N,O*-bissilyl amidates can be converted into nitriles without any catalyst under thermal conditions (>200°C).[67] However, addition of the catalyst results in better yields of nitriles at lower temperatures.



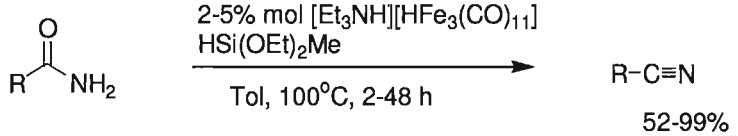
Scheme 44. Catalytic dehydration of primary nitriles in the presence of Ru-cluster

Dehydration of primary amides with silanes seems to be very unique and unusual, because silanes normally act as mild reducing agents. However, more catalytic systems have been developed since the first report on this transformation,

which could make it a general method for the synthesis of nitriles. Dehydration of amides by common organic methods usually requires acidic and very reactive compounds, such as phosphorus pentoxide, titanium tetrachloride or thionyl chloride.[68] Milder conditions can be used with trichloroacetyl chloride, pivaloyl chloride, $EtOP(O)Cl_2$ or benzensulfonyl chloride,[69] but these reagents can cause storage and waste disposal problems. Therefore, catalytic dehydration with silanes could be a valuable alternative to the existing methods.

A very general method for the dehydration of amides with silanes was reported by Beller et al.[70] Both aromatic and aliphatic amides can be converted into nitriles in the presence of TBAF (5% mol) and stoichiometric amount of H_3SiPh at 100°C. Interestingly, this reaction occurs even in the presence of secondary amido-group in the substrate, which remains unreduced. Fluoride anion is well-known to activate silanes due to the formation of a highly reactive hypervalent silyl species, which are capable of reacting with amides with the release of hydrogen and formation of an equilibrium mixture of silyl substituted amidates and amides. The latter compounds, as shown before (Scheme 44), can then undergo siloxane elimination and give nitriles at high temperature.

Catalytic dehydrogenation of amides in the presence of iron catalysts has also been recently reported by Beller's research group.[71] The best results were achieved in the presence of anionic iron carbonyl complex $[Et_3NH][HFe_3(CO)_{11}]$. Other iron complexes, such as $Fe_2(CO)_9$, $[CpFe(CO)_2]_2$, $Fe_3(CO)_{12}$, $Fe(acac)_3$ and $Fe(OAc)_2$, also showed good catalytic activity. On the other hand, $Fe(CO)_5$, $FeCl_2$ or $FeCl_3$ were totally inactive. All the reactions proceed smoothly at 100°C in the presence of 3 equivalents of $HSiMe(OEt)_2$ and are tolerant to many functional groups, such as aryl halides, C=C bonds, methoxy- and amino-groups (Scheme 45).[71]



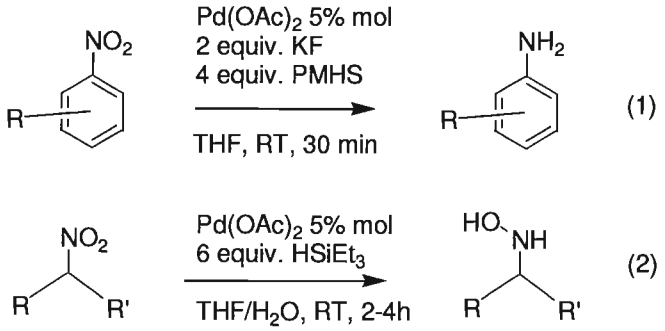
Scheme 45. Catalytic dehydration of primary amides in the presence of $[Et_3NH][HFe_3(CO)_{11}]$

II.1.5 Reduction of nitro compounds

In addition to the previously described reduction of amides, reduction of nitro compounds RNO_2 is another general method for preparation of valuable primary amines, which is usually performed with strong aluminum hydride reducing agents. The first reports on the reduction of nitroarenes with silanes appeared in 1970s. Andrianov et al. reported the preparation of anilines from nitroarenes by the reduction with different silanes in the presence of Rh-catalysts, but low yields were obtained.[72] Heterogeneous (Pd/C) reduction of $PhNO_2$ into $PhNH_2$ in 89% yield was performed in 1973 by Lipowitz and Bowman.[73] This method requires the relatively cheap PMHS as a reducing agent and the reaction proceeds smoothly within 1 h at 40-60°C in EtOH. Later, Brinkman and Miles[74] reported a more general method for preparation of aromatic amines from nitrobenzenes in the presence of Wilkinson's catalyst. Moderate to good yields (49-90%) of amines were achieved in the reduction of nitrobenzenes with $HSiEt_3$ at 110°C in toluene. Importantly, this method is tolerant to several functional group, such as chloro-, methoxy-, ester-, and aceto-groups.[74]

Rahaim and Maleczka introduced a highly effective Pd-based catalytic system, which allows for preparation of a wide range of aromatic amines (Scheme 46, eq. 1).[75] The best results were achieved with a catalytic system, which consisted of $Pd(OAc)_2$ (5% mol), 4 equiv. of PMHS, and 2 equiv. of aqueous KF in THF. However, other silanes, such as $HSiEt_3$ or $HSiMe_2OEt$, and other palladium precatalysts (Pd/C) were also quite effective. The main advantages of this catalytic system are the very high tolerance to many functional groups, mild conditions (room temperature) and short reaction times (~30 min). Thus, selective reduction of aromatic nitro-group can be performed in the presence of esters, nitriles, hydroxides, alkoxides, aromatic fluorides, amides and ketones. However, the concomitant reduction of aromatic halo and aldo-groups was observed in the reaction with corresponding nitro-compounds. Also, a very poor yield was achieved in the reduction of 4-nitrothioanisole, which could be explained by the well-known poisoning of the palladium catalysts with sulphur. The steric hindrance of substrates did not have significant influence on the reaction, which was demonstrated by the successful reduction of ortho-substituted nitroarenes. Several heteroaromatic nitro-substituted compounds were also effectively reduced into amines. Attempted reduction of aliphatic nitro-compounds under the same conditions was

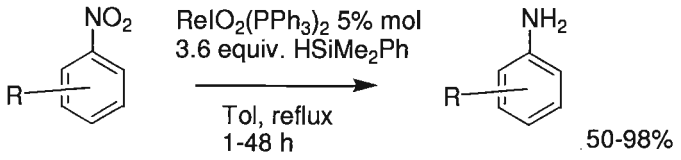
much less efficient. However, the reduction aliphatic nitro-compounds with moderate to good conversions can be performed under slightly modified reaction conditions without the addition of KF: $Pd(OAc)_2$ 5% mol, 6-10 equiv. of $HSiEt_3$, THF/H_2O. Notably, addition of water to the reaction system significantly increases the conversions of nitro-compounds. Under these conditions, primary and secondary nitro groups can be effectively reduced into the corresponding N-hydroxylamines (Scheme 46, eq. 2).[75]



Scheme 46. Reduction of aryl and alkyl nitro compounds in the presence of $Pd(OAc)_2$

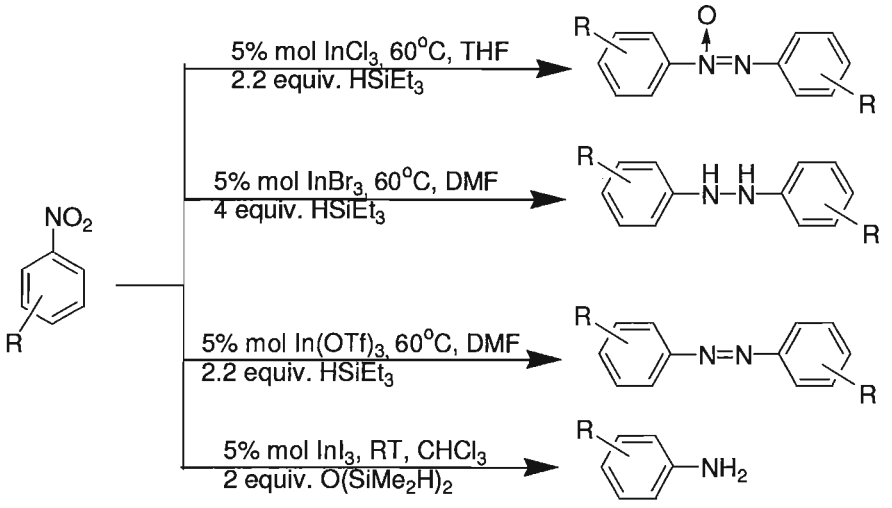
A highly chemo- and regioselective method for reduction of aromatic nitro compounds was recently reported by Fernandes et al.[4a] A wide range of different nitro-substrates was reduced into amines in the presence of rhenium oxo complexes (Scheme 47). The most active rhenium catalysts for this transformation are $ReIO_2(PPh_3)_2$ and $ReOCl_3(PPh_3)_2$. Other complexes, such as $ReOCl_3$(dppe) or Re_2O_3, also effectively catalyze the reduction of nitro groups, but the reactions are much slower. Different silanes, including PMHS, can be used as reducing agents in this method. However, the fastest conversion of 4-nitrobenzoate, which was used as a standard substrate, was achieved with H_3SiPh and $HSiMe_2Ph$ in the presence of 5% mol of $ReIO_2(PPh_3)_2$. The reactions proceed at rather high temperature (110°C) but with very high tolerance to many functional groups, such as aryl halides, esters, sulfones, lactones and alkenes. Interestingly, the regioselective reduction of the aromatic nitro group by this method is favoured over the aliphatic nitro group. Also, in the presence of two nitro substituents in the benzene ring, only one of them is usually reduced with the formation of corresponding nitroanilines in moderate to good yields. On the other hand, the reduction of aliphatic nitro compounds under standard conditions resulted in moderate conversion into nitriles instead of amines. The advantages of this catalytic system are the high yields of aromatic amines and a

relatively easy workup. Moreover, the air-stable rhenium oxo complexes can be recycled and used again in the reaction without any significant decrease in activity for up to 4 times.[4a]



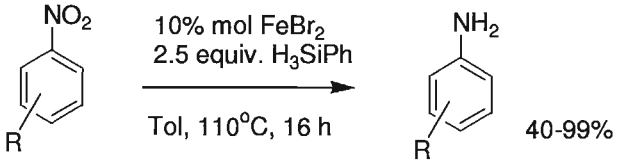
Scheme 47. Reduction of aryl nitro groups in the presence of $ReIO_2(PPh_3)_2$

Sakai et al.[4d] introduced new catalytic systems for the reduction of nitro compounds mediated by indium salts. Interestingly, four different products can be obtained by this method: azoxybenzenes, azobenzenes, diphenylhydrazines or anilines (Scheme 48). More importantly, each of these products can be selectively prepared by controlling the type of indium salt, hydrosilane, solvent, and the number of hydrosilane equivalents used in the reaction. Azoxybenzenes are the main products for the reduction of nitro compounds in the presence of 5% mol $InBr_3$ and 1-2 equiv. of $HSiEt_3$. Under these reaction conditions, azoxybenzenes can be obtained in 64-96% yield within 2-20 h at 60°C in THF, and the reactions are tolerant to halo-, cyano-, keto- and ester groups. Diphenylhydrazines derivatives can be obtained in DMF at 60°C in the presence of 5% mol $InBr_3$ and 4 equiv. of $HSiEt_3$. A wide range of nitrobenzenes with halo-, cyano-, keto- and ester groups can be effectively converted into corresponding diphenylhydrazines in 41-96% yield within 8-20 h. The synthesis of azobenzene derivatives was performed in DMF at 60°C in the presence of 5% mol $In(OTf)_3$ and 2.2 equiv. of $HSiEt_3$. The latter reaction affords 62-99% yields of azobenzenes within 5-20 h in the presence of halo-, cyano-, keto- and ester groups in the nitro-substrates. Notably, this method also allows for the quite selective preparation of some asymmetrical azobenzenes from a mixture of two different nitrobenzenes. Finally, aniline and p-toluidine were obtained from the corresponding substrates in 99% and 82% yields, respectively, at room temperature in $CHCl_3$ in the presence of 5% mol of InI_3 and 2 equiv. of $O(SiMe_2H)_2$.[4d]



Scheme 48. The reactions of aromatic nitro compounds with $HSiEt_3$ in the presence of indium salts

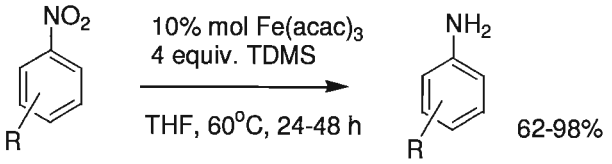
A very convenient catalytic system based on simple, environmentally friendly iron salts was discovered in 2010 by Beller et al.[4b] A wide range of nitroarenes can be reduced into the corresponding amines by H_3SiPh at 110°C in the presence of $FeBr_2$ and PPh_3 (Scheme 49). The reactions are tolerant to numerous different functional groups, including C=O, C≡N, C=C, and OH groups. Other silanes (PMHS, H_2SiPh_2, $HSiEt_3$, $HSi(OEt)_3$) as well as other iron salts ($Fe(OAc)_2$, $Fe(acac)_2$, Fe(II)stearate, $Fe(CO)_5$, $FeCl_3*_6H_2O$, or $Fe(ClO_4)_3*nH_2O$) can also be used in this method, but lower conversions of nitroarenes were achieved.[4b]



Scheme 49. Reduction of nitroarenes in the presence $FeBr_2$

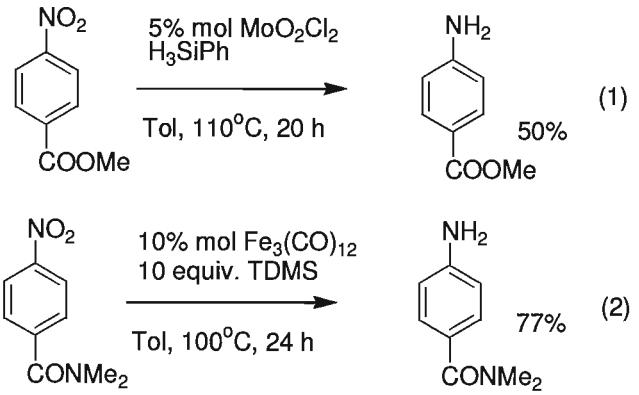
Another iron-based catalytic system was simultaneously developed by Lemaire et al.[4c] In contrast to the previously described Beller's system, cheap PMHS and TDMS can be effectively used as reducing agents in this case (Scheme 50). This method is very sensitive to the choice of iron salts and satisfactory results were only achieved with $Fe(acac)_2$ and $Fe(acac)_3$. Under the optimised conditions (10% mol $Fe(acac)_2$, 4 equiv. of TDMS, THF, 60°C) nitroarenes with cyano, ester and bromo-groups can be reduced within 24-48 h. Notably, the reaction with 1,4-dinitrobenzene

resulted in the very selective reduction of only one nitro group with the formation of 4-nitroaniline. The reduction of nitroarenes is, however, not chemoselective in the presence of aldo-group, which is also reduced into alcohol under standard conditions.[4c]



Scheme 50. Reduction of nitroarenes wih TDMS in the presence of $Fe(acac)_3$

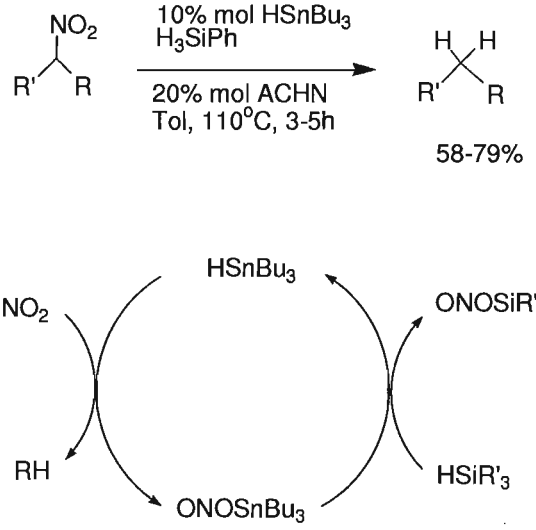
There are also several reports in literature which describe the catalytic reduction of only very specific nitro substrates with silanes. Thus, the reduction of 4-nitobenzoate into 4-aminobenzoate with H_3SiPh in the presence of MoO_2Cl_2 was reported by Fernandes and Romao (Scheme 51, eq. 1).[62] The reaction of N,N-dimethyl-p-nitrobenzamide with TDMS in the presence of $Fe_3(CO)_{12}$ afforded N,N-dimethyl-p-aminobenzamide in 77% yield (Scheme 51, eq. 2).[6b]



Scheme 51. Reduction of nitroarenes in the presence of molybdenum and iron catalysts

Fu et al.[76] showed that nitroalkanes could be also reduced into alkanes with H_3SiPh in the presence of catalytic amounts of $HSnBu_3$ (Scheme 52, top). This method is partially based on the well-known ability of $HSnBu_3$ to reduce nitroalkanes. However, the *in situ* generation of $HSnBu_3$ from the reaction with a hydrosilane in a catalytic cycle was reported for the first time, and it could be considered as a more environmentally friendly version of the stoichiometric reaction with toxic $HSnBu_3$. This method requires high temperature (110°C) and the presence of a radical initiator, such as 1,1'-azobis(cyclohexanecarbonitrile) (ACHN), but it can be used for the

reduction of a variety of nitroalkanes in the presence of different functionalities such as ethers, acetals, ketones, esters, nitriles, and mesylates. The proposed catalytic cycle for this reaction includes the reaction of $HSnBu_3$ with nitroalkane with the generation of an alkane and formation of $ONOSnBu_3$, which can be converted back into $HSnBu_3$ by the reaction with hydrosilanes (Scheme 52, bottom).[76]

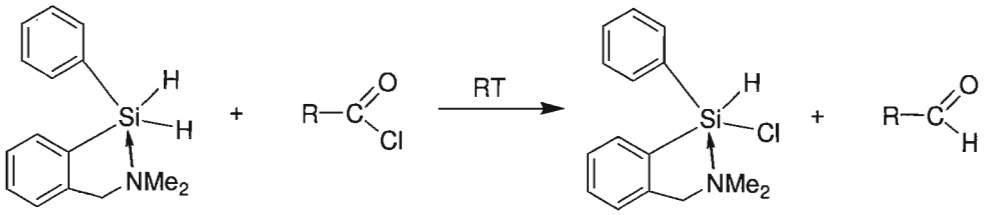


Scheme 52. Reduction of nitro compounds in the presence of $HSnBu_3$

II.1.6 Reduction of acid chlorides

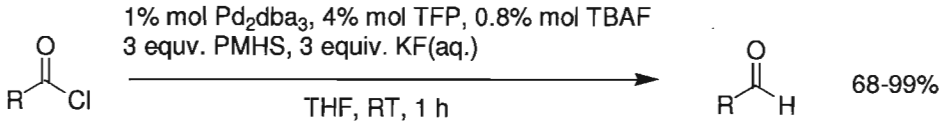
The use of hydrosilanes for dehalogenation/reduction of alkyl and aryl halides has been extensively studied and has already found important applications for these purposes.[7] On the other hand, reduction of other halogen containing compounds received much less attention. Despite the fact that conversion of acid chlorides into aldehydes is a very common transformation in organic chemistry, utilisation of hydrosilanes as reducing agents for this reaction is still very rare. In addition to the classical Rosenmund reaction, acid chlorides are usually reduced to aldehydes with different alumo- and borohydes.[77] Milder reducing agents have been also developed.[78] As an alternative method, reduction with organotin compounds has been applied.[79] However, the organotin compounds are toxic and unstable, which makes the development of new alternative procedures with hydrosilanes more desirable. Reduction of acid chlorides with hydrosilanes represents a very challenging chemoselectivity problem, which consists in stopping the reaction at the stage of highly reactive aldehydes without further reduction into silyl ethers.

The first report on the reaction of acid chlorides with silanes appeared in 1950. Jenkins and Post[80] described non-catalytic and $AlCl_3$–catalyzed reactions of acyl chlorides with $HSiPh_3$ and $HSiEt_3$, which gave low yields of aldehydes. Heterogeneous Pd-catalyzed reduction of different acid chlorides with $HSiEt_3$ was performed by Citron.[81] This more general approach allowed for the preparation of aldehydes in 40-70% yield. Reduction of acid chlorides under harsh conditions in the presence of Group 9 and 10 metal complexes was reported by Eaborn and co-workers.[81] Corriu et al.[82] reported highly reactive silanes, activated by intramolecular pentacoordination. These silanes react with acid chlororides in the absence of any catalyst with almost quantitative yields of aldehydes (Scheme 53). This method can be effectively used for the preparation of aromatic, aliphatic and heteroaromatic aldehydes, containing methoxy, ester and halo-groups in the molecule.[82]



Scheme 53. Reduction of acid chlorides with hypervalent silanes

A new method for catalytic conversion of acid chlorides into aldehydes was recently reported by Maleczka et al.[83] This method requires addition of 3 equivalents of aqueous potassium fluoride as well as catalytic amounts of $Pd_2(dba)_3$, TBAF (which facilitates phase transfer) and trifurylphosphine (TFP) to the reaction mixture. Under these conditions, aromatic and heteroaromatic acid chlorides can be reduced into aldehydes with cheap PMHS within 1 h at room temperature (Scheme 54). This method, however, cannot be used for the reduction of electron poor and alkyl acid chlorides.[83]

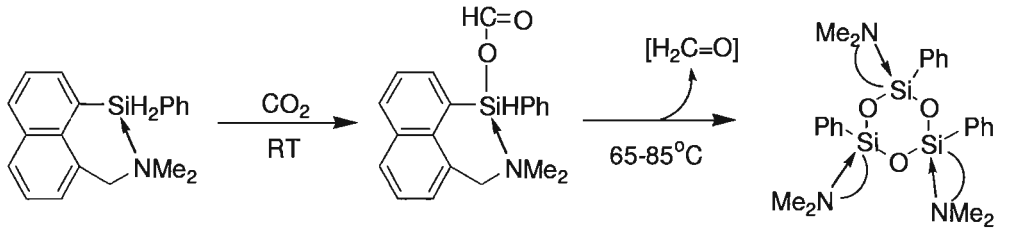


Scheme 54. Reduction of acid chlorides with PMHS in the presence of $Pd_2(dba)_3$

II.1.7 Hydrosilylation of carbon dioxide

Readily available and non-toxic carbon dioxide is a very attractive source of carbon for preparation of valuable organic compounds. However, CO_2 is a very thermodynamically stable molecule and its reduction usually requires activation for efficient transformation. Reduction of carbon dioxide under different catalytic conditions could be used for preparation of carboxylic acids, methane, methanol etc. In contrast to hydrogenation, utilization of hydrosilanes for the reduction of carbon dioxide allows to overcome the unfavourable thermodynamics due to the formation of the very stable Si-O bonds.[84] Hydrosilylation of CO_2 is still a very challenging process, but significant progress has been achieved in this field during past years.

Corriu et al.[85] demonstrated in 1988 that some highly reactive hypervalent silanes could react with CO_2 without any catalyst at room temperature. The resulting silyl formate species could be decomposed then at 65-85°C with evolution of formaldehyde, which was trapped by 2,4-dinitrophenylhydrazine (Scheme 55).[85]

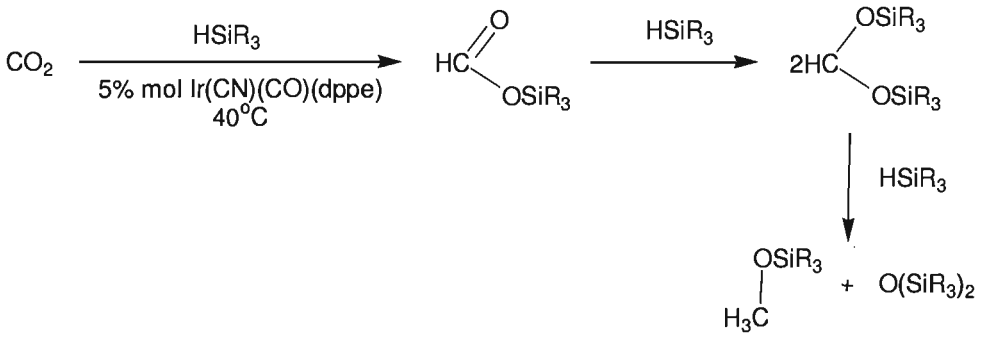


Scheme 55. The reaction of CO_2 with hypervalent silanes

Catalytic hydrosilylation of CO_2 was for the first time reported simultaneously by the research groups of Suss-Fink and Koinuma in 1981. Suss-Fink et al.[86] discovered a reaction between triethylsilane and CO_2 to give silyl formate HCO_2SiEt_3 in the presence of anionic ruthenium cluster $[N(PPh_3)_2][HRu_3(CO)_{11}]$. Koinuma et al.[87] reported the preparation of $HCO_2SiMeEt_2$ and $HCO_2SiMe(OMe)_2$ by the reaction of corresponding silanes with CO_2 in the presence of different transition metal catalysts, such as $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $Pd(PPh_3)_4$. However, in spite of the high temperature (80-120°C) and pressure of CO_2, the yields of silyl formates did not exceed 14%.

The reduction of CO_2 by hydrosilanes catalyzed by Ir(CN)(CO)(dppe) was reported by Eisenberg and Eisenschmid in 1989.[84] The reactions proceed under very

mild conditions at 40°C under one atmosphere of CO_2. Different silanes, such as $HSiMe_3$, H_2SiEt_2 or H_2SiMe_2 can be applied for the reduction. Importantly, silyl formates, which are initially formed in the reaction, can be further reduced into methoxysilanes and siloxanes by this method (Scheme 56). Unfortunately, no yields of final products were reported and long reaction times (weeks) are required under usual conditions.

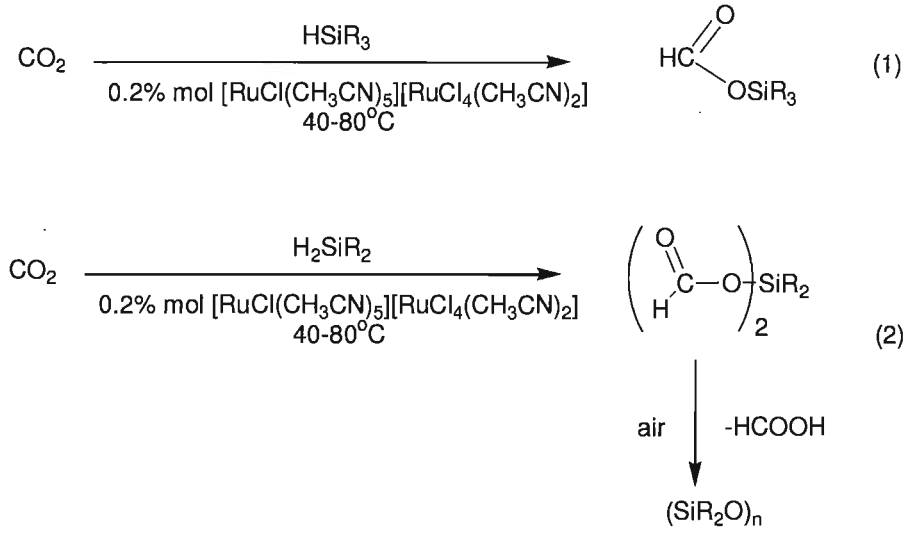


Scheme 56. Hydrosilylation of CO_2 in the presence of Ir(CN)(CO)(dppe)

Hydrosilylation of supercritical CO_2 (200-220 atm) was performed in the presence of $RuH_2(PMe_3)_4$ by Jessop.[88] The reaction proceeds at 75-100°C with good TON of 62. However, special equipment is required for this method and many catalytic reactions in liquid solvents have proven to be much more effective, which means that further improvements for the hydrosilylation of supercritical CO_2 are needed.

Pitter et al.[89] found in 2000 that hydrosilylation of carbon dioxide could be effectively catalyzed by $RuCl_3*nH_2O$ in CH_3CN. Importantly, the reaction can be performed with both aryl and alkyl silanes, which allows for preparation of a larger variety of silyl formats (Scheme 57, eq. 1). It was noticed that hydrosilylation of CO_2 in the presence of $RuCl_3*nH_2O$ can be performed only at 80°C and higher. Such a high temperature is required for the formation of ruthenium species $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$, which was isolated and characterized by X-ray structure analysis. It was found that complex $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$ by itself catalyses hydrosilylation of CO_2 with TON of 465 and TOF of 233 h^{-1}. It is one of the most active catalysts among all the known transition metal complexes, which have ever been used for this reaction. Moreover, complex $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$ effectively operates even at temperatures as low as 40°C. There is a strong dependence of the activity of the catalyst on the solvent.

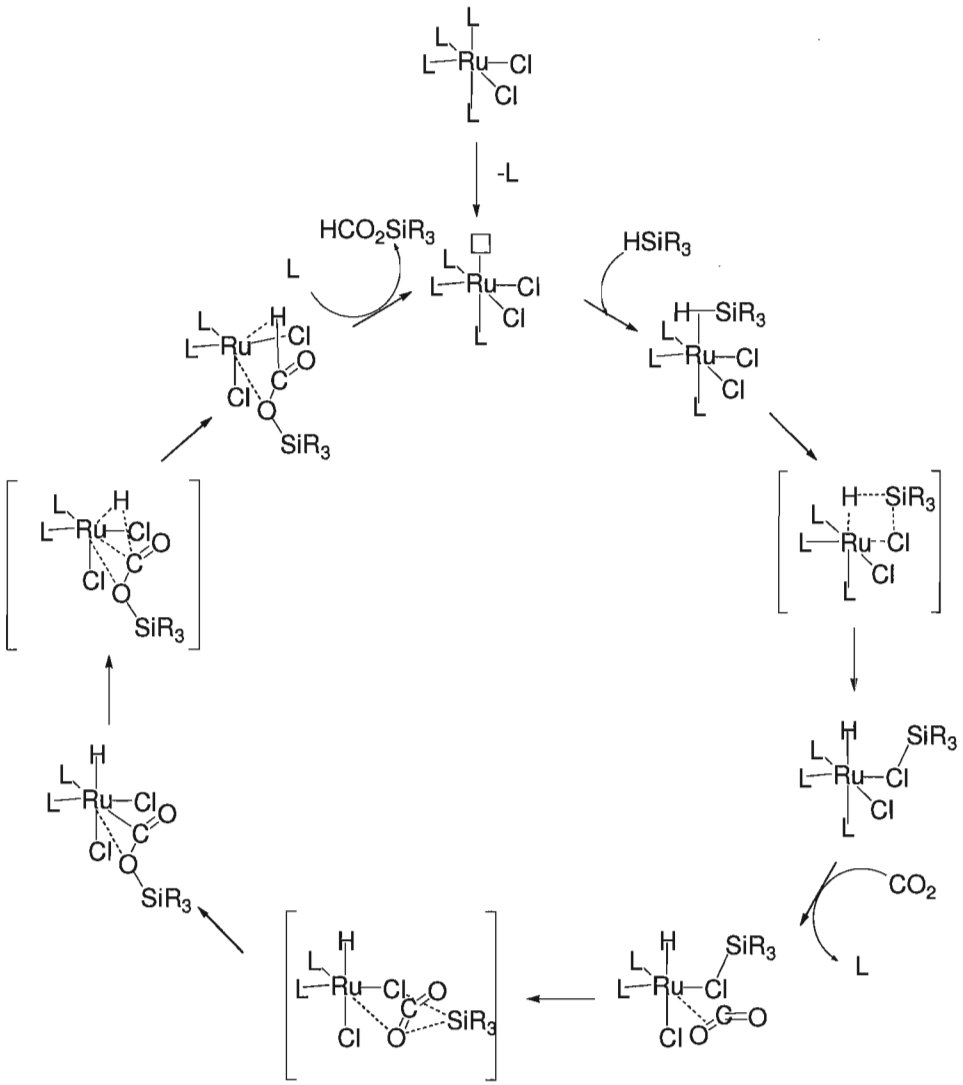
Good results were achieved in nitrile solvents, such as MeCN, EtCN, $Ph(CH_2)_2CN$. On the other hand, complex $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$ showed little or no catalytic activity in benzene, pyridine, dichloromethane and tetrahydrofuran. Addition of tertiary phosphines as well as hemilabile ligands, such as $R_2P(CH_2)_nCN$ or $R_2P(CH_2)_n(C_5H_5N)$, to the reaction mixture has proven to be beneficial for the stability of the catalyst, and improved yields of silyl formates were obtained in this case. Importantly, complex $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$ can be recycled after hydrosilylation and used again in the reaction for up to 10 times without a significant decrease in selectivity. Also, hydrosilylation of CO_2 with dihydrosilanes, such as H_2SiEt_2 or H_2SiPh_2, resulted in preparation of corresponding bis(formoxy)silanes in 80% and 39% yields, respectively (Scheme 57, eq. 2). Upon exposure to air, the latter compounds can be easily converted into a mixture of silicone oligomers and polymers with molecular weights up to 80000 g/mol (Scheme 57, eq. 2).[89]



Scheme 57. Hydrosilylation of CO_2 in the presence of $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$

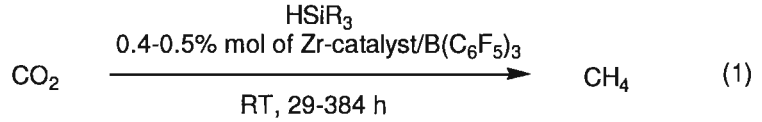
Due to the presence of both Ru(II) (cation) and Ru(III) (anion) in complex $[RuCl(CH_3CN)_5][RuCl_4(CH_3CN)_2]$, the question about the oxidation state of the actual catalyst arises. Therefore, Ru(II) complexes of the type $RuX_2(CH_3CN)_4$ and Ru(III) complexes of the type $RuX_3(CH_3CN)_3$ (X = Cl, Br) have been synthesised and used in catalysis.[89c] The best catalytic activity was observed with Ru(III) complex $RuCl_3(CH_3CN)_3$ (TOF = 390 h^{-1}), which was more active than its Ru(II) analogue $RuCl_2(CH_3CN)_4$ (TOF = 260 h^{-1} for the cis-isomer and 140 h^{-1} for the trans-isomer). Surprisingly, there is a strong dependence of catalytic activity on the type of halogen

in the precatalyst, and analogous ruthenium bromide complexes $RuBr_2(CH_3CN)_4$ and $RuBr_3(CH_3CN)_3$ were much less active. The effect of higher catalytic activity of the Ru(III) chloride complexes could be explained by the *in situ* reduction of the ruthenium complex by silane and generation of chlorosilanes $ClSiR_3$, which could possibly promote hydrosilylation. And indeed, formation of $ClSiMe_2Ph$ was observed in the reaction of $HSiMe_2Ph$ with $RuCl_3(CH_3CN)_3$. Moreover, addition of $ClSiMe_2Ph$ to the reaction mixture significantly accelerates the hydrosilylation of CO_2 in the presence of usually less active Ru(II) complex $RuCl_2(CH_3CN)_4$, but has almost no effect on the reaction mediated by $RuCl_3(CH_3CN)_3$ because it already has the potential for generating the chlorosilane.



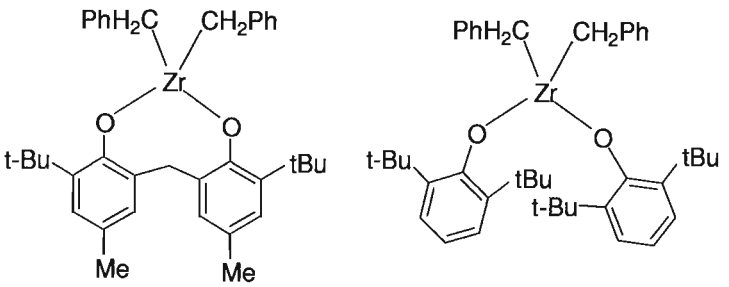
Scheme 58. The proposed mechanism of hydrosilylation of CO_2 in the presence of $RuCl_2(CH_3CN)_4$

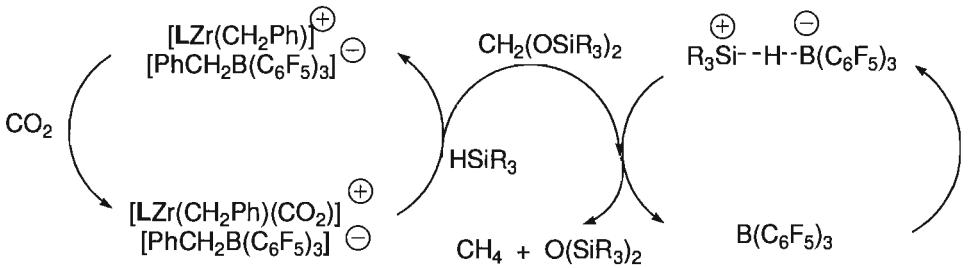
The above observations as well as DFT (BP86) calculations allowed the authors to propose a mechanism of hydrosilylation (Scheme 58), which starts with dissociation of one of the ligands in $RuCl_2L_4$ in order to free a coordination site for the subsequent reaction with silane. The resulting ruthenium σ-complex $RuCl_2(\eta^2\text{-}HSiR_3)L_3$ then rearranges into a ruthenium hydride complex with coordinated chlorosilane, $HRuCl(ClSiR_3)L_3$. The latter could react with a molecule of CO_2 after dissociation of one of the labile ligands L with the formation of complex $HRuCl(ClSiR_3)(\eta^2\text{-}CO_2)L_2$. The silyl group then migrates to the coordinated carbon dioxide affording complex $HRuCl_2(\eta^2\text{-}CO_2SiR_3)L_2$, which rearranges into $RuCl_2(HCO_2SiR_3)L_2$ *via* hydride transfer to carbon. Finally, addition of ligand L and elimination of silyl formate regenerates the catalyst.[89c]



(1)

Examples of Zr-catalysts:

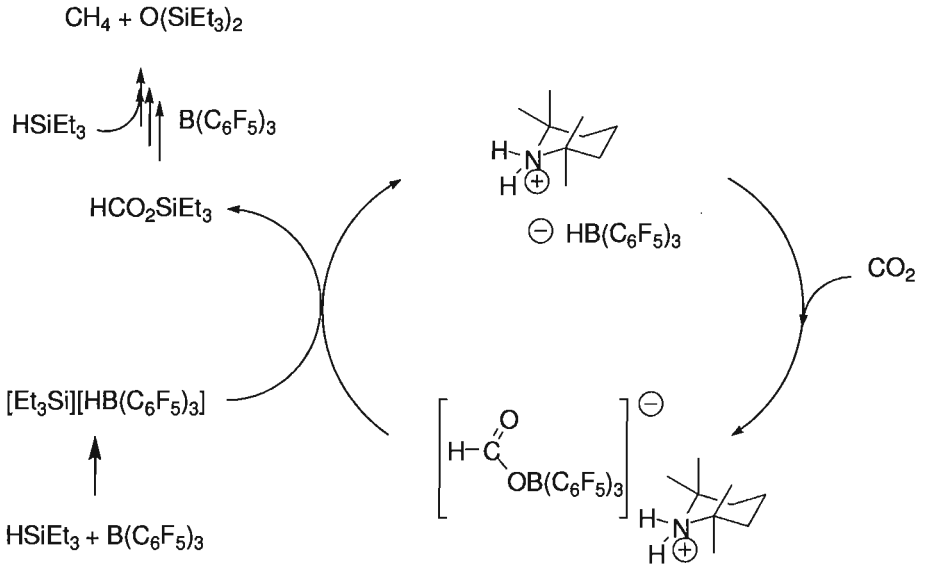




Scheme 59. Reduction of CO_2 in the presence of $LZr(CH_2Ph)_2/B(C_6F_5)_3$

The reduction of carbon dioxide with hydrosilanes catalyzed by cationic zirconium complexes was discovered by Matsuo and Kawaguchi.[90] An interesting feature of this system is that it allows for the reduction of carbon dioxide into methane

(Scheme 59, eq. 1). Importantly, the reduction of CO_2 can be effectively performed even at room temperature with tertiary, secondary and primary silanes. Also, this method should be considered for preparation of valuable siloxanes, which are formed as by-products of the reaction. In addition to the zirconium dibenzyl complexes, the procedure also requires catalytic amounts of $B(C_6F_5)_3$. Presumably, coordination of CO_2 to the electrophilic zirconium centre promotes hydrosilylation with the formation bis(silyl)acetal $H_2C(OSiR_3)_2$ (Scheme 59, bottom), which was detected by NMR spectroscopy in the reaction mixture. Addition of $B(C_6F_5)_3$ to the reaction does not only generate the catalytically active cationic zirconium species $[LZr(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ from $LZr(CH_2Ph)_2$, but also catalyzes the conversion of (silyl)acetal $H_2C(OSiR_3)_2$ into methane and siloxanes.[90]



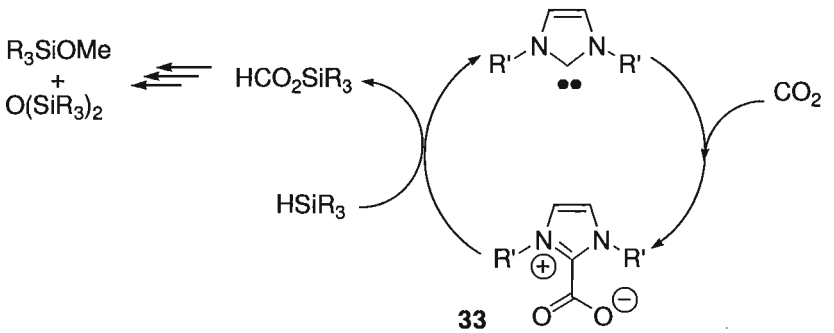
Scheme 60. Reduction of CO_2 in the presence of frustrated Lewis pair and $B(C_6F_5)_3$

A closely related catalytic system has been recently reported by Piers et al.,[91] who performed reduction of CO_2 into CH_4 catalyzed by frustrated Lewis pair consisting of 2,2,6,6-tetramethylpiperidine (TMP) and $B(C_6F_5)_3$. The ammonium borohydride $[HB(C_6F_5)_3][TMPH]$, which was prepared by the reaction TMP with $B(C_6F_5)_3$ in the presence of H_2, can effectively bind CO_2 affording formatoborate $[HCO_2B(C_6F_5)_3][TMPH]$ (Scheme 60). The latter compound does not react with $HSiEt_3$ under normal conditions. However, the reaction with $HSiEt_3$ proceeds smoothly with the formation of silyl formate HCO_2SiEt_3 and the starting ammonium borohydride $[HB(C_6F_5)_3][TMPH]$ in the presence of $B(C_6F_5)_3$, which activates silane

via formation of silyl borohydride intermediate $[Et_3Si][HB(C_6F_5)_3]$. Therefore, a catalytic cycle depicted on Scheme 60 becomes feasible. The silyl formate HCO_2SiEt_3, which is initially formed in the reaction, is then converted into CH_4 and $O(SiEt_3)_2$ by a sequence of borane catalyzed reactions.[91]

Another transition metal free catalytic system for the reduction of CO_2 was discovered by Ying et al.[92] It was shown, that heterocyclic carbenes (NHC) catalyze the reaction between silane and CO_2 with formation of CH_3OSiR_3 and $O(SiR_3)_2$ (Scheme 61, eq. 1). Importantly, this reaction can be performed at room temperature with very small loadings of the catalyst (0.05% mol). Heterocyclic carbenes showed remarkable catalytic activity (TON of 1840 and TOF of 25.5 h^{-1}) with dihydrosilanes. On the other hand, the reactions with monohydrosilanes were sluggish or did not proceed. Little is known about the mechanism of the reaction, but the proposed catalytic cycle includes coordination of CO_2 to carbene to give imidazolium carboxylate **33** (Scheme 61, bottom), which could then react with silane with the formation of silyl formate HCO_2SiR_3. The latter then undergoes several carbene catalyzed transformations yielding the final products of the reaction.[92]

$$CO_2 + 3HSiR_3 \xrightarrow[\text{DMF, RT, 72 h}]{\text{0.05\% mol NHC}} R_3SiOMe + O(SiR_3)_2 \quad (1)$$

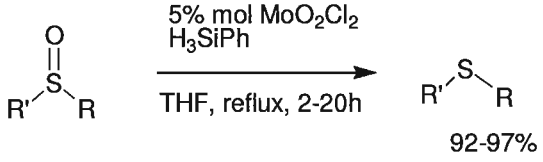


Scheme 61. Reduction of CO_2 in the presence of heterocyclic carbenes

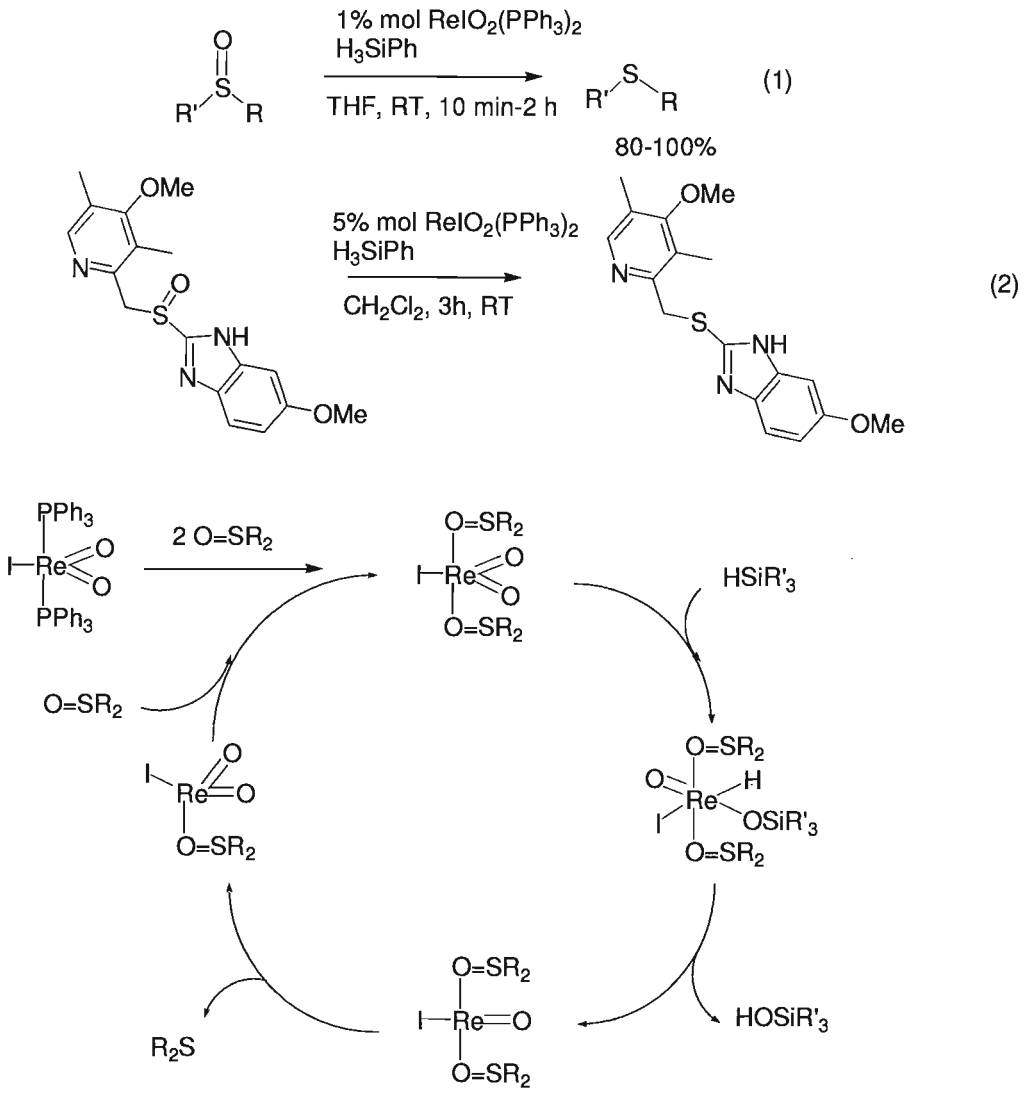
II.1.8 Reduction of sulfoxides, amine N-oxides and phosphine oxides

Hydrosilylanes are very effective reducing agents for a large number of abundant classes of organic compounds. On the other hand, there are also many applications of hydrosilanes for the reduction of less common substrates, which are still of great interest for more specific purposes. One of these applications is the reduction (deoxygenation) of sulfoxides, amine N-oxides and phosphine oxides.

The reduction of sulfoxides into corresponding sulfides is an important transformation in organic synthesis. There are many different procedures developed to reduce sulfoxides, but most of them require elevated temperature or the use of stoichiometric amounts of metal hydride or borohydride reagents, which are usually not selective to many functional groups.[93] On the other hand, catalytic reduction of sulfoxides with silanes could be very selective in the presence of appropriate catalysts. Fernandes and Romao[94] disclosed a very convenient protocol for the preparation of sulfides from sulfoxides in the presence of oxo molybdenum complex MoO_2Cl_2. Under optimized conditions, the reduction of sulfoxides proceeds smoothly in refluxing THF and is tolerant to halo-, ester- and alkene-groups (Scheme 62). The reactions can be performed with different silanes, including PMHS, H_3SiPh and $HSiEt_3$. Some of the sulfoxides can be effectively reduced even in water in the presence of air stable $MoO_2Cl_2(H_2O)_2$, which opens new horizons for the development of environmentally friendly procedures. However, more consistent results in the reactions mediated by $MoO_2Cl_2(H_2O)_2$ were achieved in organic solvents, such as THF and methanol.[93]



Scheme 62. Reduction of sulfoxides in the presence of MoO_2Cl_2

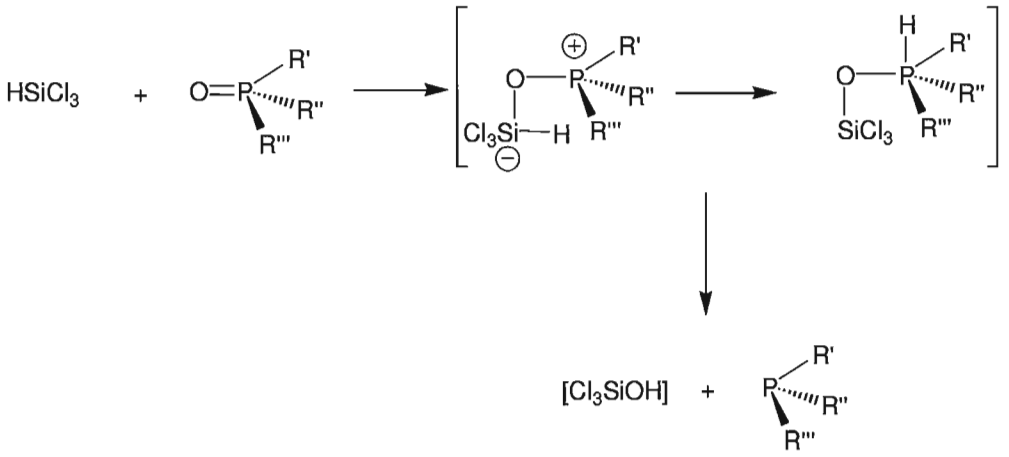


Scheme 63. Reduction of sulfoxides in the presence of $ReIO_2(PPh_3)_2$

Fernandes et al.[5a] also introduced another catalytic system for the reduction of sulfoxides, which showed remarkable tolerance to many functional groups, such as –CHO, $-CO_2R$, –Cl, $-NO_2$, and double or triple bonds. This system is based on the application of rhenium oxo complexes, which effectively catalyze reduction of sulfoxides with PMHS or H_3SiPh at room temperature (Scheme 63, eq. 1). Surprisingly, many different rhenium complexes showed good to excellent catalytic activity at room temperature, with $ReIO_2(PPh_3)_2$ being the most active catalyst. Unprecedented activity and selectivity of this catalytic system was also utilized for the reduction of a complex substrate with multiple functional groups, omeprazol, which was successfully reduced into the sulfide derivative in good yield (Scheme 63, eq. 2).

The proposed mechanism of rhenium-catalyzed reactions (Scheme 63, bottom) includes formation of the bis(sulfoxide) rhenium complex $ReIO_2(O{=}SR_2)_2$, which could react with silane *via* addition of Si-H bond across one of the Rh=O bonds. Elimination of silanol from the resulting complex $HReIO(OSiR'_3)(O{=}SR_2)_2$ gives monooxo Rh(III) complex $ReIO(O{=}SR_2)_2$, which could be converted into complex $ReIO_2(O{=}SR_2)_2$ with liberation of sulfide R_2S. Finally, the latter rhenium complex could react with another molecule of $O{=}SR_2$, which regenerates the starting rhenium complex in the catalytic cycle.[5a]

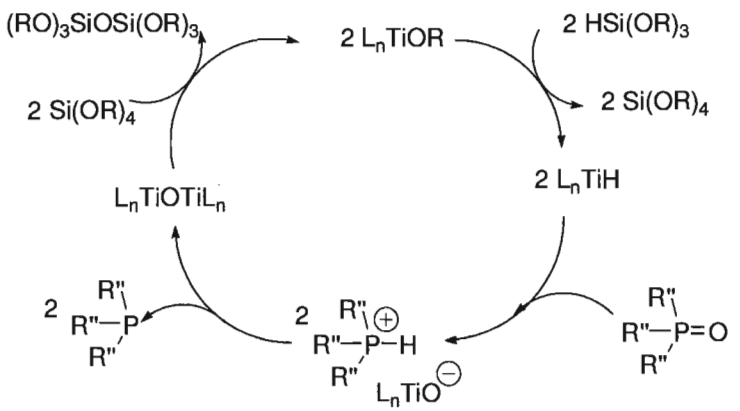
Reduction of phosphine oxides into corresponding phosphines is of significant importance to organometallic chemistry, as phosphines are one of the most abundant ligands for a large number of transition metal complexes and catalysts. Hydrosilanes, especially trichlorosilane, have been used for this reaction for decades.[95] A large number of different phosphine oxides can be reduced with $HSiCl_3$ without addition of any catalyst (Scheme 64). Interestingly, this reaction can be performed with inversion or retention of configuration of optically active phosphines, which could be controlled by addition of appropriate bases.[95a] The retention of configuration was observed in the presence of weak bases, such as pyridine and dimethylaniline. On the other hand, the reaction proceeds with inversion in the presence of stronger bases, such as triethylamine.[95a] This simple procedure has already become one of the standard methods for reduction of phosphine oxides and has been used numerous times in literature.[95] However, the yields of corresponding phosphines are usually quite moderate.



Scheme 64. Reduction of phosphine oxides with $HSiCl_3$

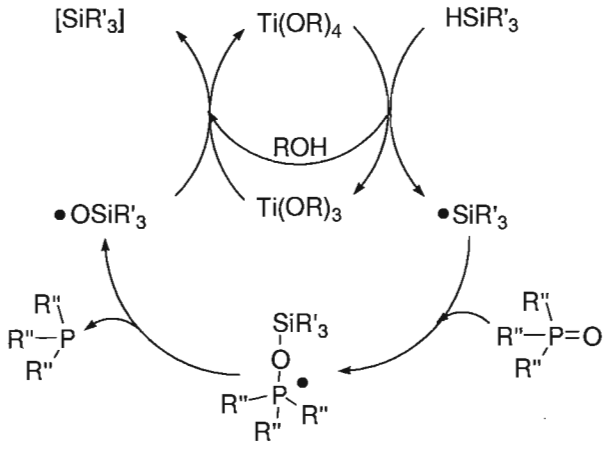
Phenylsilane was also successfully applied for the reduction of phosphine oxides in the absence of any catalyst. Marsi used this silane for preparation of a number of phosphines in high yields (87-96%).[95b] Notably, the reactions with phenylsilane proceed with very selective retention of configuration, which allows for preparation of optically pure phosphines.

Despite of the simplicity, the above methods of reduction of phosphine oxides require high temperatures and/or aqueous workup, which could result in oxidation of the product. To avoid these problems, a new catalytic method of reduction was developed by Lawrence et al.[16] This method is based on the use of the titanium catalytic system $Ti(Oi\text{-}Pr)_4/HSi(OEt)_3$, which was originally developed by Buchwald and Berk for the reduction of esters (see above). A wide range of phosphine oxides was reduced by this method at 67°C in THF. The phosphines were easily isolated from the reaction mixture by extraction with hexanes or crystallization of corresponding phosphonium salts. Notably, all the reactions proceed with the retention of configuration at phosphorus. Importantly, PMHS can be also effectively used as a reducing agent by this method, because $HSi(OEt)_3$ is known to cause explosions due to generation of pyrophoric SiH_4. The original mechanism of this reaction (Scheme 65) includes the formation of titanium hydride species $HTiL_n$, which could react with phosphine oxide to give the protonated phosphine [HPR'R''R''']$OTiL_n$. The latter could further react with another titanium hydride complex to afford the free phosphine, and the catalyst can be regenerated by the reaction with silane.[16]



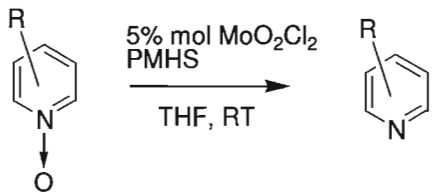
Scheme 65. The proposed mechanism for the reduction of phophine oxides with Lawrence's catalytic system

However, later Lemaire et al.[5c] proposed a different mechanism for this reaction with tetramethyldisiloxane (TMDS), which was based on the observation of paramagnetic Ti(III) species by EPR spectroscopy in the reaction mixture. According to this mechanism (Scheme 66), the titanium tetraalkoxide $Ti(OR)_4$ reacts with silane with the formation of titanium(III) complex $Ti(OR)_3$ and a silyl radical, which could further react with phosphine oxide to produce the free phosphine and another silyl radical species. The latter then reacts with $Ti(OR)_3$ to regenerate the catalyst.



Scheme 66. The proposed catalytic cycles for the reduction of phosphine oxides with Lemaire's system

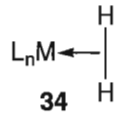
The reduction of N-oxides has received much attention especially because this reaction is one of the steps in the synthesis of many heteroaromatic compounds. Several silanes, such as Si_2Cl_6 or R_6Si_2 are capable of reducing N-oxides without any catalyst, but high temperatures are usually required and a very limited number of substrates were examined.[95a, 96] Catalytic deoxygenation of aromatic N-oxides at room temperature can be performed with Me_6Si_2 in the presence of NBu_4F (5% mol).[97] Fernandes and Romao[94] reported a very convenient method for the reduction pyridine N-oxides in the presence of catalytic amount of MoO_2Cl_2. The main advantages of this method are utilization of cheap PMHS as a reducing agent and very mild conditions of the reactions (Scheme 67).



Scheme 67. Reduction of pyridine N-oxide in the presence of MoO_2Cl_2

II.2 *Silane σ-complexes of transition metals*

In 1984, Kubas et al.[98] discovered a new type of non-classical dihydrogen complexes **34** (Figure 3, top). This finding has become one of the greatest discoveries of the late 20th century with a huge impact on the development of transition metal chemistry and catalysis.[12c] In general, by non-classical bond we assume delocalization of σ-bonds over three or more centres.[12c] The model of 3 centre-2 electron (3c-2e) interactions had been previously used for description of molecules like trihydrogen cation H_3^+, methonium cation CH_5^+, and polyboranes (Figure 3).[12c] Introduction of this concept to the organometallic chemistry allowed for much better understanding of activation of inert bonds by transition metal complexes. Since the Kubas' discovery a large number of non-classical complexes have been obtained with important implications to catalysis.[12a, 12d, 99]



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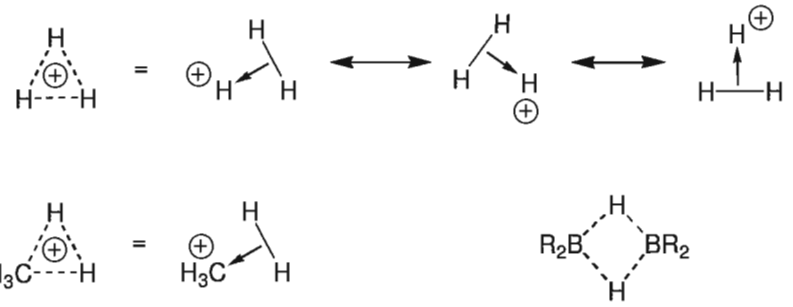


Figure 3. Molecules with (3c-2e) interactions

The first transition metal complex with non-classical Si···H interaction was the binuclear rhenium silane complex **35** (Figure 4), which was obtained by Graham et al. in 1969. Since then, due to the rapid development of various catalytic hydrosilylation reactions, numerous silane σ-complexes **36** have been obtained or postulated as important intermediates in different catalytic transformations.[12c] Also, new classes of non-classical silane complexes have been introduced (Figure 4).[12c] One of them, the agostic complexes **37**, differs from the σ-complexes **36** in the presence of a bridge between the metal and silicon atoms, which could consist of a direct M-Si bond or several atoms. New types of non-classical complexes with interligand

hypervalent interactions (IHI), as in complex **38**, and multiple silicon hydride interactions (complex **39**) have also been discovered. The main difference of the latter complexes from σ-complexes **36** is that non-classical bonding in **38** and **39** is delocalized over four and more centres. This bonding also requires a specific orientation of the silyl group and has a different dependence of structural parameters on the nature of substituents at silicon.[12c]

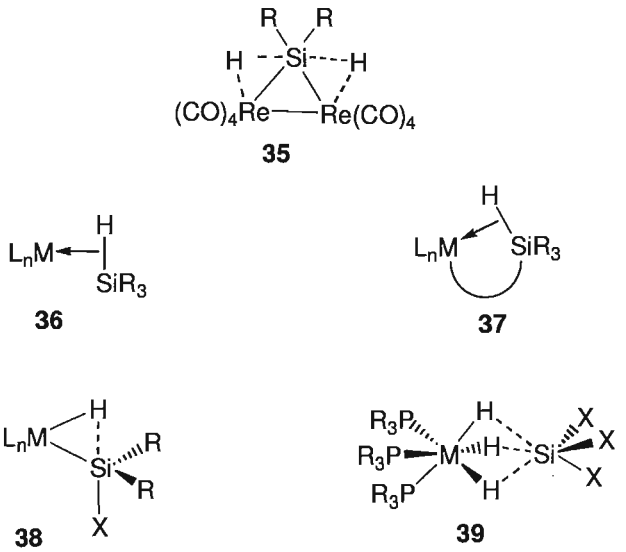
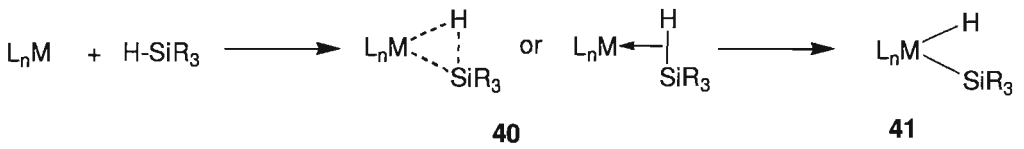


Figure 4. Examples of non-classical silane complexes

The activation of the Si-H bond by transition metal complexes is schematically depicted on Scheme 68. Cleavage of the Si-H bond with the formation of complex **41** can be viewed as a completed Si-H bond activation (oxidative addition), which also results in the formal oxidation of the metal centre due to formation of new M-H and M-Si bonds. In this case, the silane σ-complexes **40** can be described as complexes with incomplete Si-H bond activation, and the extent of this activation could vary depending on the nature of silanes and metal compounds.[12b]



Scheme 68. Schematic activation of Si-H bond by transition metals

In terms of molecular orbital theory, the formation of silane σ-complexes **40** (Scheme 68) can be explained using the well-known Dewar-Chatt-Duncanson (DCD)

diagram, which was originally suggested for the description of olefin complexes. In this case, the non-classical bonding consists of interaction of σ(Si-H) bonding and σ*(Si-H) antibonding orbitals with the orbitals of the metal centre (Figure 5).[12c] The strength of the σ*(Si-H) – metal interaction (backdonation) controls the extent of Si-H bond activation (oxidative addition), and complexes with strong backdonation tend to be closer in properties to the hydridosilyl complexes **41** (Scheme 68) with fully activated Si-H bond.[12c]

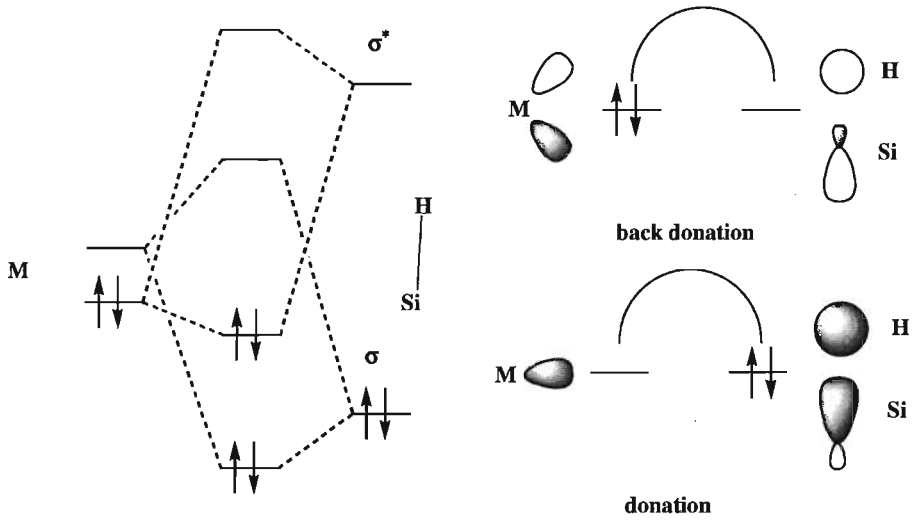


Figure 5. Dewar-Chatt-Duncanson model for the Si-H-M bonding

There are several factors which can influence the σ-bonding of silanes. One of them is the nature of substituents at silicon atom. Electron-donating groups at silicon increase the energy of both σ(Si-H) and σ*(Si-H) orbitals, which favours the donation component but decreases the backdonation.[12c] On the other hand, electron-withdrawing groups drive both bonding and antibonding orbitals lower in energy decreasing the donation but increasing the backdonation, which could lead to full oxidative addition of Si-H bond to the metal centre in an ultimate case.[12c] The other factor, which can influence the extent of Si-H bond activation, is the nature of the metal complex. Generally, the metals from the first transition series, metals in high oxidation state or cationic metal complexes have weak backdonation due to rather contracted d-orbitals. Relatively poor backdonation is also observed in the presence of π-acidic ancillary ligands (CO, PF_3) or strongly electron-withdrawing ligands in the metal complex.[12c]

II.2.1 Structural and spectroscopic features of silane σ-complexes

It can be assumed that a larger extent of oxidative addition of the Si-H bond to the metal centre results in shorter M-H and M-Si bonds and longer Si-H distance. However, assigning the presence or absence of Si-H interaction by using these structural parameters could be often problematic and not obvious.[12c] First of all, the structural data from the X-ray diffraction studies usually does not provide accurate information on the location of hydrogen atoms in the vicinity of heavy atoms, and the neutral diffraction studies of σ-complexes are scarce.[12c] As a result, there is a rather large inaccuracy in the lengths of M-H and Si-H bonds. However, there is a very rough criterion for the Si-H distance of 2.0 Å being the shortest non-bonding Si-H contact.[100] The M-Si distance is the only parameter, which can be reliably determined by X-ray crystallography, but the M-Si bonds depend significantly on the substitution at silicon, steric factors and the nature of ligands. In this case a proper choice of a classical reference silyl complex is required for the accurate comparison with a given silane σ-complex.[12c] It also should be mentioned that short distance between atoms in a metal complex could be also a result of steric forces, which could even create a repulsive interaction between these atoms.[12c]

Due to inaccuracy of X-ray structure analysis and high cost and complexity of neutron diffraction experiments, the NMR spectroscopy has become the most abundant method for characterization of silane σ-complexes. Corriu et al. found for that the silicon hydride coupling constant J(Si-H) of 65 Hz in the silane σ-complex $Mn(\eta^2\text{-H-SiPh}_3)(CO)_2Cp'$ is much higher than in classical silyl hydride complexes (J(Si-H) = 3-10 Hz).[101] Later, Schubert suggested to consider the values of 10-20 Hz as an approximate borderline between classical and non-classical silyl hydride complexes, with all the transition metal silane complexes which exhibit the J(Si-H) of more than 20 Hz to have a direct Si-H bond.[100] Obviously, there is an upper limit of the silicon proton coupling constant in silane σ-complexes, which cannot exceed the value of J(Si-H) in free hydrosilanes $HSiR_3$ (150-200 Hz for R = aryl, alkyl). Since then, this spectroscopic criterion of 20 Hz has been used for identification of the majority of silane σ-complexes. It is generally believed that with the increase of the oxidative addition of the Si-H bond to a metal centre the value of J(Si-H) decreases. However, the presence of substituents at silicon could significantly complicate this general trend. According to the Bent's rule,[102] in the presence of substituents with

different electoronegativities, the bonds of silicon to more electropositive substituents receive more of silicon s character, which makes these bonds shorter. On the other hand, the bonds to more electronegative substituents become longer due to increased p character of silicon.[12c] As a result, for example, the J(Si-H) of 370 Hz in free trichlorosilane $HSiCl_3$ is much larger than in hydrosilanes $HSiR_3$ with more electropositive alkyl and aryl substituents R (150-200 Hz).[12c] Thus, for the same extent of oxidative addition to a metal centre, the J(Si-H) of complexes with $HSiCl_3$ will be higher than for complexes with alkyl or aryl chlorosilanes. And indeed, Fenske-Hall calculation of $Mn(HSiCl_3)(CO)_2Cp$ revealed almost full oxidative addition of the silane to manganese.[103] However, the observed J(Si-H) of 55 Hz in the closely related complex $Mn(HSiCl_3)(CO)_2Cp'$ suggested the presence of significant Si-H interaction.[12e] As has already been discussed, this superficial contradiction is a result of the large s character in the weak Si-H bond of the mentioned above manganese complexes.

It should be noted that the observed silicon coupling constant in silane σ-complexes is actually a sum of a one bond (direct Si-H) and two-bond (H-M-Si) interactions: $J^{obs}(Si\text{-}H) = |{}^1J(Si\text{-}H) + {}^2J(Si\text{-}H)|$.[12c] The direct Si-H interactions usually have a negative sign of ${}^1J(Si\text{-}H)$ due to negative gyromagnetic ratio of silicon and two bond silicon proton coupling constants are in most cases positive.[12c] As a result, a problem could arise if the magnitudes of ${}^1J(Si\text{-}H)$ and ${}^2J(Si\text{-}H)$ are similar. In this case the possibly large absolute value of the direct ${}^1J(Si\text{-}H)$ could be compensated by the two-bond component ${}^2J(Si\text{-}H)$, and the resulting small value of $J^{obs}(Si\text{-}H)$ could be erroneously accounted for the absence of significant Si-H interactions.[12c] Therefore, it is usually safe to assign a non-classical bonding for the silane σ-complexes with relatively large J(Si-H) of 70-160 Hz. On the other hand, complexes with small values of J(Si-H) could require an independent investigation, such as, for example, the calculation of the sign of J(Si-H), for reliable conclusions on the type of bonding.[12c]

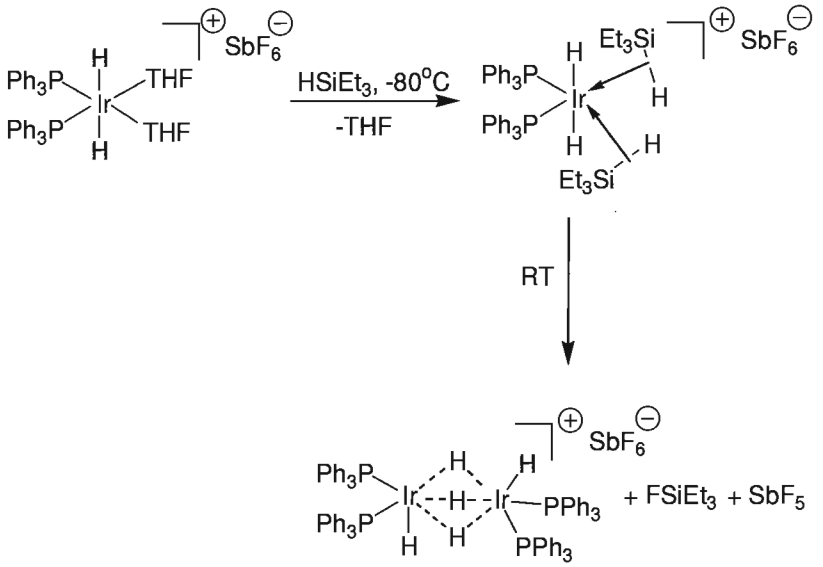
Silane σ-complexes usually exhibit a clear shift of the Si-H stretches to longer wavelengths in IR spectra. However, this trend becomes more complicated in the case of significant Si-H bond oxidative addition to metal due to the coupling of the Si-H and M-H vibrations.[12c]

II.2.2 Cationic silane σ-complexes

In comparison with the amount of known neutral silane σ-complexes, analogous cationic compounds are extremely rare. Such a big discrepancy is mostly explained by the instability and high reactivity of most of the cationic silane σ-complexes.[12b] Coordination of a silane to a cationic metal center significantly polarizes the Si-H bond and creates a highly electrophilic silicon atom, which is similar to the silicon in the silylium cations R_3Si^+. Therefore, the isolation of cationic silane σ-complexes requires elimination of any nucleophiles, which can potentially react with the coordinated silane. This usually rules out the employment of regular non-coordinative counter anions, such PF_6^-, BF_4^-, OTf^-, and only perfluorinated borates BAr'_4^- remain relatively inert. There is also a big problem with the dryness of appropriate solvents for the reactions, because cationic complexes are usually not soluble in non-polar solvents, and drying CH_2Cl_2 or PhCl over CaH_2 usually does not eliminate all traces of water, which could immediately react with the cationic silane σ-complex with the formation of silanols and siloxanes. Therefore, the preparation of cationic silane σ-complexes is a challenging task, and most of these compounds were obtained and characterized only at low temperature. However, all the efforts on preparation are usually rewarded by the discoveries of unique properties and/or high catalytic activities of cationic silane σ-complexes, which will be discussed further.

The first cationic silane σ-complex was obtained and investigated by Luo and Crabtree in 1989.[104] The iridium complex $[Ir(PPh_3)_2(H)_2(\eta^2\text{-}HSiEt_3)_2]SbF_6$ was obtained by the reaction of the cationic dihydride complex $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ with $HSiEt_3$ at -80°C (Scheme 69). The complex $[Ir(PPh_3)_2(H)_2(\eta^2\text{-}HSiEt_3)_2]SbF_6$ was characterized by NMR spectroscopy. Two hydride signals were observed in ^1H NMR: a triplet at -9.85 (J(P-H) = 16 Hz), which corresponds to the *trans* hydrides in the complex, and a multiplet at -12.75 ($J(P\text{-}H)_{trans}$ = 85 Hz), which was assigned to the silicon bound protons. Importantly, the latter $J(P\text{-}H)_{trans}$ is considerably smaller than typical values for classical iridium hydride complexes. Reduced phosphorus proton coupling constants are very typical for σ-complexes, which makes the J(P-H) one of the most valuable parameters for assigning σ-bonding. The deuterium labelling experiments revealed a fast exchange between the iridium and silicon bound protons, which could be explained by the presence of an equilibrium between the complex

$[Ir(PPh_3)_2(H)_2(\eta^2\text{-}HSiEt_3)_2]SbF_6$ and the silyl dihydrogen isomer $[Ir(PPh_3)_2(H)(H_2)(SiEt_3)(\eta^2\text{-}HSiEt_3)]SbF_6$. However, the latter has never been observed by NMR spectroscopy. Interestingly, complex $[Ir(PPh_3)_2(H)_2(\eta^2\text{-}HSiEt_3)_2]SbF_6$ is stable only at low temperature and the reaction of $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ with $HSiEt_3$ at room temperature resulted in preparation of iridium hydrogen bridged dimer $[Ir_2(H)_2(PPh_3)_4(\mu\text{-}H)_3]SbF_6$, $FSiEt_3$ and SbF_5 (Scheme 69). The formation of fluorosilane and SbF_5 can be explained by the reaction between the highly reactive cation $^+SiEt_3$, which was generated by the σ-complex, and counter anion SbF_6^-. An attempt to prepare a more stable σ-complex by the reaction of $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ with bis(silane) $H(SiEt_2)_2H$ was also unsuccessful, as the initially obtained σ-complex decomposes at room temperature in the same way.[104]

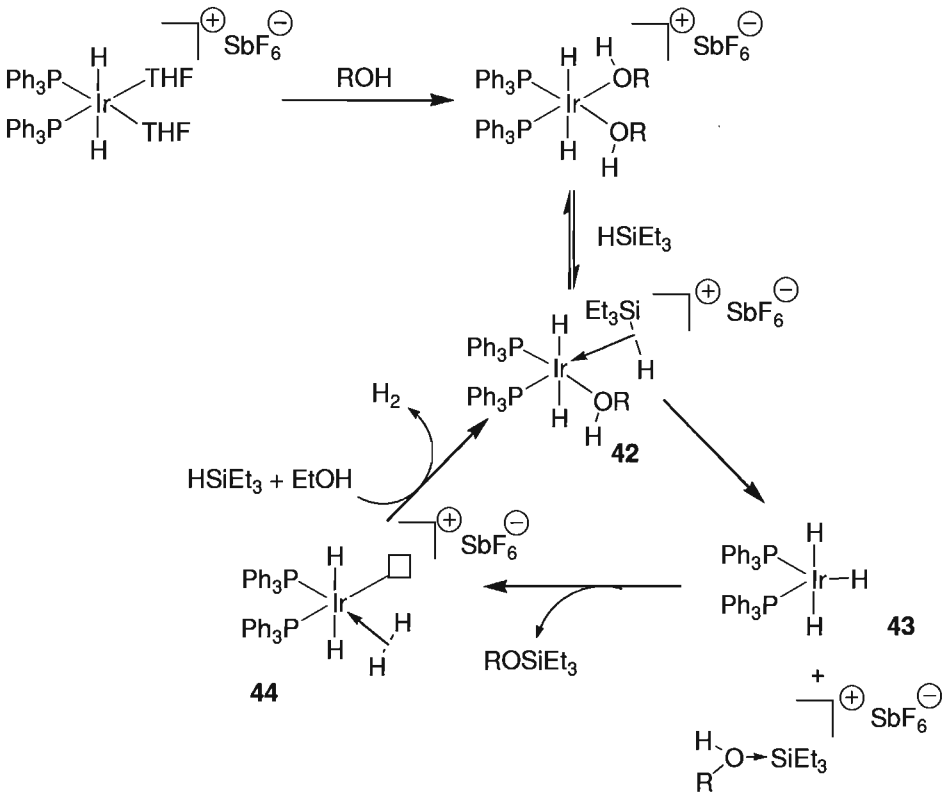


Scheme 69. The preparation of iridium complex $[Ir(PPh_3)_2(H)_2(\eta^2\text{-}SiEt_3)_2]SbF_6$

The complex $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ effectively catalyzes alcoholysis of silanes (Scheme 70, eq. 1).[104] A wide range of different alcohols undergo fast dehydrogenative coupling with $HSiEt_3$ at room temperature. The catalytic activity of complex $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ strongly depends on the nature of the counter anion in the complex. The best results were achieved with the SbF_6^- counter anion. On the other hand, complexes with BF_4^- and PF_6^- anions were less active due to faster deactivation of the catalyst. Extremely high catalytic activity of complex $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$ (up to 130000 h^{-1}) can be explained by the fact, that it can generate two vacant sites for both the silane and alcohol substrate, and the reaction

could go faster due to intramolecular interactions. And indeed, methanolysis of $HSiEt_3$ catalyzed by $[IrH(H_2O)(bq)(PPh_3)_2]SbF_6$, which can generate only one vacant site, was 60 times slower than the same reaction in the presence of $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$. Another unusual feature of this system is an irregular order in rates of the reactions with primary, secondary and tertiary alcohols: 2-butanol > *n*-butanol > *tert*-butanolthat (primary alcohols are usually the most active substrates). Presumably, primary alcohols, as better donors in comparison with secondary alcohols, bind stronger to the iridium centre and occupy both of the available vacant sites, which results in a slower reaction with silane.

$$ROH + HSiEt_3 \xrightarrow[CH_2Cl_2]{\text{0.4\% mol of } [Ir(PPh_3)_2(H)_2(THF)_2]SbF_6} ROSiEt_3 + H_2 \qquad (1)$$



Scheme 70. The proposed catalytic cycle for the alcoholysis of silanes in the presence of $[Ir(PPh_3)_2(H)_2(THF)_2]SbF_6$

The proposed mechanism of this reaction, which was based on the kinetic studies, involves the formation of cationic σ-complex **42** (Scheme 70, bottom), which

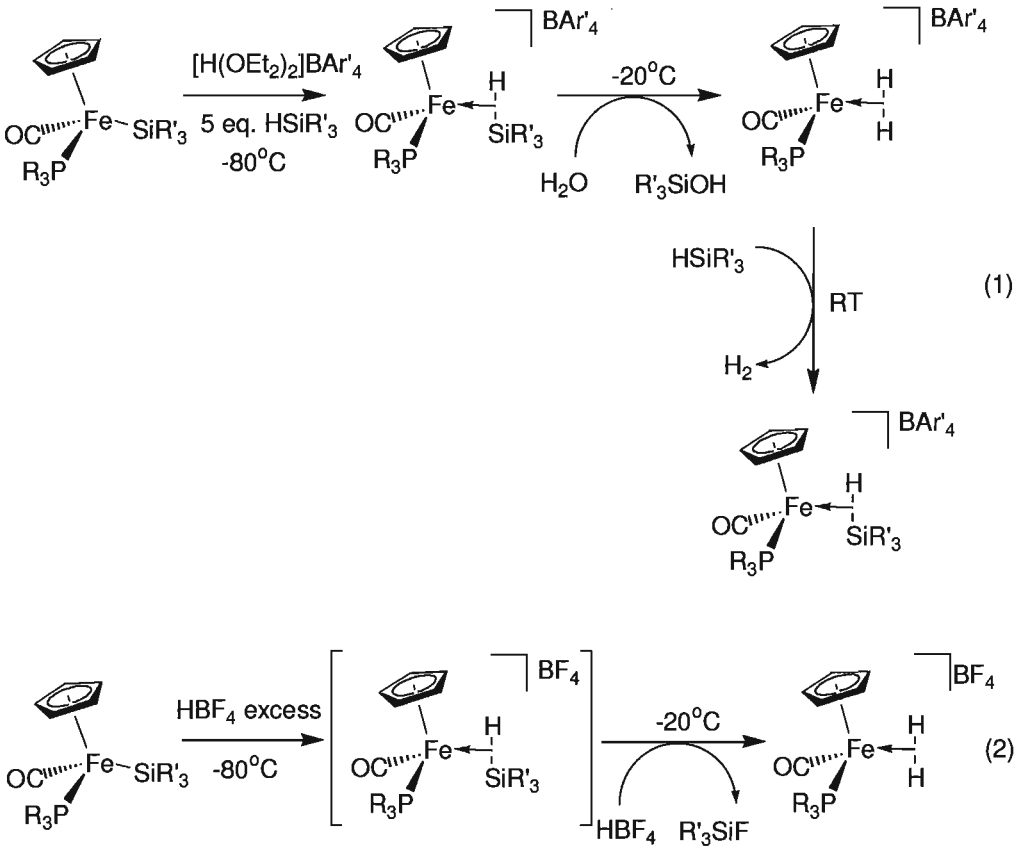
could undergo heterolitic splitting of the Si-H bond with the formation of a neutral iridium trihydride complex **43** and a silylium cation adduct with alcohol. Proton transfer from the latter to the iridium hydride could result in the formation of iridium dihydrogen complex **44** and a silyl ether. The release of hydrogen from **44**, followed by the reaction with alcohol and silane regenerates the catalyst.[104]

Cationic ruthenium silane σ-complex was, for the first time, obtained by Lemke in 1994.[105] Bis(phosphine) ruthenium σ-complex $[CpRu(PMe_3)_2(\eta^2\text{-}HSiCl_3)]^+$ was prepared by the reaction of the ruthenium silyl complex $CpRu(PMe_3)_2(SiCl_3)$ with $H(OEt_2)_2BAr'_4$ (Scheme 71). It was isolated in 88% yield and characterized by NMR spectroscopy. Compound $[CpRu(PMe_3)_2(\eta^2\text{-}HSiCl_3)]^+$ exhibits a triplet at –9.87 ppm with silicon satellites in ^1H NMR (J(P-H) = 11 Hz, J(Si-H) = 48 Hz). The value of J(P-H) is significantly smaller than the same parameter for classical ruthenium hydride complexes (~30 Hz).[105] In addition, the J(Si-H) in the compound $[CpRu(PMe_3)_2(\eta^2\text{-}HSiCl_3)]^+$ is relatively large, which is consistent with postulating of σ-bonding of silane to the ruthenium centre. Later, the structure of $[CpRu(PMe_3)_2(\eta^2\text{-}HSiCl_3)]^+$ was also confirmed by X-ray crystallography,[105b] which revealed an elongated Ru-Si distance (2.329 Å) and a short Si-H contact (1.77 Å). This is a very rare example of a cationic silane σ-complex, which was isolated at room temperature and characterized by X-ray crystallography.[105b]

Scheme 71. The synthesis of cationic complex $[CpRu(PMe_3)_2(\eta^2\text{-}HSiCl_3)]BAr'_4$

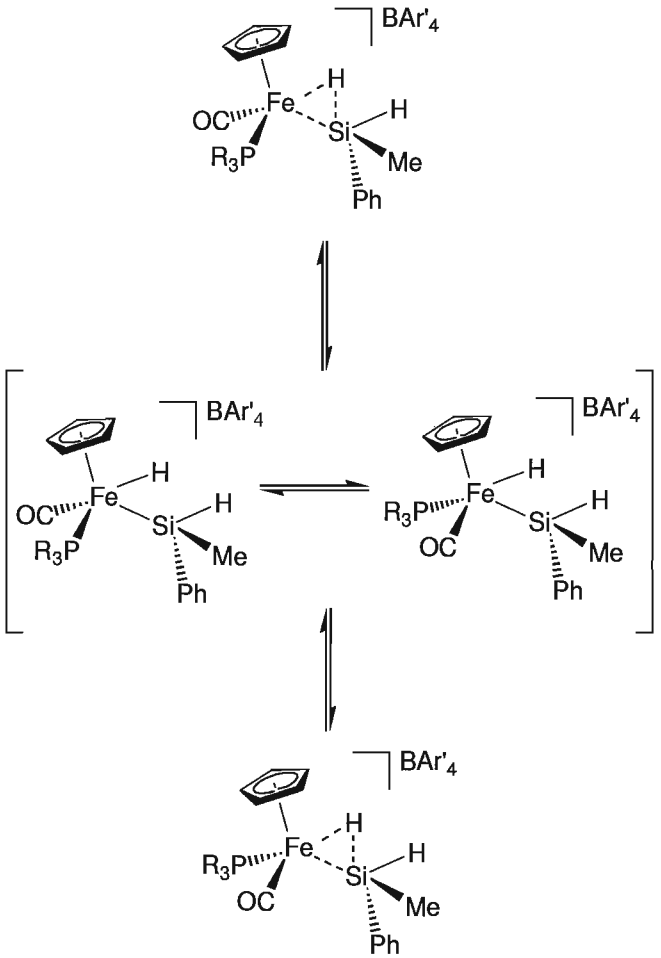
Brookhart et al.[106] prepared a series of cationic iron complexes, which were characterized by NMR spectroscopy. Treatment of the iron silyl complex $CpFe(PR_3)(CO)(SiR_3)$ with $H(OEt_2)_2BAr'_4$ at -78°C resulted in a clean formation of silane σ-complex $[CpFe(PR_3)(CO)(\eta^2\text{-}HSiR_3)]^+$, which reacts with traces of water at temperature higher than -40°C to give the cationic iron dihydride complex $[CpFe(PR_3)(CO)(\eta^2\text{-}H_2)]^+$ (Scheme 72, eq. 1). However, in the presence of excess silane corresponding silane σ-complexes can be obtained even at room temperature by further substitution of dihydrogen molecule in $[CpFe(PR_3)(CO)(\eta^2\text{-}H_2)]^+$ with silane

(Scheme 72, eq. 1). This procedure allowed for preparation of five new iron σ-complexes of type $[CpFe(CO)(PR_3)(\eta^2\text{-}HSiR'_3)]^+$ (PR_3=PEt_3 or PPh_3, SiR'_3= $SiHPh_2$, SiHMePh, SiH_2Ph, $SiEt_3$). These complexes exhibit relatively small J(P-H) in comparison with classical iron hydride compounds. The values of J(Si-H) fall in the range of 20-70 Hz, which is typical for silane σ-complexes. These observations strongly support the presence of the η^2-$HSiR'_3$ motif in the complexes. The stability of the above cationic iron σ-complexes depends on the nature of counter anion. Thus, the reaction of iron silyl complex $CpFe(PR_3)(CO)(SiR_3)$ with HBF_4 gave a mixture of dihydride complex $[CpFe(PR_3)(CO)(\eta^2\text{-}H_2)]^+$ and fluorosilane even at -90°C (Scheme 72, eq. 2). Therefore, stable cationic silane σ-complexes of iron could be prepared only in the presence of highly inert counter anions, such as BAr'_4^-. These complexes are extremely sensitive to any nucleophiles. For example, diethyl ether could to some extent abstract the silylium cation from the complex $[CpFe(CO)(PPh_3)(\eta^2\text{-}HSiEt_3)]BAr'_4$ with the formation of neutral iron monohydride $CpFe(PPh_3)(CO)H$ and $[Et_3Si(OEt_2)]BAr'_4$.[106]



Scheme 72. The synthesis of cationic iron silane σ-complexes

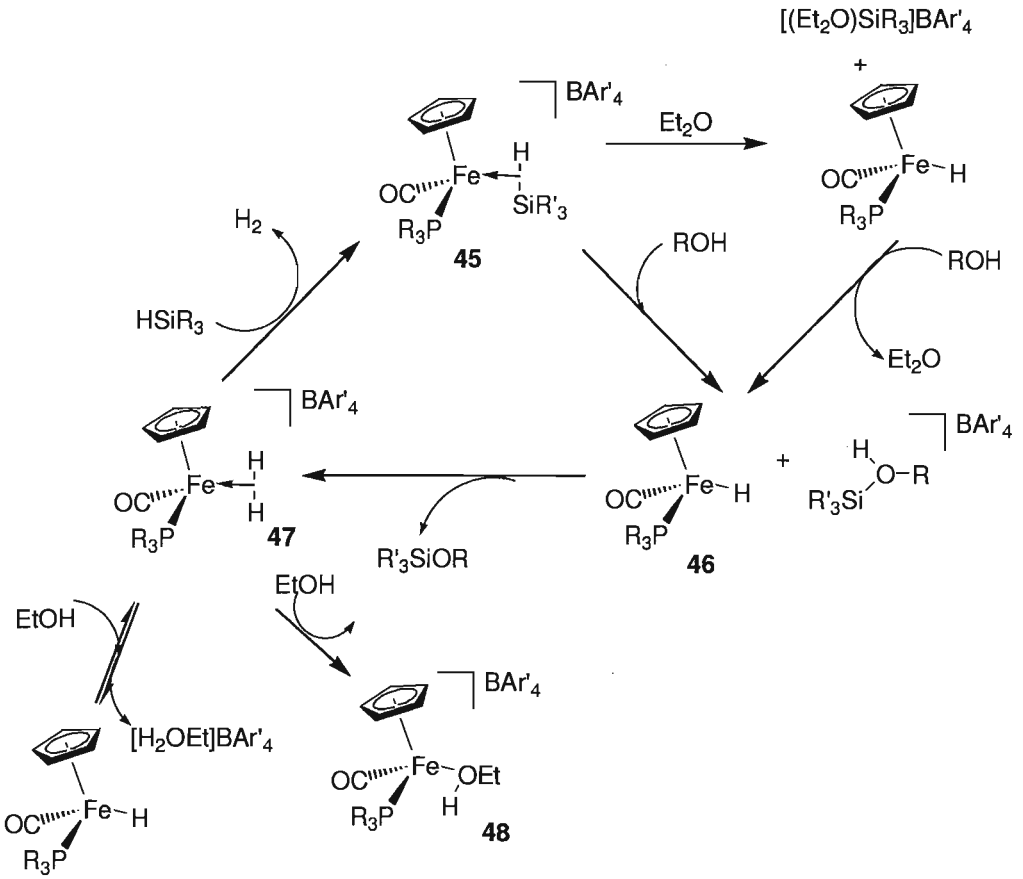
Interesting dynamic behaviour was observed for the cationic complex $[CpFe(CO)(PEt_3)(\eta^2\text{-}HSiHMePh)]BAr'_4$, which exists in a solution as an equilibrium mixture of two diastereomers.[106] Both of them can be observed by ^1H NMR at -80°C. Upon heating, the signals of two diastereomers coalesced, which supports the presence of an equilibrium between them. The interconversion of two diastereomers was proposed to undergo through a pseudorotation process, which involves full oxidative addition of silane followed by a switch of the CO and PEt_3 ligands.[106]



Scheme 73. Dynamic behaviour of complex $[Cp(CO)(PEt_3)Fe(\eta^2\text{-}HSiHMePh)]BAr'_4$ in the solution

Complex $[CpFe(PPh_3)(CO)(\eta^2\text{-}HSiH_2Ph)]BAr'_4$ catalyzes dehydrogenative coupling of $HSiEt_3$ with PhOH and EtOH.[107] Interestingly, fast alcoholysis was observed only in the reaction with PhOH. On the other hand, the reaction with EtOH was slow due to fast deactivation of the catalyst. Brookhart et al.[107] were able to

monitor the course of reactions at low temperature and observed most of the common deactivation pathways for the reaction with EtOH.

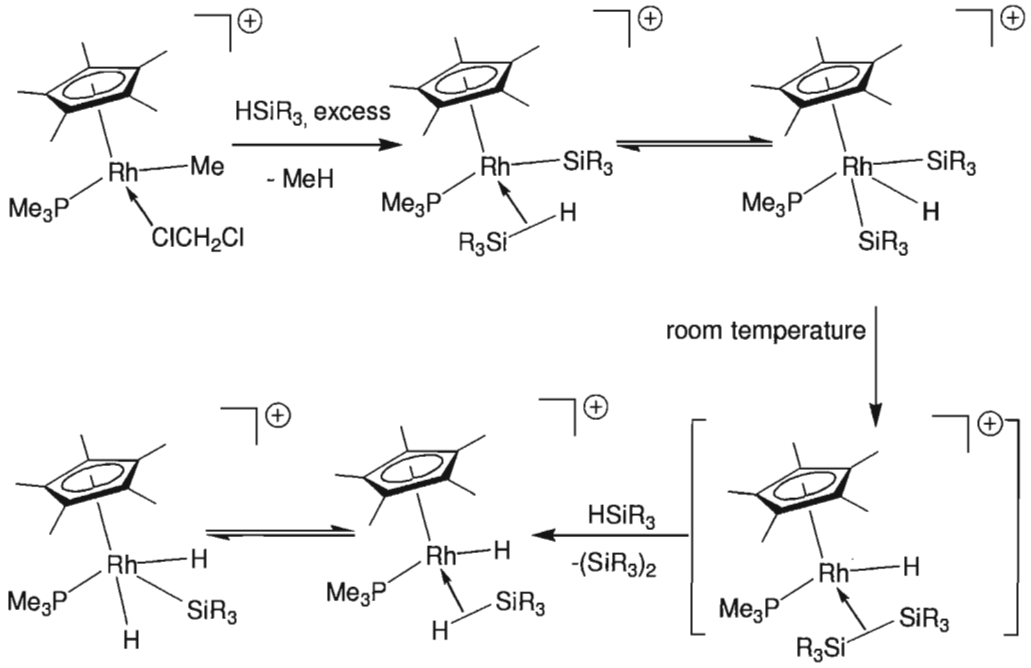


Scheme 74. The proposed mechanism of iron-catalyzed alcoholysis of silanes

The proposed general mechanism for the catalytic reaction is depicted on Scheme 74. The reaction starts with abstraction of the silylium cation from **45** with ROH followed by proton transfer to the iron hydride complex **46**. The resulting dihydrogen complex **47** could then react with silane and regenerate the catalyst. There is also a concomitant reaction of the silane σ-complex **45** with Et_2O, which comes from the starting $[H(OEt_2)_2]BAr'_4$. This reaction could generate small amounts of iron hydride complex and $[Et_3Si(OEt_2)]BAr'_4$. Also, a reversible reaction between iron dihydrogen complex and ethanol was observed, which results in the formation of iron monohydride and $[H_2OEt]BAr'_4$. Alternatively, the latter reaction could also lead to irreversible formation of complex **48**, which deactivates the catalyst. Notably, no reaction of dihydrogen complex **47** with PhOH was observed, which explains the high catalytic activity of the iron complex $[CpFe(PPh_3)(CO)(\eta^2\text{-}HSiH_2Ph)]BAr'_4$ in

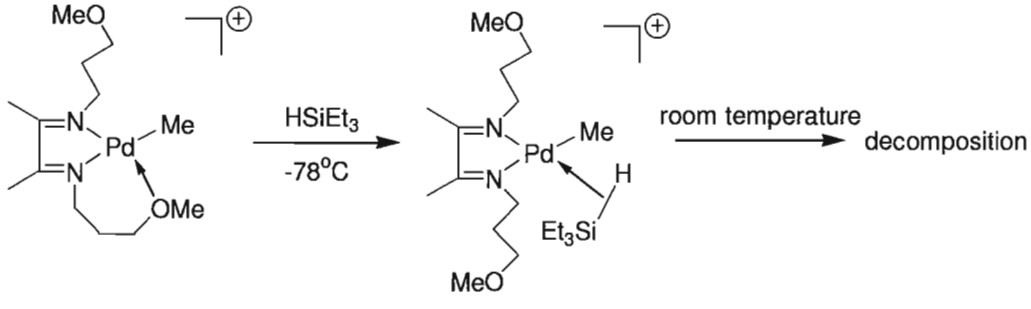
reactions with this alcohol.[107] Later, DFT calculations by Buhl and Mauschick[108] confirmed the proposed catalytic cycle, in which the replacement of dihydrogen in $[CpFe(PR_3)(CO)(\eta^2\text{-}H_2)]^+$ with silane was found to be the rate determining step. Interestingly, the calculations also predicted higher catalytic activity of the iron complexes with substituted Cp-ring.[108]

Treatment of the rhodium complex $Rh(Me)(ClCD_2Cl)(PMe_3)Cp^*$ with excess silanes at low temperature resulted in the formation of cationic silyl (η^2-silane) complexes $Rh(\eta^2\text{-}HSiR_3)(SiR_3)(PMe_3)Cp^*$, which were characterized by NMR spectroscopy (Scheme 75).[109] These complexes are very fluxional due to fast exchange of hydride between silyl and η^2-silane ligands. Therefore, the coupling constants J(Si-H) observed by NMR spectroscopy (28.5 Hz for R = Me and 27.8 Hz for R = Et) would be average of $J(\text{Si-H})_{terminal}$ in $Rh(H)(SiR_3)_2(PMe_3)Cp^*$ and $J(\text{Si-H})_{\eta 2}$ in $Rh(\eta^2\text{-}HSiR_3)(SiR_3)(PMe_3)Cp^*$. Since the value of $J(\text{Si-H})_{terminal}$ is small, the $J(\text{Si-H})_{\eta 2} = 2*J(\text{Si-H})_{observed}$ = 57 Hz (R = Me) or 55.6 Hz (R = Et). The latter coupling constants are in a good agreement with the proposed η^2-silane moiety in complexes $Rh(\eta^2\text{-}HSiR_3)(SiR_3)(PMe_3)Cp^*$. Another exchange process between the free and coordinated silane in $Rh(\eta^2\text{-}HSiR_3)(SiR_3)(PMe_3)Cp^*$ was found for R = Et, which was concluded from broadening of the hydride signal and the signal of free silane at 10°C. At room temperature, complexes $Rh(\eta^2\text{-}HSiR_3)(SiR_3)(PMe_3)Cp^*$ rearrange into new compounds $Rh(H)(\eta^2\text{-}HSiR_3)(PMe_3)Cp^*$ after elimination of disilane $R_3Si\text{-}SiR_3$ and addition of another molecule of $HSiR_3$ (Scheme 75). Alternatively, compounds $Rh(H)(\eta^2\text{-}HSiR_3)(PMe_3)Cp^*$ could be formulated as classical silyl hydrides $RhH_2(SiR_3)(PMe_3)Cp^*$. The final decision on the structure could not be made due to the absence of data on coupling constant J(Si-H), which was not observed either because of very small value or because of very fast exchange between the terminal hydride and the η^2-silane moiety. Interestingly, analogous iridium compound was formulated as a classical Ir(V) complex $[IrH_2(SiMe_3)(PMe_3)Cp^*]^+$.[110]



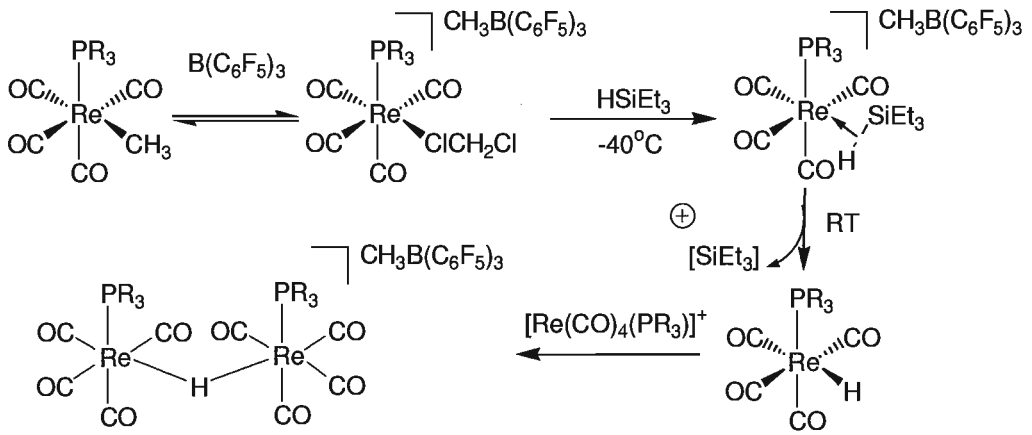
Scheme 75. The synthesis of cationic rhodium silane σ-complex

The only example of a cationic palladium silane σ-complex was reported by Kubas et al.[111] The reaction of the cationic diimine complex $[Pd(Me)(N(O(CH_2)_3OMe)=CMe)_2)]^+$ with $HSiEt_3$ gave the silane σ-complex $[Pd(Me)(N(O(CH_2)_3OMe)=CMe_2)(\eta^2\text{-}HSiEt_3]^+$, which was characterized only by ^1H NMR spectroscopy at -78°C (Scheme 76). This complex decomposes at room temperature with the formation Et_3SiCl and $O(SiEt_3)_2$, which are presumably produced by heterolytic cleavage of the Si-H bond coordinated to palladium by the chlorinated solvent and traces of water.[111]

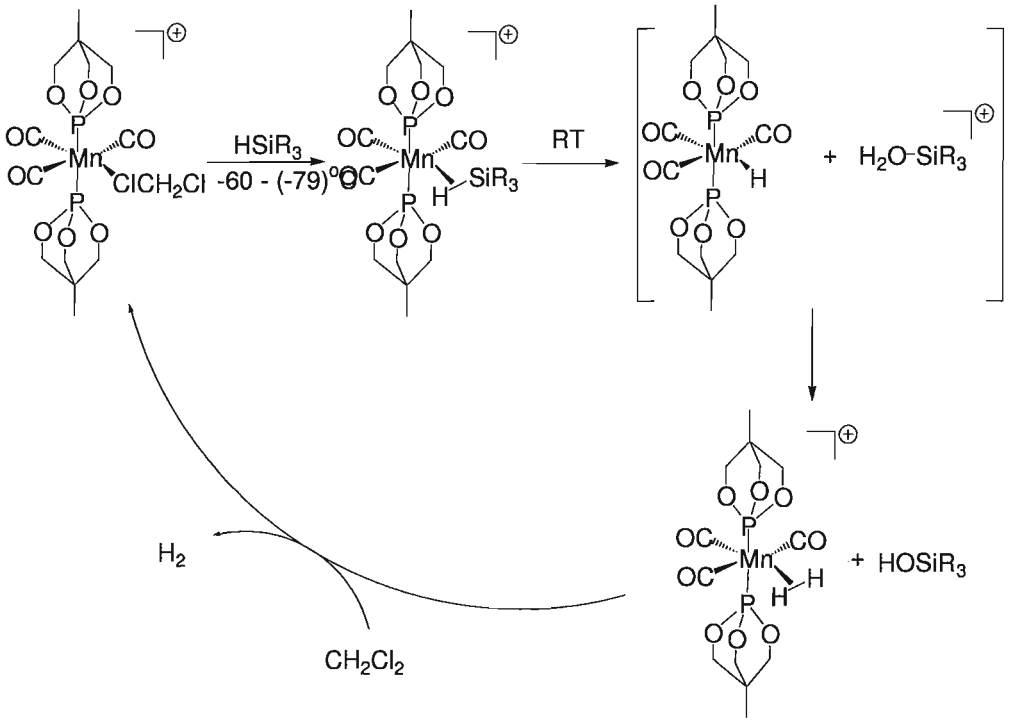


Scheme 76. The sunthesis of palladium silane σ-complex

Kubas et al. also obtained and characterized by low temperature NMR spectroscopy several cationic rhenium silane σ-complexes.[112] Treatment of complex $[Re(CO)_4(PR_3)(ClCH_2Cl)][CH_3B(C_6F_5)_3]$ with $HSiEt_3$ at -40°C resulted in quantitative formation of σ-complex $[Re(CO)_4(PR_3)(\eta^2\text{-}HSiEt_3)][CH_3B(C_6F_5)_3]$ (Scheme 77). The assignment of σ-character of silane bonding to rhenium was based on characteristic upfield doublets with ^{29}Si satellites in ^1H NMR of $[Re(CO)_4(PR_3)(\eta^2\text{-}HSiEt_3)][CH_3B(C_6F_5)_3]$ at -8.89 ppm (J(P-H) = 10.5 Hz, J(Si-H) = 60.9 Hz for R = Ph) or at -9.41 ppm (J(P-H) = 9.3 Hz, J(Si-H) = 61.6 Hz for R = Cy). The reported J(P-H) are considerably smaller than the values for classical rhenium hydride complexes (J(P-H) ~ 20Hz). In addition, J(Si-H) fall in the range 20-70 Hz. The increasing of temperature of the solution of $[Re(CO)_4(PR_3)(\eta^2\text{-}HSiEt_3)][CH_3B(C_6F_5)_3]$ to 0°C resulted in fast decomposition with the formation of hydride complex $Re(CO)_4(PR_3)(H)$ as well as bimetallic hydrogen bridged complex $[Re_2(CO)_8(PR_3)_2(\mu\text{-}H)][CH_3B(C_6F_5)_3]$ (Scheme 77). The silyl part of complex $[Re(CO)_4(PR_3)(\eta^2\text{-}HSiEt_3)][CH_3B(C_6F_5)_3]$ was converted into different products depending on the type of counter anion in the rhenium complex. Triethylmethyl silane $MeSiEt_3$ was obtained as the main silyl product upon heating up silane σ-complexes, which contained $MeB(C_6F_5)_3^-$ as a counter anion. On the other hand, a mixture of $O(SiEt_3)_2$ and $FSiEt_3$ was observed for analogous complexes with $B(C_6F_5)_4^-$ as the counter anion. The formation of $MeSiEt_3$ and $FSiEt_3$ can be explained by the reaction of the highly active $^+SiEt_3$ species with counter anions, and $O(SiEt_3)_2$ could be formed as a result of reaction of $^+SiEt_3$ with adventitious water in the reaction mixture.[112]



Scheme 77. The synthesis of cationic rhenium silane σ-complexes

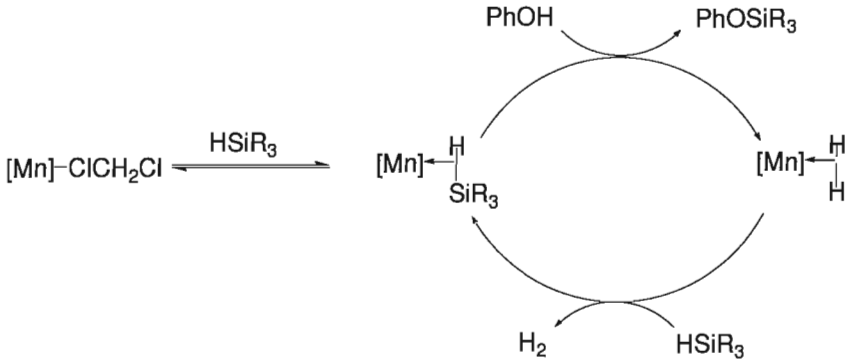


Scheme 78. The sysnthesis of cationic manganese silane σ-complexes

Another report by Kubas et al.[113] was devoted to preparation of highly unstable manganese silane σ-complexes, which were observed by NMR spectroscopy at low temperature. Both $HSiEt_3$ and H_3SiPh could react with highly reactive cationic manganese complex $[Mn(CO)_3(PR_3)_2(ClCH_2Cl)]^+$ and displaced coordinated dichloromethane in it (Scheme 78). Full conversion into corresponding silane σ-complexes was, however, observed only with $HSiEt_3$ at -78°C. Phenyl silane reacted only at higher temperature (-60°C) with only 20% conversion. Complexes $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ were characterized by NMR spectroscopy and gave similar triplets at high field in ^1H NMR at -16.1 ppm for SiR_3' = $SiEt_3$ and -15.3 ppm for SiR_3' = SiH_2Ph, which were assigned to protons of coordinated silanes. Phosphorus proton coupling constants in $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ (J(P-H) = 15.9 Hz for SiR_3' = $SiEt_3$ and 15.5 Hz for SiR_3' = SiH_2Ph) are smaller than for classical phosphine Mn-H complexes (J(P-H) = 40-60 Hz). Therefore, σ-complexation of silanes to manganese was proposed. Unfortunately, the J(Si-H) values were not measured due to manganese quadruple broadening.[113] Later, Kubas et al.[114] also communicated a similar phosphite rhenium complex, which was fully characterized by NMR spectroscopy. The Si-*H* protons of the complex

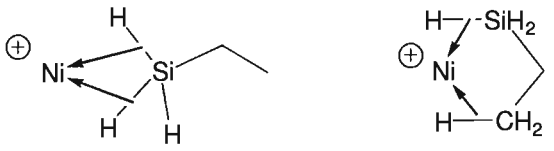
$[Re(CO)_3(PR_3)_2(\eta^2\text{-}HSiEt_3)]BAr'_4$ appeared as triplets with silicon satellites in ^1H NMR at -10.43 ppm (J(P-H) = 12.7 Hz, J(Si-H) = 66 Hz). The J(Si-H) of this complex falls in the region of 20-70 Hz, which is a strong evidence for σ-bonding of silane to rhenium centre.[114]

Compounds $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ showed typical reactivity for silane σ-complexes. Thus, when a solution of $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ was brought up to room temperature, a mixture of compounds was obtained, which contained significant amount of siloxanes.[113] Formation of the latter can be easily explained by heterolytic splitting of the Si-H bond in $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ by adventitious water in the reaction mixture (Scheme 78). The manganese hydride species $Mn(CO)_3(PR_3)_2(H)$, which was not detected NMR spectroscopy, could undergo fast protonation followed by displacement of dihydrogen by dichloromethane. Analogously to other silane σ-complexes, compounds $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ catalyze alcoholysis of silanes.[113] The major manganese complex observed during the catalysis was the dihydride complex $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}H_2)]^+$, which could be produced in the reaction of $[Mn(CO)_3(PR_3)_2(\eta^2\text{-}HSiR'_3)]^+$ with PhOH in the proposed catalytic cycle depicted on Scheme 79.[113]



Scheme 79. The proposed catlytic cycle for manganese-catalyzed alcoholysis of silanes

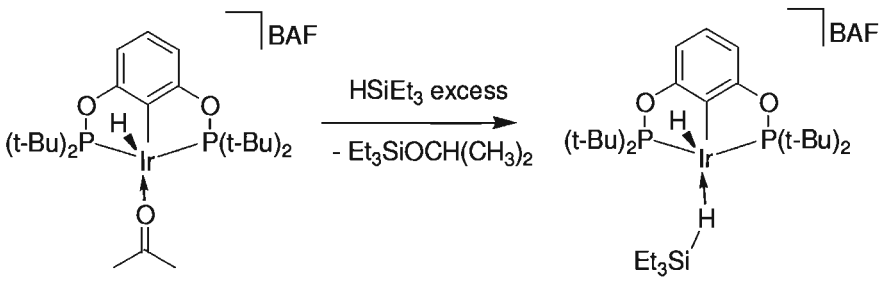
Cationic silane σ-complexes of nickel were computationally studied by B3LYP calculations and an AIM study.[115] The investigation of the gas phase interaction of H_3SiEt and Ni^+ revealed complex $[(\eta^2\text{-}H_3SiEt)Ni]^+$ (Figure 6, **49**) as the most stable species. Analogous structure with a chelate ligand (Figure 6, **50**) was less stable.



49 **50**

Figure 6. Cationic silane σ-complexes of nickel

The first example of a cationic silane σ-complex with η^1-$HSiR_3$ moiety was reported by Brookhart et al. in 2008.[116] The iridium silane σ-complex [(PCP)Ir(H)(η^1-$HSiEt_3$)]BAF was obtained by the reaction of the pincer complex [(PCP)Ir(H)(η^1-$O{=}C(CH_3)_2$)]BAF with an excess of $HSiEt_3$ in dichloromethane at room temperature (Scheme 80). Complex [(PCP)Ir(H)(η^1-$HSiEt_3$)]BAF is fluxional at room temperature due to fast exchange of terminal and bridging hydrides. At -70°C, the signal of the bridging hydride appears in ^{1}H NMR as a singlet with silicon satellites at -4.9 ppm (J(Si-H) = 79 Hz). Interestingly, the terminal hydride resonates in very high field at –44.2 ppm, which is indicative of the hydride position trans to a vacant site in the complex. The reported high value of J(Si-H) is very typical for all σ-complexes and, therefore, could not be used for the assignment of the η^1-$HSiR_3$ *vs.* η^2-$HSiR_3$ modes. However, the X-ray structure of [(PCP)Ir(H)(η^1-$HSiR_3$)]BAF revealed a very long Ir-Si distance (3.346 Å), which is 0.97Å longer than a sum of the covalent radii of Ir and Si atoms, and a large Ir-H-Si angle (157°). In addition, computational studies also confirmed the proposed η^1-$HSiEt_3$ structure, which is dictated by the bulky substituents on phosphorus.[116]

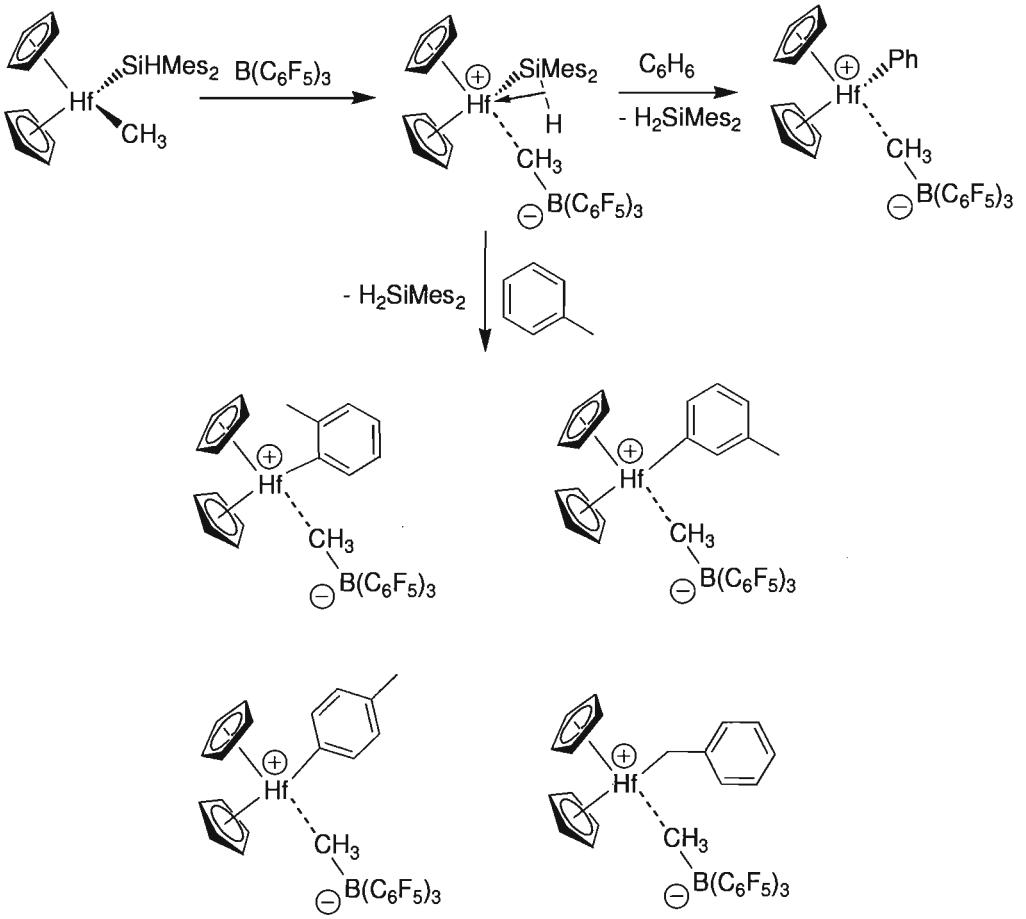


Scheme 80. The synthesis of [(PCP)Ir(H)(η^2-$HSiR_3$)]BAF

II.2.3 Cationic agostic M···H-Si complexes

α-Agostic complexes

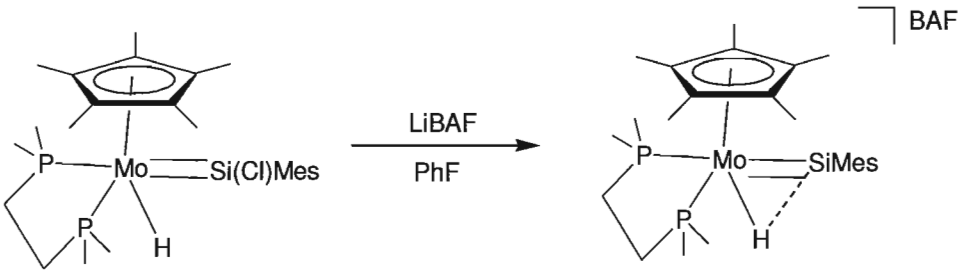
A very rare example of a cationic α-agostic M···H-Si complex was reported by Tilley and Sadow.[117] The hafnium complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ was obtained by the reaction of the hafnium methyl silyl complex $Cp_2Hf(Me)(SiHMes_2)$ with $B(C_6F_5)_3$ (Scheme 81). Complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ is highly reactive and decomposes quickly in fluorobenzene, hexafluorobenzene, chlorobenzene, and bromobenzene. However, compound $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ is relatively stable in toluene solution at -40°C, which allowed for full characterization by NMR spectroscopy. In the ^1H NMR spectrum, the resonance of the silicon bound proton appears at 1.80 ppm, which is considerably shifted upfield in comparison with terminal silicon bound protons. The J(Si-H) value of 57 Hz is also consistent with an α-agostic structure of the molecule. Additional evidence comes from IR data, which revealed a red-shifted Si-H frequency at 1415 cm^{-1}. Notably, the reactivity studies of the complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ revealed the capability of this complex to activate both aryl and alkyl C-H bonds. Thus, complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ reacts with benzene at room temperature forming cationic benzyl hafnium compound $[Cp_2Hf(C_6H_5)][MeB(C_6F_5)_3]$ and free silane H_2SiMes_2 (Scheme 81). Also, treatment of complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ with toluene resulted in the formation of a mixture of hafnium cationic complexes, which correspond to the activation of aromatic or methyl C-H bonds of toluene. The α-agostic interaction in complex $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ could also play an important role in the C-H activation processes. For example, analogous cationic hafnium silyl complexes, that did not have α-Si-H protons, were found to be completely inert in the above C-H bond activation reactions. Also, a relatively small kinetic isotope effect ($k_{SiHMes2}/k_{SiDMes2}$ = 1.1) could indicate that α -agostic interaction is also present in the transition state of the C-H activation. Unfortunately, all attempts to perform catalytic dehydrosilylation of benzene to produce $(C_6H_5)SiR_3$ have been unsuccessful so far.[117]



Scheme 81. The synthesis of $[Cp_2Hf(\eta^2\text{-}SiHMes_2)][MeB(C_6F_5)_3]$ and C-H activation reactions

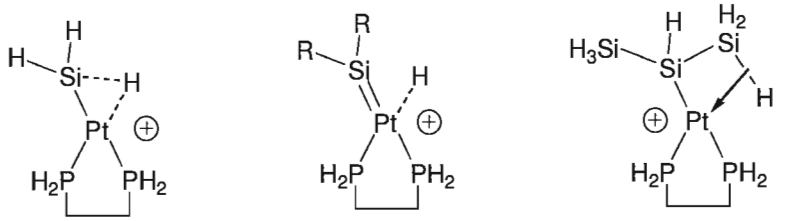
Tilley and Mork[118] reported a very unusual hydridosilylyne molybdenum complex [Mo(H)(=SiMes)(dmpe)Cp*][BAF], which was prepared by the reaction of compound Mo(H)(=SiClMes)(dmpe)Cp* with LiBAF (Scheme 82). Complex [Mo(H)(=SiMes)(dmpe)Cp*][BAF] exhibits downfield-shifted ^{29}Si NMR resonance at 289 ppm and a relatively small coupling constant J(Si-H) of 15 Hz, which suggests a hydridosilylyne structure. However, X-ray crystallography and preliminary DFT calculations revealed the presence of Si-H interaction in [Mo(H)(=SiMes)(dmpe)Cp*][BAF]. According to the X-ray structure analysis, the silylyne ligand in [Mo(H)(=SiMes)(dmpe)Cp*][BAF] has a linear geometry with very short Si-Mo and Si-H distances of 2.219(2) Å and 1.39(5) Å, respectively. In addition, NMR spectroscopy studies revealed the C_s symmetry of complex [Mo(H)(=SiMes)(dmpe)Cp*][BAF] at room temperature, which changes to C_1

symmetry at -40°C. The latter result is consistent with a fast migration of hydrogen between the metal centre and silicon.[118]



Scheme 82. The synthesis of hydridosilylyne molybdenum complex

The DFT (B3LYP) calculations of the cationic silyl platinum complexes $[Pt(SiHR_2)(H_2PCH_2CH_2PH_2)]^+$ found the α-agostic structure (Figure 7, **51**) as a global minimum for R = H.[119] Substitution of silicon with σ-donating (Me) or π-donating groups (Cl, OMe, SMe, NMe_2) stabilizes the silylene structure (Figure 7, **52**). Also, β-agostic coordination of the silyl ligand (Figure 7, **53**) was found for R = SiH_3.

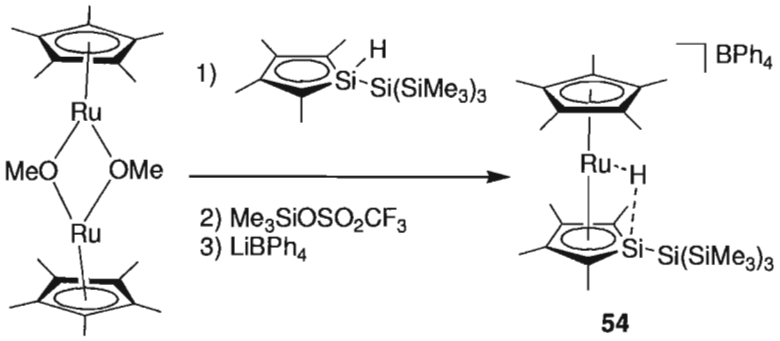


51 **52** **53**

Figure 7. The cationic silyl platinum complexes

β-Agostic complexes

Tilley et al.[120] reported cationic ruthenium complex **54** (Scheme 83) with a silacyclopentadienyl ligand, which was obtained by the reaction of $Me_4C_4SiH(Si(SiMe_3)_3)$ with $[Cp^*Ru(\mu\text{-}OMe)]_2$ in the presence of $Me_3SiOSO_2CF_3$, followed by addition of $NaBPh_4$. An interesting feature of complex **54** is the presence of significant Si-H interaction, which was evidenced by the relatively large coupling constant *J*(Si-H) of 41 Hz. In addition, the X-ray structure of **54** revealed a short Si-H distance of 1.70(7) Å and a deflection of the $Si(SiMe_3)_3$ group from the silacyclopentadienyl plane by 19.0°, which is a result of agostic interaction.



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Scheme 83. The synthesis of cationic ruthenium silacyclopentadienyl complex

The computational study of the gas phase interaction between $H_2C{=}C(H)SiH_3$ and Ni^+ was performed by Yanez et al.[115, 121] The B3LYP calculations revealed agostic species **55** (Figure 8). Interestingly, coordination of the double bond to the nickel centre is not symmetrical. The interaction with the C_β atom of the double bond was substituted by the donation of the Si-H bond to the metal. According to calculations, the agostic complex **55** is more stable than the analogous classical π-complex without agostic bonding by more than 28 kJ/mol. In contrast, the π-complex was the global minima for the coordination of $HC{\equiv}CSiH_3$ to the nickel cation. The corresponding agostic complex was only 2.9 kJ/mol less stable than the π-complex.[119]

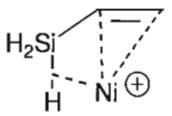

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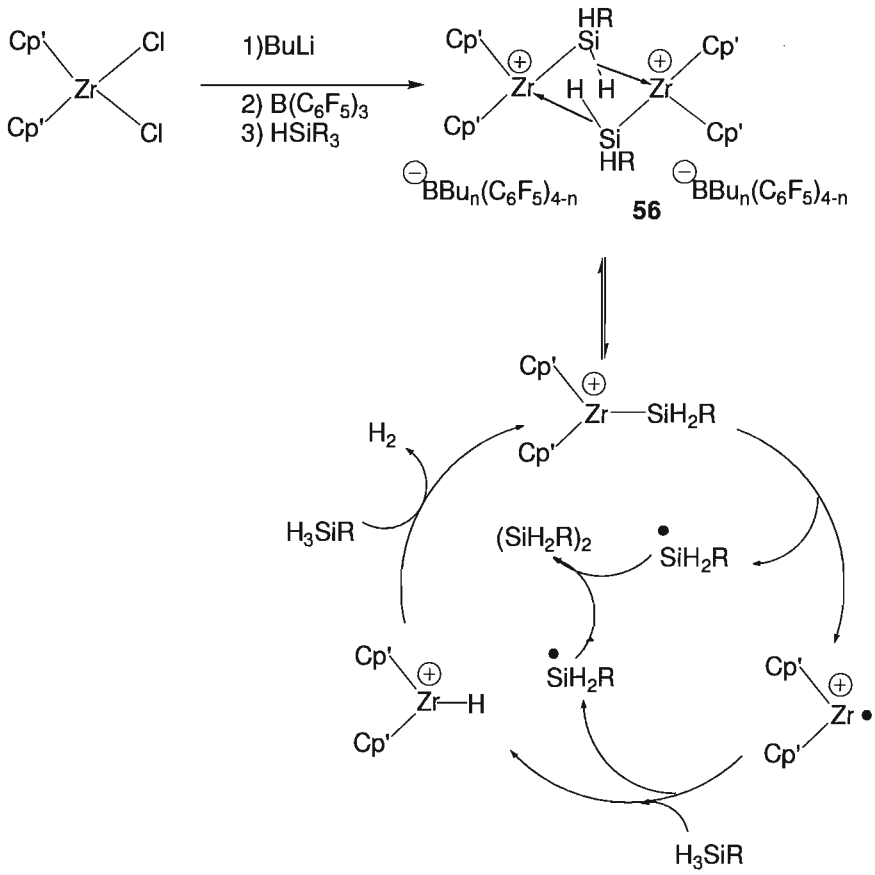
Figure 8. Cationic agostic silane nickel complex

γ-Agostic complexes

An excellent example of using NMR spectroscopy for identification of the structure of an unknown compound was demonstrated by Dioumaev and Harrod.[122] A series of new zirconium complexes were obtained by the reaction of zirconocene dichloride Cp'_2ZrCl_2 with BuLi, $B(C_6F_5)_3$, and H_3SiPh at -20°C (Scheme 84). The proposed structures of zirconocene hydridosilyl compounds **56** (Scheme 84) were confirmed by extensive multinuclear and multidimensional NMR spectroscopy studies. The ^1H-^{29}Si HSQC experiments revealed two distinct silicon coupled protons with relatively small and large silicon proton coupling constants. According to ^{29}Si NMR spectroscopy, the J(Si-H)s equal 32.2 Hz and 203.5 Hz (R = Ph, Cp' = Cp),

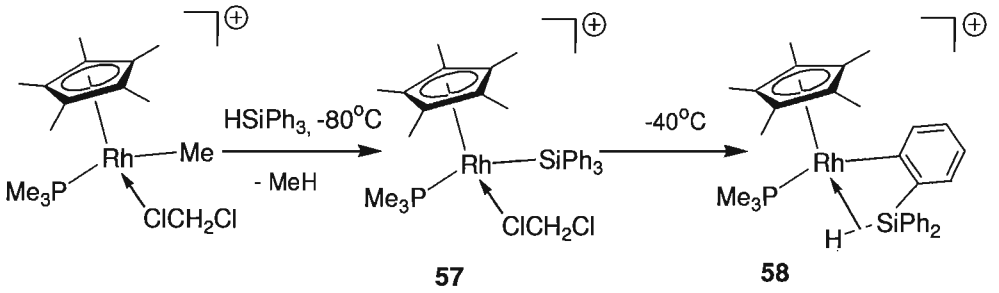
which supports the presence of a coordinated Si-H bond as well as a silicon-bound terminal proton, respectively. The positive charge in complexes **56** is delocalized between the silicon and zirconium atoms. However, reactions of complexes **56** with CsF resulted in the formation of new Zr-F bonds without any evidence of Si-F bonds, which is indicative of a positive charge being predominantly at the metal centre. Fast polymerization of phenyl silane was observed when complex **56** was generated in the presence of an excess of silane. Stoichiometric reactions of Cp_2ZrCl_2 with BuLi and $B(C_6F_5)_3$ at room temperature revealed formation of paramagnetic zirconocene radicals (as evidenced by EPR spectroscopy), which were assumed to be catalytically active species in the proposed catalytic cycle (Scheme 82).[122]



Scheme 84. The synthesis of cationic zirconium agostic silane complexes and the proposed catalytic cycle for the polymerization of H_3SiPh

A cationic γ-agostic silane complex of rhodium was prepared by the reaction of complex $Rh(Me)(ClCD_2Cl)(PMe_3)Cp^*$ with $HSiPh_3$ (Scheme 85).[109] In this reaction, a cationic silyl rhodium complex $Rh(SiPh_3)(ClCD_2Cl)(PMe_3)Cp^*$ is initially formed as a result of C/Si exchange at -80°C. On warming to -40°C, complex **57**

(Scheme 85) rearranges into the agostic compound $Rh((C_6H_4)(\eta^2\text{-}HSiPh_2))(PMe_3)Cp^*$, which gives rise to a hydride signal in ^1H NMR spectrum at -8.95 ppm (J(Si-H) = 84 Hz).[109] Large value of coupling constant J(Si-H) strongly suggests the presence of η^2-$HSiPh_2$ interaction. Interestingly, the full oxidative addition of the Si-H bond to the metal centre was reported for a related iridium complex $Ir(H)((C_6H_4)(SiPh_2))(PMe_3)Cp^*$.[123]



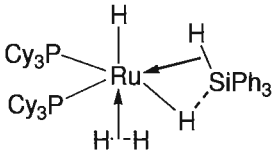
Scheme 85. The synthesis of γ-agostic silane complex of rhodium

III. Results and Discussion

III.1 *Cyclopentadienyl(Cp) silane complexes of ruthenium*

III.1.1 Neutral silane σ-complexes of ruthenium with interligand Si···Cl interactions

Transition metal silane σ-complexes, which are often postulated as intermediates in a large number of catalytic transformations of organosilicon compounds, have been intensively studied during the last decades, and the main features of these complexes as well as representative examples are summarized in the corresponding chapter of the historical. Notably, the majority of previous studies were devoted to investigation of neutral silane σ-complexes of type $L_nM(\eta^2\text{-}HSiR_3)$, where the influence of ligands L on the coordinated silane was limited to indirect interaction, mostly by changing the electronic and steric parameters of metal complexes. The importance of secondary interactions between the η^2-coordinated silane and other ligands in the metal complexes has been realized only recently. Thus, Sabo-Etienne et al.[124] reported the presence of *secondary interactions between silane and hydride* (SISHA) ligands in the ruthenium hydrido silane complex $Ru(PCy_3)_2(H)_2(H_2)(\eta^2\text{-}HSiPh_3)$ (Figure 9, **59**). Also, Nikonov et al.[13b] discovered and structurally characterized the complex $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$ which exhibits first example of significant Si···Cl interaction between a η^2-coordinated silane and the chloride ligand on ruthenium (Figure 9, **60**). The latter example is of special interest due to the recent reports of Pitter and Hofmann et al.,[89a, b] who revealed the pivotal role of such secondary Si···Cl interactions in the Ru-catalyzed hydrosilylation of CO_2.



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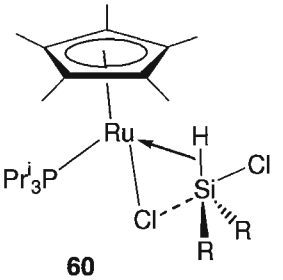

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Figure 9. Examplex of silane σ-complexes with secondary interligand interactions

Analogously to the previously described interligand Si···H interactions, the extent of secondary Si···Cl interactions could be varied by changing the electronic and steric parameters of the supporting ligands in metal complexes. Nikonov group has previously investigated the effect of ancillary ligands on the Si-H interactions in the dihydride silyl complexes $Cp'Ru(PR_3)H_2(SiR'_3)$ that exhibit interligand hypervalent interactions (IHI) and found an unexpected interplay of steric and electronic factors.[13a] In contrast to the compound $CpRu(PPh_3)H_2(SiMe_2Cl)$, where the presence of IHI was proven using X-ray crystallography, analogous complex with the Cp*-ligand lacked IHI (Figure 10, **61** and **62**, respectively). This unexpected result could be explained by steric repulsions between the bulkier Cp* ring and the $SiMe_2Cl$ group, which prevents the right orientation of the silyl group necessary for IHI. Therefore, the electronic effect of the Cp* ligand favourable for the IHI was fully compensated by the unfavourable steric factor.[13a]

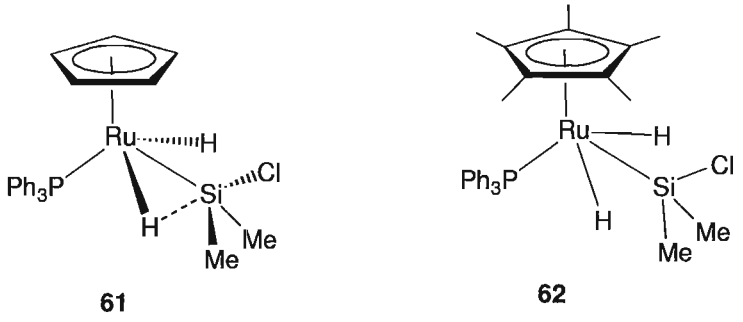


Figure 10. The influence of Cp-ring on the IHI in half-sandwich hydridosilyl ruthenium complexes

Strong influence of ancillary ligands on the extent of secondary Si···Cl interactions can be also expected for complexes $Cp'Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$. Thus, the synthesis and structural investigation of complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$ could potentially provide additional valuable information about unusual Si···Cl interligand interactions in transition metal silane σ-complexes.

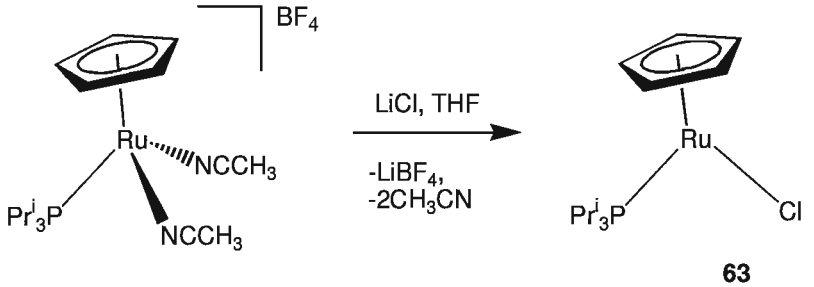
Synthesis of the precursor complex $CpRu(PPr^i_3)Cl$

Our initial attempts to synthesize Cp analogues of the previously described Cp* complexes $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$ (**60**) by the reaction of the readily available compounds $CpRu(PR_3)(PR'_3)Cl$ with chlorosilanes were unsuccessful. Substitution of one of the phosphines with silane proceeds only at elevated

temperature, and the target products $CpRu(PR_3)Cl(\eta^2\text{-}HSiR''_2Cl)$ decompose under these conditions with formation of a mixture of silyl dihydrides $CpRu(PR_3)H_2(SiR''_nCl_{3-n})$ and monohydrides $CpRu(PR_3)(PR'_3)H$.[13a]

The complexes **60** have been previously prepared by the reaction of the readily available precursors $Cp^*Ru(PPr^i_3)Cl$[125] with silanes.[13b] In this case, the starting compound $Cp^*Ru(PPr^i_3)Cl$ can be easily obtained by the reaction of $[Cp^*RuCl]_4$ with the bulky phosphine PPr^i_3 or by the reduction of $Cp^*Ru(PPr^i_3)Cl_2$ with zinc.[125] Unfortunately, both of these methods are not applicable for the synthesis of $CpRu(PR_3)Cl$. Therefore, we focused on the development of a new synthetic procedure for the preparation of unsaturated complex $CpRu(PR_3)Cl$, which was required for the synthesis of the target ruthenium silane σ-complexes $CpRu(PR_3)Cl(\eta^2\text{-}HSiR_2Cl)$. Notably, the chemistry of ruthenium complexes based on the $CpRu(PR_3)$ platform is barely developed in comparison with analogous Cp*-compounds. Due to the much lower price of the Cp-ligand than its substituted analogues, the preparation of new Cp-based ruthenium precursors, such as the presumably highly reactive complex $CpRu(PR_3)Cl$ could provide new opportunities for the development of the chemistry of half-sandwich ruthenium complexes.

We found that complex $CpRu(PPr^i_3)Cl$ (**63**) can be obtained by the reaction of the readily available complex $[CpRu(PPr^i_3)(CH_3CN)_2]BF_4$ with dry LiCl in THF (Scheme 86). The driving force of this reaction is the precipitation of the lithium salt $LiBF_4$ that is insoluble in THF. The solubility of lithium salt in THF, presumably, plays the crucial role in this synthesis as the reaction of the analogous cationic ruthenium complex with the PF_6^- counter anion affords the target complex **63** in only trace amounts. This fact can be explained by the higher solubility of the $LiPF_6$ salt.



Scheme 86. The synthesis of unsaturated complex $CpRu(PPr^i_3)Cl$

Unsaturated complex **63** was obtained as a brown crystalline solid in 46% isolated yield. Only broad signals were observed at ambient temperature in the ^1H

NMR spectrum of this compound, corresponding to the peaks of the Cp ring (4.25 ppm) and isopropyl groups (2.10 and 1.25 ppm). At lower temperature, the Cp-signal decoalesces and three new singlets, at 4.48, 4.33 and 4.03 ppm, appear at 225 K. At the same temperature, three singlets were also detected in the ^{31}P NMR spectrum (Figure 11). Such a behaviour can be explained by the presence of an equilibrium between a monomer and, presumably, two isomers of the dimer (*cis* and *trans*) (Scheme 87).

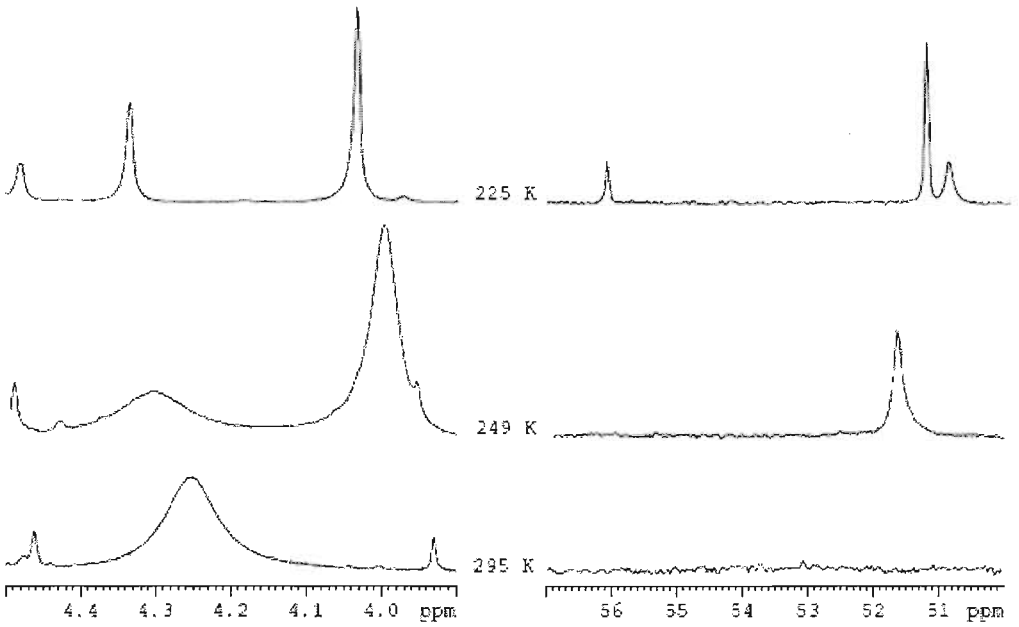
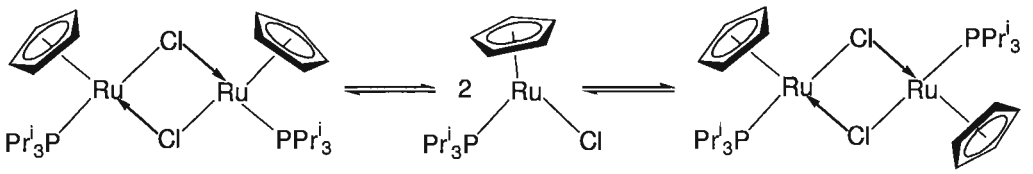


Figure 11. ^{1}H NMR of Cp ring (left) and ^{31}P NMR (right) of $CpRu(PPr^{i}_{3})Cl$ at different temperatures.



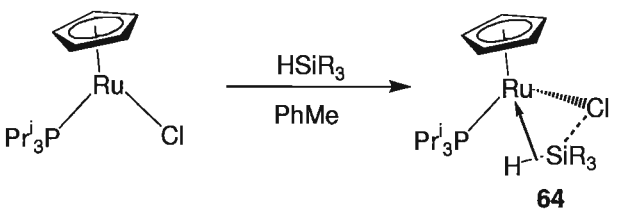
Scheme 87. Monomer-dimer equilibrium of $CpRu(PPr^{i}_{3})Cl$

Interestingly, the analogous complex $Cp^{*}Ru(PPr^{i}_{3})(Cl)$ does not show any evidence of fluxionality and the X-ray analysis revealed a monomeric structure with a very short Ru-Cl bond.[125c] The multiple character of the Ru-X bond in complexes

$Cp^*Ru(PR_3)(X)$ was proven by several X-ray diffraction studies and further supported by Huckel calculations.[125c, 126] Therefore, partial saturation of the formally 16-electron complex $Cp^*Ru(PPr^i_3)(Cl)$ is achieved mostly by the π-donation of a lone pair from the chloride ligand. The stabilization by dimerization is precluded by steric factors. On the other hand, dimerization plays significant role in the saturation of compound **63**, which can be explained by the reduced bulkiness of the Cp ligand. This is also supported by the fact that with smaller ligands L complexes $[Cp^{\wedge}Ru(L)(Cl)]_2$ ($Cp^{\wedge}$ = C_5Me_4Et, L = CO, C_2H_4, Py) exist as dimers with chlorides in the bridging positions.[127] In addition, monomer-dimer equilibrium has been previously observed by NMR spectroscopy for the unsaturated monophosphine complexes $Cp^*Ru(PPr^i_2Me)Cl$[128] and Cp"$Ru(PBu_3)Cl$ (Cp" = 1–methoxy-2,4-tert-butyl-3-neopentylcyclopentadienyl).[129]

The synthesis of silane σ-complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_3)$.

The treatment of complex $CpRu(PPr^i_3)Cl$ with silanes $HSiR_3$ resulted in immediate formation of silane σ-complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_3)$ (**64**) (SiR_3 = $SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), $SiMe_2Ph$ (**f**)), which was visually observed by a fast colour change of the reaction mixture from dark brown to yellow with the last drop of the added silane. All the silane σ-complexes were characterized by NMR spectroscopy.



64

Scheme 88. The synthesis of $Cp(Pr^i_3P)RuCl(\eta^2\text{-}HSiR_3)$

The stability of silane σ-complexes **64** strongly depends on the type of silane used. Most stable derivatives were obtained with chlorosilanes. On the other hand, the ruthenium complex with phenyl silane $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiH_2Ph)$ exhibits very broad signals of the Si-*H* protons in ^1H NMR, which could be indicative of a fluxional process. The complex with dimethylphenyl silane $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Ph)$ decomposes quickly at room temperature into a mixture of unidentified compounds. Notably, the stability of silane σ-complexes **64** resembles that of Cp*-analogues,

which showed a similar trend, with the complex Cp*(Pr^i_3P)RuCl(η^2-$HSiMe_2Ph$) being stable only at -90°C.[13b]

All complexes **64** exhibit a characteristic upfield signal of the η^2-Si-*H* proton in ^1H NMR, which appears as a doublet at -9.67 – (-10.30) ppm flanked with silicon satellites (J(P-H) = 24.9 – 27.1 Hz, J(Si-H) = 33.3 – 50.0 Hz) (Table 1).[i] The large values of Si-H coupling constants (J(Si-H) > 20 Hz) along with the red shift of Ru-H stretches in IR (SiR_3 = $SiCl_3$: 1995 cm^{-1}, $SiCl_2Me$: 1976 cm^{-1}, $SiClMe_2$: 1975 cm^{-1}, SiH_2Ph: 1985 cm^{-1}) strongly support the σ-coordination of the Si-H bond to Ru. Interestingly, there is a noticeable trend of increasing of the value of J(Si-H) in complexes **64** with decreasing Lewis acidity of the coordinated silane, e.g. in the chlorosilyl series the J(Si-H) increases from 33 Hz for $SiCl_3$ to 50 Hz for $SiMe_2Cl$ (Table 1). Also, a red-end shift of the corresponding Ru-H stretches in the IR spectrum was observed (Table 1). These observations suggest larger extent of oxidative addition of the Si-H bond for more acidic silanes, which is in agreement with the general trend observed for silane σ-complexes. As it was mentioned before, this observation can be explained by lowering the energy of the anti-bonding σ*(Si-H) orbital, which results in a better back-donation from the metal centre.

Table 1. Selected spectroscopic parameters of complexes Cp'(Pr^i_3P)RuCl(η^2-$HSiR_3$)

	$SiCl_3$	$SiMeCl_2$	$SiMe_2Cl$	SiH_2Ph	$SiMe_2Ph$
J*(Si-H) (Hz); Cp'=Cp	<6[13b]	19[13b]	34[13b]	-	32[13b]
***J*(Si-H) (Hz); Cp'=Cp**	33	45	50	39	46
υ(SiHRu) (cm^{-1}); Cp'=Cp	1995	1976	1975	1985	-

There are two main factors, which should be taken into account when comparing the half-sandwich Cp-complexes with their Cp*-analogous: the sterics and electron donating ability of Cp'-ligands. Bulky Cp* could potentially prevent complete oxidative addition of a silane to the metal centre due to the steric factor. On the other hand, the Cp* is a better electron donor, which could promote increased

[i] See Appendix (Figure 27) for a representive example of ^1H NMR.

back donation from the metal centre onto the anti-bonding σ*(Si-H) orbital and result in a more advanced oxidative addition of the Si-H bond. Therefore, it is difficult to predict *a priori* the relative magnitude of these conflicting factors and, therefore, the extent of resulting Si-H bond activation. Additional experimental or computational data are usually required. Based on the NMR data, complexes **64** exhibit much stronger Si-H interaction in comparison with their Cp*-analogues, which can be seen from the increased *J*(Si-H) values (Table 1). Therefore, in silane σ-complexes $Cp'Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR_2Cl)$ (Cp'= Cp, Cp*) the electronic effect of the ring on the activation of the Si-H bond dominates over the steric factor. As mentioned before, the opposite situation is observed in related complexes $Cp'Ru(PPr^i_3)H_2SiR_2Cl$, where the steric demands of the ring control the orientation of the silyl ligand and the extent of Si-H interaction.[13a]

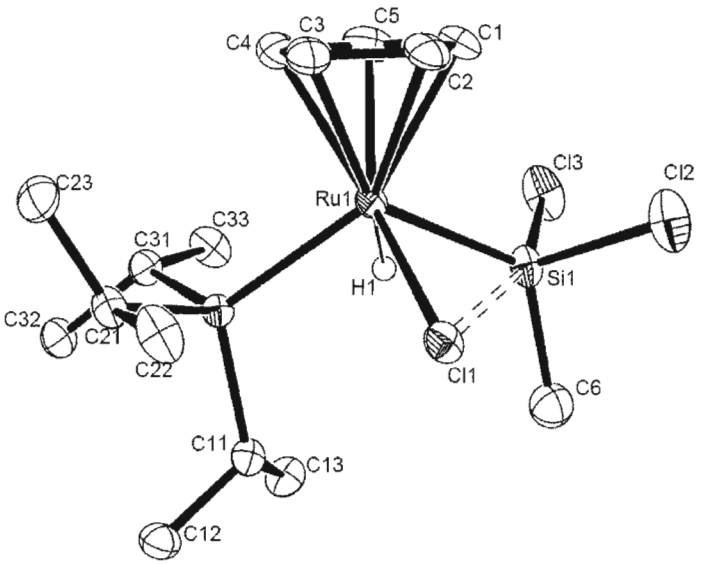


Figure 12. Molecular structure of $Cp(Pr^i_3P)RuCl(\eta^2\text{-}HSiMeCl_2)$ (H atoms, except Si-H, are omitted for clarity)

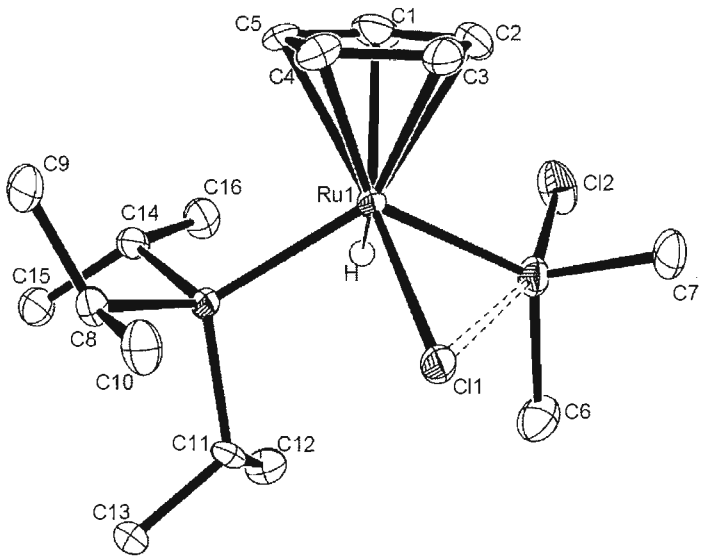


Figure 13. Molecular structure of $Cp(Pr^i_3P)RuCl(\eta^2\text{-}HSiMe_2Cl)$ (H atoms, except Si-H, are omitted for clarity)

The NMR data for complexes **64**, however, do not provide evidence for additional interactions between the silyl and chloride ligands. The most reliable conclusions about the presence of secondary interactions can be made from the X-ray structures of these compounds. Fortunately, we were able to grow crystals of complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMeCl_2)$ and $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$, which were suitable for X-ray analysis. The main structural features of complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMeCl_2)$ and $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$ (Figure 12 and Figure 13) resemble those of the Cp* analogue $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$.[13b] Thus, the silyl group is located between the chloride and hydride ligands, and the Si-bound chloride occupies the position *trans* to the Ru-bound chloride (the angle RuCl-Si-Cl is 164.06° in SiR_3=$SiMeCl_2$ and 162.50° in SiR_3=$SiMe_2Cl$). The Ru-Si bonds in both structures (Table 2) are considerably longer than in related half-sandwich silyl complexes of ruthenium: 2.3564(7) Å (SiR_3=$SiMeCl_2$) versus the range of 2.2950(5)-2.3099(9) Å for complexes $Cp^*Ru(PR_3)H_2SiMeCl_2$[130] and 2.4035(2) Å (SiR_3=$SiMe_2Cl$) versus the range of 2.302(3)-2.364(2) Å[13a,125b,130-131] for the ruthenium complexes with the SiR_2Cl ligands. The latter values are longer than the Ru-Si bond in $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$ (2.3982(7) Å),[13b] which is consistent with a stronger silane σ-complex character of $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$. The

presence of a short RuCl···SiCl contact is a distinguished feature of complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMeCl_2)$ (2.896 Å) and $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$ (2.873 Å). The RuCl···SiCl distances in the latter Cp complexes are considerably shorter than the same parameter in the Cp* derivative $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$ (3.014 Å),[13b] which is indicative of even stronger Si-Cl interaction in Cp-complexes.

Table 2. Selected bond lengths (Å) and angles (°) for $Cp'Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR'_3)$

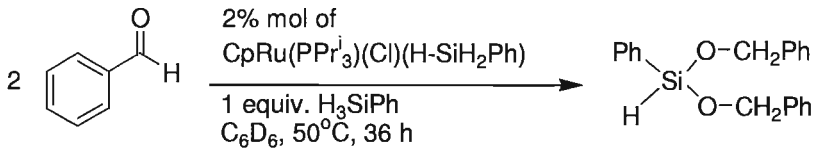
	Cp'/SiR'$_3$		
	Cp*/SiClMe$_2$[13b]	Cp/SiClMe$_2$	Cp/SiCl$_2$Me[a]
Ru-Si	2.3982(7)	2.4035(17)	2.3564(7)
Ru-Cl	2.4129(6)	2.4213(14)	2.4199(6)
Si-Cl	2.155(1)	2.132(2)	2.1104(9)
Si...Cl	3.014(1)	2.873(2)	2.8965(9)
Si-H	2.05(3)	2.15(6)	1.86(3)
Cl-Si...Cl	165.61(3)	162.50(9)	164.06(4)
Ru-P	2.3813(6)	2.3481(15)	2.3571(6)
P-Ru-Cl	87.60(2)	88.47(5)	88.12(2)
Cl-Ru-Si	77.59(2)	73.10(5)	74.65(2)

[a] The $SiMeCl_2$ is rotationally disordered

As one can see, the shortest RuCl···SiCl contact was observed for the complex $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMe_2Cl)$, which also exhibits the strongest Si-H interaction among all X-ray characterized complexes. Therefore, we can conclude that the extent of RuCl···SiCl interaction depends inversely on the extent of Si-H activation by the metal. This conclusion is also in agreement with the observation of almost completely added Si-H bonds in complexes $Cp^*Ru(PR_3)(Cl)(H)(SiCl_3)$ (PR_3 = PPr^i_3, PPr^iMe_2), which exhibit much longer RuCl···SiCl distances (3.110 and 3.102 Å).[13b] In other words, we can say that the RuCl···SiCl interaction anchors the silane in the coordination sphere of ruthenium and helps to saturate the silicon centre in the case when back-donation from the metal is small.

Catalytic activity of silane σ-complexes CpRu(PPr$^i_3$)Cl(η^2-HSiR$_3$).

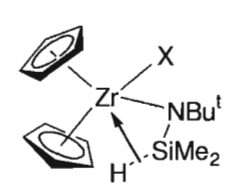
Complex CpRu(PPr$^i_3$)Cl(η^2-HSiH$_2$Ph) showed moderate catalytic activity in hydrosilylation of benzaldehyde with H$_3$SiPh. According to NMR monitoring, full conversion of benzaldehyde into (PhCHO)$_2$SiHPh happened after 36 h at 50 °C in the presence of 2% mol of CpRu(PPr$^i_3$)Cl(η^2-HSiH$_2$Ph).



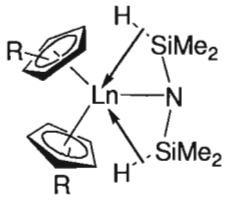
Scheme 89. Catalytic hydrosilylation of PhCHO mediated by Cp(Pr$^i_3$P)RuCl(η^2-HSiH$_2$Ph)

III.1.2 β-Agostic silylamido complexes of ruthenium

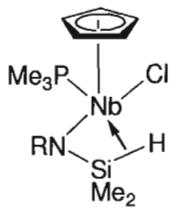
Agostic silane complexes are often considered as intramolecular analogues of silane σ-complexes. However, the presence of a bridge between the silicon and metal centres often puts restrictions on the activation of the Si-H bond by metal.[12c] Among different types of agostic complexes, the β-agostic compounds (when the bridge between the silicon and metal consists of only one atom, such as carbon, phosphorus or nitrogen) have been known for the longest time.[12c] Most of β-agostic silane complexes exhibit relatively large coupling constants *J*(Si-H) of usually more than 100 Hz, which is much larger than normally observed in silane σ-complexes (40-80 Hz). Therefore, the Si-H interaction in β-agostic complexes is usually stronger, and the complexation of the Si-H bond to the metal is weaker. Most of silane σ-complexes with a comparable extent of Si-H activation are too unstable and usually cannot be isolated or characterized by common techniques.[12c]



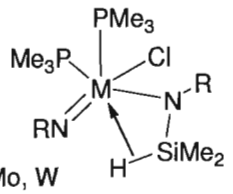
J(Si-H) =113 -135 Hz



J(Si-H) =133 -155 Hz

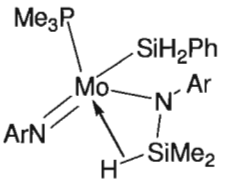


J(Si-H) = 97 -113 Hz



M = Mo, W

J(Si-H) = 96 -129 Hz



J(Si-H) = 113 Hz

Figure 14. Examples of silylamido agostic complexes

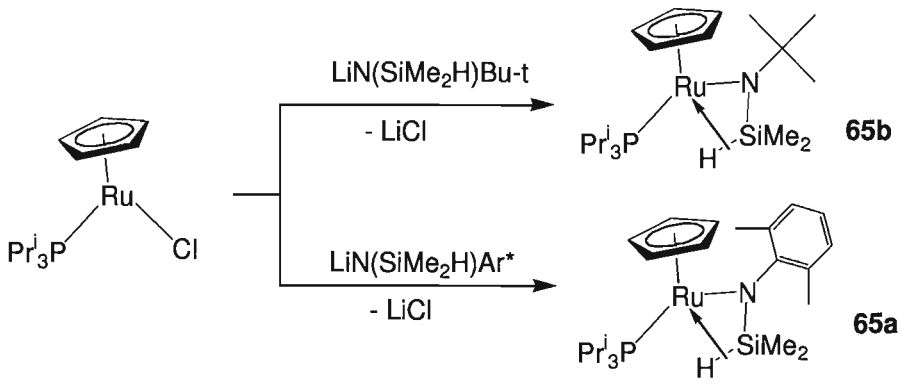
The additional stabilization of agostic complexes comes from the bridging atom, which holds the Si-H bond in close proximity to metal.[12c] Therefore, investigation of agostic complexes provides a unique opportunity to study the properties of Si-H bond in the early stage of oxidative addition, which makes the preparation of the corresponding complexes of great interest. There is a handful of

examples of β-agostic complexes with a nitrogen bridge (silylamido complexes), and all of them are early transition metal complexes (Zr, Nb, Mo, W) (Figure 14).[25, 132] Some of these agostic silylamido complexes exhibit interesting structural features and/or show remarkable reactivity towards the activation of small molecules as well as promising catalytic activity.[25]

Thus, as part of our broad research programme on studying non-classical Si-H interactions in late transition metal complexes, we attempted to prepare and investigate the first examples of the ruthenium β-agostic silylamido complexes.

The synthesis of β-agostic silylamido complexes CpRu(PPr$^i_3$)(N(η^2-HSiMe$_2$)R).

Our synthetic approach to the ruthenium β-agostic silylamido complexes is based on reactions of the previously described unsaturated complex CpRu(PPr$^i_3$)Cl with lithium salts LiN(SiMe$_2$H)R (Scheme 90). The reactions result in precipitation of LiCl and formation of new complexes CpRu(PPr$^i_3$)(N(η^2-HSiMe$_2$)R) (**65**) (R= Ar (**a**) or Bu^t (**b**)). Unfortunately, the complex **65a** is too unstable and quickly decomposes at room temperature. On the other hand, the complex **65b** is stable enough to allow performing NMR experiments with this compound at room temperature. Both complexes **65** exhibit upfield hydride signals in ^{1}H NMR, at -11.02 ppm (**65a**) and -11.63 ppm (**65b**), which appear as doublets with silicon satellites (J(P-H) = 19.5 Hz, J(Si-H) = 63 Hz for **65a**) and J(P-H) = 17.5 Hz, J(Si-H) = 64 Hz for **65b**).



Scheme 90. The synthesis of ruthenium β-agostic complexes

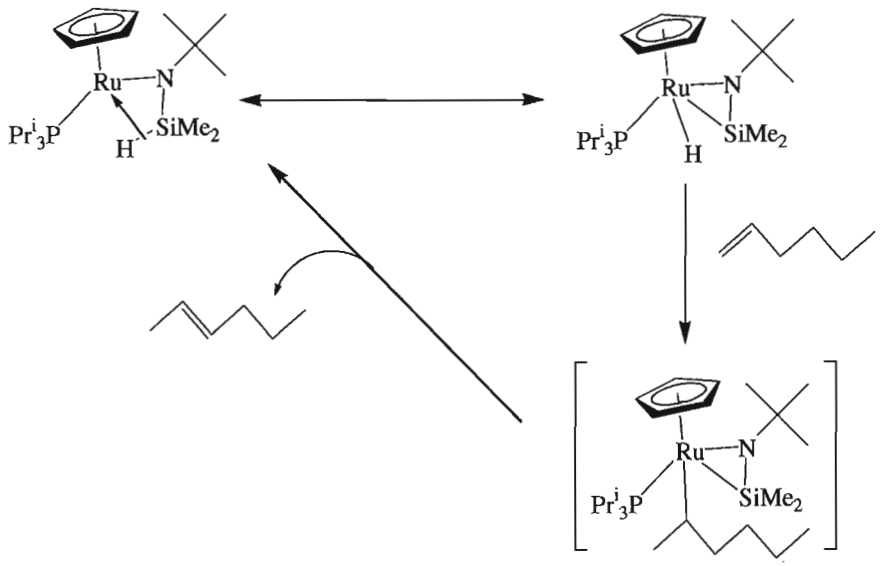
As can be seen from the NMR data, the nature of substituents on the nitrogen bridge in the agostic complexes does not significantly impact on the extent of Si-H activation. In this case, the difference in stability of complexes **65** can be explained by the steric factor. The J(Si-H) values in complexes **65** are significantly larger than in

related σ-complexes $Cp(Pr^i_3P)RuCl(\eta^2\text{-}HSiR_3)$ (J(Si-H) = 33.3 – 50.0 Hz), and, correspondingly, much smaller values of J(P-H) were observed. These observations confirm that Si-H interactions in the agostic complexes **65** are stronger than in related σ-complexes $Cp(Pr^i_3P)RuCl(\eta^2\text{-}HSiR_3)$.

Notably, the ruthenium complexes $CpRu(PPr^i_3)(N(\eta^2\text{-}HSiMe_2)R)$ are the first late transition metal compounds with agostic NSi-H···M interactions. The J(Si-H) values in these complexes are the smallest among all known β-agostic silylamido compounds, which can be easily explained by stronger back-donation from the electron-rich late transition metal.

Catalytic activity of β-agostic silylamido complex $CpRu(PPr^i_3)(N(\eta^2\text{-}HSiMe_2)Bu^t)$.

Addition of hexene-1 to a solution of complex **65b** resulted in izomerization of the starting alkene into a mixture of hexenes with the internal double bond. This process can be also performed catalytically, as the agostic ruthenium complex decomposes only slightly during the reaction. This reaction requires additional studies, which could help to determine the mechanism and the nature of catalytically active species. Possibly, the izomerization proceeds *via* an intermediate formation of a hydrido silanimine complex, which could undergo insertion of hexene-1 into the Ru-H bond followed by β-hydrogen elimination (Scheme 91). This possible mechanism is based on the previous work in the Nikonov group,[25] who studied the reactivity of β-agostic silylamido molybdenum complexes and demonstrated the intermediate formation of a silanimine molybdenum species.



Scheme 91. The proposed mechanism of isomerization of hexene-1 in the presence of $CpRu(PPr^i_3)(N(\eta^2\text{-}HSiMe_2)Bu^t)$

III.1.3 Cationic silane σ-complexes of ruthenium

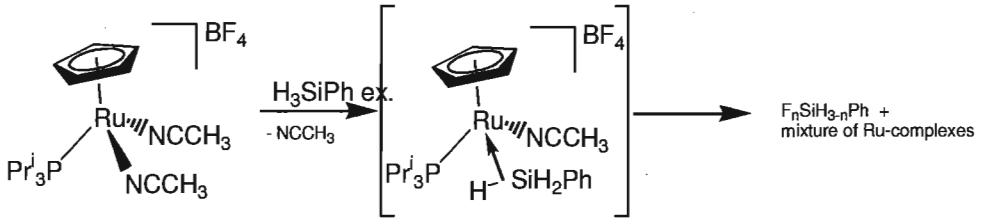
As previously described in the historical section, cationic silane σ-complexes are relatively rare and usually very unstable. Some of the known compounds of this type exhibit unique properties and show remarkable catalytic activity. Due to the aforementioned difficulties in their preparation and the very limited number of available cationic silane σ-complexes, virtually nothing is known about the substituent effects on the Si–H interaction in these species. Activation of the Si-H bond by transition metal complexes is usually a crucial process in most of catalytic hydrosilylation reactions. Therefore, knowing the influence of substituents on the extent of Si-H activation is of great importance.

The dependence of Si-H bond oxidative addition on the substituents at silicon and on the metal ligands is well-established for neutral σ-complexes, and it is tempting to extend these trends to their cationic analogues. However, one should take into account that electron deficient metal centres in cationic σ-complexes cannot provide the same extent of back-donation on the antibonding σ*(Si-H) orbital, which could potentially affect the general rules of Si-H bond activation.

As part of our research on non-classical silyl ruthenium complexes, we attempted to prepare a series of cationic silane ruthenium compounds and perform a systematic study of substituent effects on the Si–H interaction for this rare type of non-classical silane complexes.

The synthesis of cationic silane σ-complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]^+$

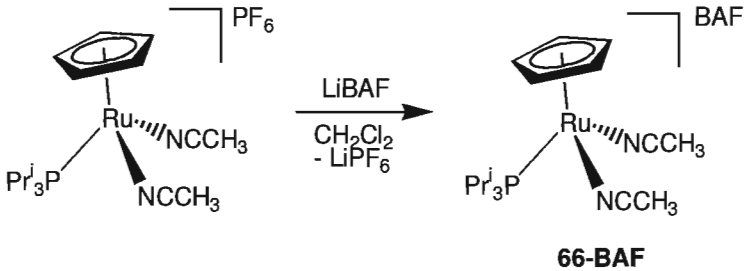
Our basic strategy for the synthesis of cationic ruthenium silane σ-complexes was based on the substitution of the labile acetonitrile ligands in the cationic monophosphine precursors $[CpRu(PR_3)(CH_3CN)_2]^+$ (PR_3 = PPr^i_3 (**66**) or PPh_3 (**67**)) with different hydrosilanes. Unfortunately, we observed only a mixture of decomposition products in the reaction of H_3SiPh with $[CpRu(PR_3)(CH_3CN)_2]PF_6$ ((PR_3 = PPr^i_3 (**66-BF$_4$**) or PPh_3 (**67-BF$_4$**)). This fact can be attributed to the well-known ability of coordinated silanes to react with counter-anions, such as $[PF_6]^-$ or $[BF_4]^-$, with the formation of fluorosilanes and neutral metal complexes (Scheme 92).



Scheme 92. The reaction of $[CpRu(PR_3)(CH_3CN)_2]PF_6$ with H_3SiPh

Interestingly, the reaction of **66-BF$_4$** with excess $HSiMeCl_2$ gave the previously described neutral silane σ-complex $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiMeCl_2)$ as one of the major products (>60%), which could be a result of the Si-Cl bond activation. The latter complex can be easily isolated from the reaction mixture by extraction with benzene. Therefore, this reaction could be potentially used as an alternative method for the synthesis of silane σ-complexes $CpRu(PR_3)Cl(\eta^2\text{-}HSiR_nCl_{3-n})$ avoiding the preparation of 16e-complex $CpRu(PPr^i_3)Cl$.

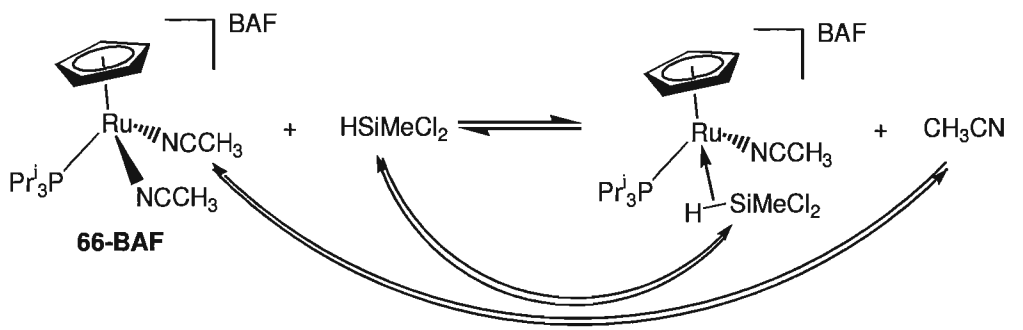
Due to the above results, we reckoned that the cationic complexes with the inert BAF counter anion, $[CpRu(PR_3)(CH_3CN)_2]$BAF ($PR_3 = PPr^i_3$ (**66-BAF**) or PPh_3 (**67-BAF**)) (BAF= tetrakis(pentafluoroborate)), would be a better starting material for the preparation of the target cationic silane σ-complexes. We found that these complexes can be synthesized by the reaction of **66-PF$_6$** or **67-PF$_6$** with LiBAF in CH_2Cl_2 *via* exchange of counter anions, thanks to precipitation of the lithium salt $LiPF_6$ in this solvent (Scheme 93). It was, however, important to obtain **66-BAF** and **67-BAF** in analytically pure form, without even traces of the PF_6^- counter anion. Fortunately, in contrast to the starting complexes **66-PF$_6$** and **67-PF$_6$**, which are not soluble in ether, the solubility of complexes **66-BAF** and **67-BAF** is relatively high, which allowed for the effective separation of these compounds.



Scheme 93. The synthesis of $[CpRu(PPr^i_3)(CH_3CN)_2]$BAF

Addition of silane to the cationic ruthenium complexes **66-BAF** and **67-BAF** leads to substitution of one of the acetonitrile ligands with silane and formation of cationic silane σ-complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ ($PR_3 = PPr^i_3$ (**68**) or PPh_3 (**69**); $SiR'_3 = SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), SiHMePh (**e**), $SiMe_2Ph$ (**f**)). The stability of the latter complexes strongly depends on the nature of silane, and is significantly reduced in comparison with related neutral compounds $Cp(Pr^i_3P)Ru(Cl)(\eta^2\text{-}HSiR_3)$. However, when compared with other known cationic silane σ-complexes, **68** and **69** should be considered as remarkably stable. For example, whereas most of cationic silane σ-complexes can be prepared only at low temperature in inert polar solvents, such as PhCl or CH_2Cl_2, compounds **68a** and **68b** can be generated in chloroform and can be stored in the solution for several days at room temperature without significant decomposition!

The reactions of complexes **66-BAF** and **67-BAF** with silanes are reversible. Thus, the treatment of complex **66-BAF** with 2 equiv. of $HSiMeCl_2$ resulted in an equilibrium mixture of **66-BAF** (45%) and $[CpRu(PPr^i_3)(CH_3CN)(\eta^2\text{-}HSiMeCl_2)]BAF$ (55%) (Scheme 94). The EXSY NMR experiment confirmed the presence of an equilibrium and also revealed an exchange between the coordinated and free silane in $[CpRu(PPr^i_3)(CH_3CN)(\eta^2\text{-}HSiMeCl_2)]BAF$ as well as between the coordinated and free nitrile in **66-BAF** (Figure 15). However, no exchange of coordinated and free acetonitriles was observed in the silane σ-complex $[CpRu(PPr^i_3)(CH_3CN)(\eta^2\text{-}HSiMeCl_2)]BAF$, suggesting that the second molecule of acetonitrile does not dissociate.



Scheme 94. The equilibrium between $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ and silane σ-complex

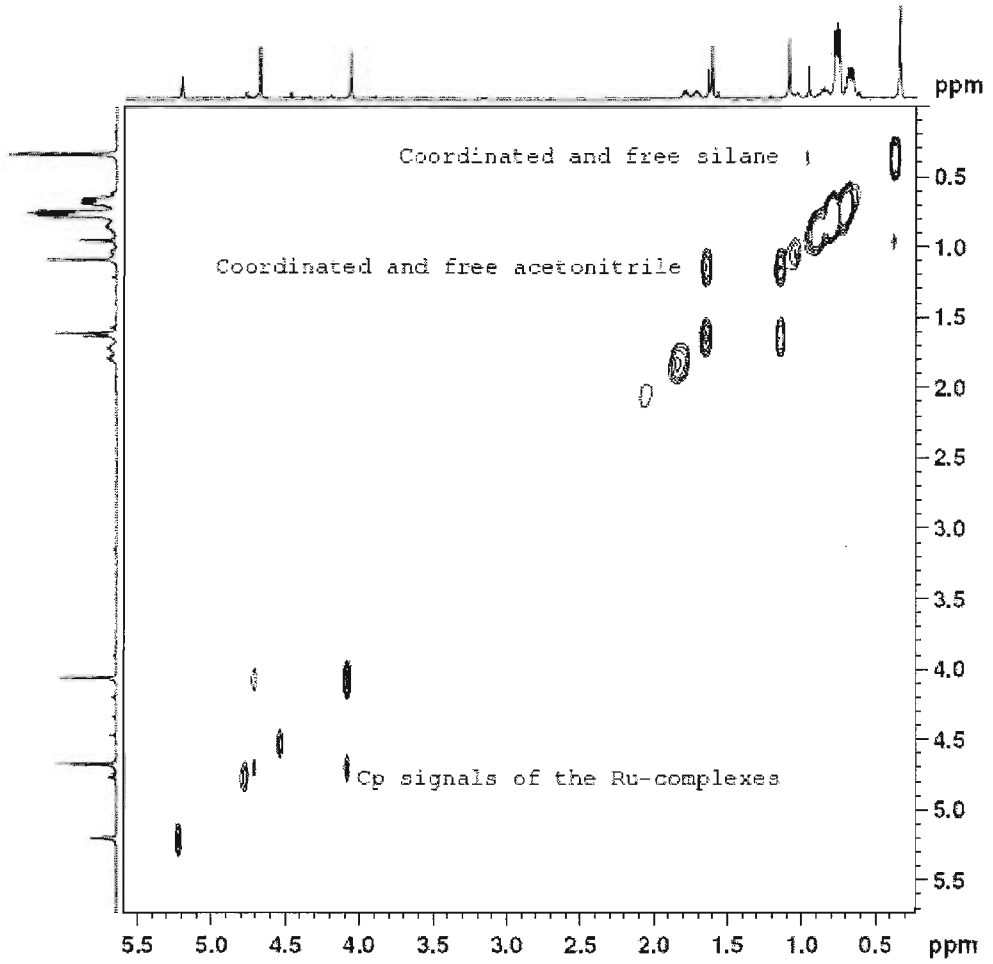


Figure 15. EXSY NMR spectrum for the reaction of 66-BAF with $HSiMeCl_2$

Due to the competition between the silane and acetonitrile for a coordination site on ruthenium, pure cationic silane σ-complexes can be obtained by this method only in the presence of excess silane and after the removal of all free acetonitrile under vacuum. In some cases, such as the reaction with $HSiMe_2Cl$, even dissolving the compound **66-BAF** in neat silane does not result in complete reaction and only an equilibrium mixture is obtained. Complexes $[CpRu(PPr^i_3)(CH_3CN)(\eta^2\text{-}HSiR_3)]BAF$ (SiR_3 = SiHMePh or $SiMe_2Ph$) were also generated in neat silanes, but a small amount of PhCl was added to increase the solubility of the starting ruthenium compound.

In the ^1H NMR spectrum of the σ-complexes **68**, the Si-*H* resonances appear as doublets flanked with ^{29}Si satellites, which allowed us to measure the coupling constant *J*(Si-H) and evaluate the extent of Si–H activation. All the Si-H coupling

constants observed are relatively large, which is a typical feature for silane sigma-complexes. Interestingly, the substituents on silicon do not influence the coupling much, and the values of J(Si-H) fall in the narrow range 49 ± 4 Hz (Table 3).

Table 3. The J(Si–H) values (in Hz) for silane σ-complexes [CpRu(PR_3)(CH_3CN)(η^2-HSiR'$_3$)]BAF and calculated J(Si–H) (in Hz) and Si–H bond lengths (in Å) in analogous complexes

	SiR'$_3$					
	$SiCl_3$	**$SiCl_2Me$**	**$SiClMe_2$**	**SiH_2Ph**	**SiHMePh**	**$SiMe_2Ph$**
J(Si-H) $PR_3=PPr^i_3$ **(68)**	53	45	45	48	48	50
J(Si-H) $PR_3=PPh_3$ **(69)**	59	48	47	-	-	-
$^{Calc.}J$(Si-H) $PR_3=PPr^i_3$	–34.8	–19.9	–17.8	-	-	–34.2
$^{Calc.}$Si–H, Å	1.996	1.980	1.947	-	-	1.889

Surprisingly, the largest J(Si-H) was observed for complex [CpRu(PPr^i_3)(CH_3CN)(η^2-$HSiCl_3$)]BAF, which contains the most acidic silane $HSiCl_3$. Also, there is a slight V-type dependence of the J(Si-H) on the electron-withdrawing ability of the SiR_3 group, first decreasing from 53 Hz for $SiR_3 = SiCl_3$ to 45 Hz for $SiR_3 = SiClMe_2$ and then increasing to 50 Hz for $SiR_3 = SiMe_2Ph$. Exactly the same trend for the J(Si-H) constants was observed for complexes **69** supported by the significantly less donating phosphine ligand PPh_3, albeit only slightly larger values of J(Si-H) were detected in this case. Such a behavior of J(Si-H) in silane σ-complexes is very unusual. For comparison, the J(Si–H) in neutral complexes CpRu(PPr^i_3)Cl(η^2-$HSiR_2Cl$) show the opposite trend, and the complex with $HSiCl_3$ exhibits the smallest J(Si-H) (Table 1).

These observations suggest the significantly reduced back-donation from the cationic Ru center in **68** and **69**, and the effect of enhanced back-donation for more acidic silanes on the value of J(Si–H) is compensated by the change of hybridization at Si. Therefore, the relatively large values of J(Si-H) for the complexes [CpRu(PR_3)(CH_3CN)(η^2-$HSiCl_3$)]BAF with $HSiCl_3$ do not necessary mean the lesser extent of Si-H activation in these complexes. It is well-known that more chlorinated silanes exhibit enhanced 3s character of silicon in the Si-H bond, which influences the

coupling constant J(Si-H).[102] Thus, the J(Si-H) in free chlorosilanes changes in the series $J(\text{Si-H})_{HSiCl3}$ = 366 Hz > $J(\text{Si-H})_{HSiMeCl2}$ = 283 Hz > $J(\text{Si-H})_{HSiMe2Cl}$ = 223 Hz. Therefore, in spite of the slightly larger values of J(Si-H) in complexes [CpRu(PR_3)(CH_3CN)(η^2-$HSiCl_3$)]BAF, the extent of Si-H activation in these complexes could be actually higher. This conclusion is also in agreement with the relative stability of silane σ-complexes in the presence of free acetonitrile. Under similar reaction conditions (6 equiv. of silane per 1 equiv. of **66-BAF**), there was >99% conversion of the starting ruthenium complex for $HSiCl_3$ and 81% conversion for $HSiMeCl_2$, whereas the equilibrium mixture in pure $HSiMe_2Cl$ contained only 78% of complex [CpRu(PPr^i_3)(CH_3CN)(η^2-$HSiMe_2Cl$)]BAF. Presumably, the aforementioned influence of hybridization at silicon on the J(Si-H) weakens with the increasing oxidative addition of silane to the metal centre. Therefore, neutral complexes CpRu(PPr^i_3)(Cl)(η^2-$HSiR_3$) demonstrate a different and more common for silane σ-complexes dependence of J(Si-H) on the substituents at silicon, where the compounds with more acidic silanes exhibit smaller values of the J(Si-H) due to the stronger back-donation from the metal (in comparison with cationic complexes) onto the antibonding σ*(Si-H) orbital, and, as a consequence, better oxidative addition of silanes.

In addition to experimental spectroscopic data, the η^2-silane coordination in compounds **68** and **69** was confirmed by DFT calculations of model complexes [CpRu(PPr^i_3)(NCMe)(η^2-$HSiR_3$)]$^+$ (SiR_3=$SiCl_3$, $SiMeCl_2$, $SiMe_2Cl$, and $SiMe_3$), which were performed by Prof. Vyboishchikov (Univ. of Gerona, Spain). In contrast to neutral complexes CpRu(PPr^i_3)Cl(η^2-$HSiR_2Cl$) that exhibit significant Si···Cl bonding, no Si···N interligand interactions were observed in the calculated structures of [CpRu(PPr^i_3)(NCMe)(η^2-$HSiR_3$)]$^+$. The calculated Si–H coupling constants in complexes [CpRu(PPr^i_3)(NCMe)(η^2-$HSiR_3$)]$^+$ are all negative, which is indicative of the presence of a direct Si-H bond.[ii]

It is important that the dependence of the calculated J(Si-H)s on the substituents at silicon corresponds to experimental values, albeit systematically lower J(Si-H)s were obtained. Additional evidence for the significant influence of hybridization at silicon on the Si-H coupling constants comes from the absence of direct correlation between the magnitude of Si–H coupling and Si–H distance. Thus,

[ii] Silicon has negative gyromagnetic ratio, which results in the direct Si-H coupling having negative values.

the complex $[CpRu(PPr^i_3)(NCMe)(\eta^2\text{-}HSiMe_3)]^+$ with the shortest Si–H bond (1.889 Å) shows almost the same J(Si–H) as the complex $[CpRu(PPr^i_3)(NCMe)(\eta^2\text{-}HSiCl_3)]^+$ with the longest Si–H bond (1.996 Å). Also, despite of the graduate increase in the absolute value of J(Si-H) in the order $HSiMe_2Cl < HSiMeCl_2 < HSiCl_3$, the calculated Si-H distances in the complexes **68** show the opposite trend, which corresponds to the increasing extent of Si-H oxidative addition. As previously described, such an abnormal behaviour of the Si-H coupling constants can be explained by a significantly different contribution of the 3s orbital of silicon in the Si-H bonds of complexes **68**.

III.2 *Catalytic reactions mediated by $[CpRu(PR_3)(CH_3CN)_2]^+$*

The cationic complexes $[CpRu(PR_3)(CH_3CN)_2]^+$ (PR_3 = PPr^i_3 (**66**) or PPh_3 (**67**)) can be easily generated in one step from the commercially available compound $[CpRu(CH_3CN)_3]^+$. Both types of ruthenium complexes are relatively stable in air and can be stored in desiccators for long periods of time. Also, due to the low solubility of cationic ruthenium complexes in non-polar solvents, these compounds can be easily separated from many organic substances by simple filtration or decantation of hexane or ether solutions. Moreover, the separated catalysts can be potentially recycled and used again. These valuable features of complexes **66** and **67** make them very attractive for practical applications, and the catalytic activity of these complexes in a variety of hydrosilylation reactions will be further discussed in this section.

III.2.1 Hydrosilylation of carbonyls

Reduction of carbonyls is a process of high importance as it allows for preparation of alcohols, which are widely used in many fields of chemistry. Hydrosilanes have been used as reducing reagents for this reaction for a long time.[1, 17d] The reduction of carbonyl compounds with hydrosilanes is distinguished by high levels of selectivity, broad substrate scope, mild and environmentally friendly conditions. Most importantly, the hydrosilylation of carbonyls results in the direct formation of silylated protected alcohols, which are often used in organic synthetic chemistry.[133]

The reactivity studies of catalytic hydrosilylation of carbonyls and esters

The complex $[CpRu(PPr^i_3)(NCMe)_2]^+$ was found to catalyze hydrosilylation of carbonyls under mild conditions. To establish the scope of silane reactivity for this reaction (Table 4), benzaldehyde was used as a standard substrate. Of several silanes screened in the reaction, the fastest rate was observed with $HSiMe_2Ph$ (Table 4, entry 1). The reduction of benzaldehyde with triethylsilane proceeds only at elevated temperature and stops at 82% conversion (Table 4, entry 2). The hydrosilylation can be also performed with dihydrosilane $H_2SiMePh$ and trihydrosilane H_3SiPh, but longer reaction times are required (Table 4, entries 3,4).

Table 4. Hydrosilylation of benzaldehyde with different silanes in the presence of $[CpRu(PPr^{i}_{3})(NCMe)_2]^+$ in $CDCl_3$[a]

N	Substrate	Silane	Time	Conv.[b]	Products
1	PhCHO	$HSiMe_2Ph$	30 min	100%	$PhCH_2OSiMe_2Ph$
2		$HSiEt_3$	36 h, 50 C	82%	$PhCH_2OSiEt_3$
3		$H_2SiMePh$	20 h	100%	$PhCH_2OSiHMePh$
4		H_3SiPh	4 h 20 h	60% 99%	$PhCH_2OSiH_2Ph$ + $(PhCH_2O)_2SiHPh$

[a] In a general procedure to a solution of benzaldehyde and silane in chloroform was added $[CpRu(PPr^{i}_{3})(NCMe)_2]^+$ (5% mol). [b] Based on NMR data.

Notably, the most efficient hydrosilylation of benzaldehyde with $HSiMe_2Ph$ was achieved in chloroform, and the reactions in dichloromethane and acetone were sluggish and do not go to completion.

Hydrosilylation of benzaldehyde with H_3SiPh proceeds efficiently also in the presence of the cationic complex $[CpRu(PPh_3)(NCMe)_2]^+$, which contains the less electron donating phosphine PPh_3. However, the above complex was totally inactive in the reduction of benzaldehyde with $HSiMe_2Ph$, which demonstrates a very high sensitivity of this reaction to the type of phosphine ligand in the ruthenium catalyst.

The hydrosilylation of ketones with $HSiMe_2Ph$ mediated by $[CpRu(PPr^{i}_{3})(NCMe)_2]^+$ is sluggish, and the reactions do not reach completion for bulkier ketones (Table 5). Thus, only cyclohexanone was fully converted into the corresponding silyl ether (Table 5, entry 1). On the other hand, hydrosilylation of PhC(O)Me and MeC(O)Et resulted in only 30% and 11% conversions, respectively, after 24 h at room temperature (Table 5, entries 2,3).

Table 5. Hydrosilylation of ketones with $HSiMe_2Ph$ in the presence of $[CpRu(PPr^{i}_{3})(NCMe)_2]^+$ in $CDCl_3$[a]

N	Substrate	Silane	Time	Conv.[b]	Products
1	$C_6H_{10}O$	$HSiMe_2Ph$	18 h	100%	$C_6H_{11}OSiMe_2Ph$
2	PhC(O)Me	$HSiMe_2Ph$	24 h	30%	$PhCH(OSiMe_2Ph)Me$
3	MeC(O)Et	$HSiMe_2Ph$	24 h	11%	s-$BuOSiMe_2Ph$

[a] In a general procedure, to a solution of ketone and silane in chloroform was added $[CpRu(PPr^{i}_{3})(NCMe)_2]^+$ (5% mol). [b] Based on NMR data.

Due to the lack of catalytic activity of complex $[CpRu(PPr^i_3)(NCMe)_2]^+$ in chlorinated solvents, we turned our attention to the solvent-free hydrosilylation reactions. This type of reactions is of high interest as it has several important advantages over reactions in solvent media. First of all, the reactions under solvent-free conditions are more environmentally friendly due to the absence of the often toxic solvent waste. Second, these reactions usually proceed faster because of higher concentrations of reagents. Third, the isolation of the final product does not require an extra step of solvent removal (decreased time and energy consumption). Finally, this method is usually cheaper as it allows one to save money on solvents and separation.[134]

Table 6. Hydrosilylation of carbonyls with $HSiMe_2Ph$ under solvent-free conditions in the presence of $[CpRu(PPr^i_3)(NCMe)_2]BAF$ (0.7% mol)[a]

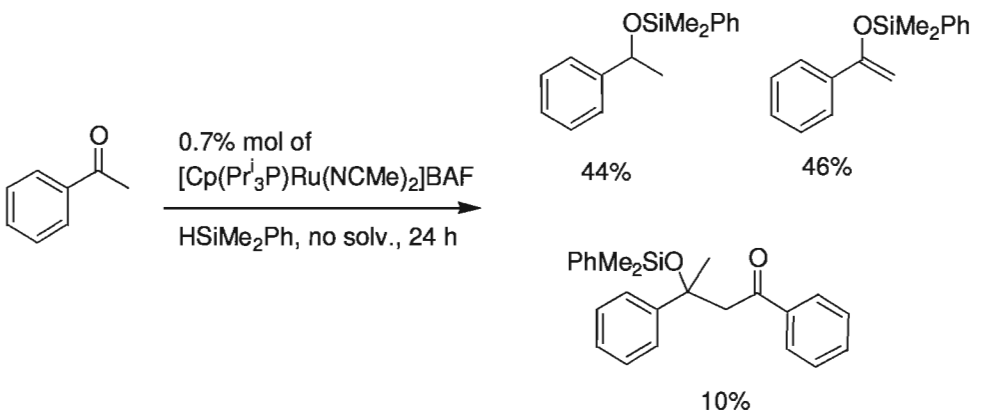
N	Substrate	Time	Conv.[b]	Products
1	PhCHO	30 min	100%	$C_6H_{11}OSiMe_2Ph$
2	PhCH=CHCHO	24 h	60%	mixture
3	PhC(O)Ph[c]	24 h	100%	$Ph_2CHOSiMe_2Ph$
4	$Pr^iC(O)Pr^i$	24 h	100%	$(Pr^i)_2CHOSiMe_2Ph$
5	PhC(O)Me	24 h	100%	$PhCH(OSiMe_2Ph)CH_3$ (44%), $PhC(OSiMe_2Ph)=CH_2$ (46%), $PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$ (10%)
6	$p\text{-}NO_2(C_6H_4)C(O)CH_3$[c]	24 h	100%	$p\text{-}NO_2(C_6H_4)CH(OSiMe_2Ph)CH_3$ (50 %), $p\text{-}NO_2(C_6H_4)C(OSiMe_2Ph)=CH_2$ (50%)
7	$CH_3C(O)CH_3$	48 h	100%	$(CH_3)_2CHOSiMe_2Ph$ (84%), $CH_3C(OSiMe_2Ph)=CH_2$ (16%)
8	$CH_3C(O)CH_2CH_3$	48 h	100%	$CH_3CH(OSiMe_2Ph)CH_2CH_3$ (57 %), $CH_2=C(OSiMe_2Ph)CH_2CH_3$ (19 %), $CH_3C(OSiMe_2Ph)=CHCH_3$ (24 %)
9	PhC(O)Me[d]	24 h	100%	$PhCH(OSiMe_2Ph)CH_3$ (4%), $PhC(OSiMe_2Ph)=CH_2$ (76%), $PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$ (20%)

[a] In a general procedure, to a mixture of ketone and silane was added $[CpRu(PPr^i_3)(NCMe)_2]BAF$ (~0.7% mol). [b] Based on NMR data. [c] 2 eq. of PhCl was added. [d] Complex $[CpRu(PPh_3)(NCMe)_2]BAF$ was used as a catalyst

Importantly, the hydrosilylation of carbonyls under solvent free conditions can be performed in the presence of much lower quantities of the catalyst $[CpRu(PPr^i_3)(NCMe)_2]^+$ (0.7% mol *vs.* 5% mol in solvents). However, we found that reactions are very sensitive to the type of the counter anion in the ruthenium complex.

Thus, the hydrosilylation of PhC(O)Me with $HSiMe_2Ph$ in the presence of 1% mol of **66-PF_6** stops after only 2% conversion of the starting ketone. Presumably, a fast decomposition of the catalyst occurs under these conditions. On the other hand, the reactions mediated by **66-BAF** (0.7% mol) proceed with 100% conversions, which can be explained by the higher inertness of the BAF counter anion. Hydrosilylation of benzaldehyde with $HSiMe_2Ph$ under solvent-free conditions proceeds to completion with the formation of $PhCH_2OSiMe_2Ph$ within just 30 min at room temperature (Table 6, entry 1). Unfortunately, the reaction with a conjugated aldehyde, PhCH=CHCHO, gave a mixture of compounds with only 60% conversion of the starting aldehyde after 24 h (Table 6, entry 2). The reduction of ketones requires longer reaction times, but sterically challenging substrates, such as $(i\text{-}Pr)_2C{=}O$ and $Ph_2C{=}O$, can be fully converted into the corresponding silyl ethers within 1 day at room temperature (Table 6, entries 3,4).

Unexpectedly, the hydrosilylation of PhC(O)Me resulted in the formation of a mixture of three compounds: $PhCH(OSiMe_2Ph)CH_3$ (44%), $PhC(OSiMe_2Ph){=}CH_2$ (46%), and $PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$ (10%) (Scheme 95; Table 6, entry 5).



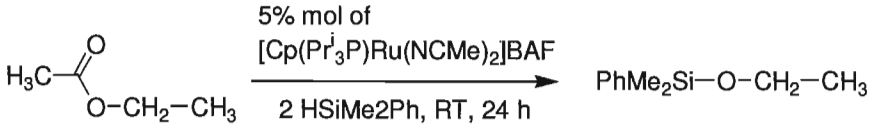
Scheme 95. Hydrosilylation of acetophenone under solvent-free conditions in the presence of [CpRu(PPr$^i_3$)(NCMe)$_2$]BAF

Introduction of an electron-withdrawing NO_2-group into the phenyl ring of the substrate did not change the ratio of silyl enols and alcohols significantly, but no product of condensation of two ketones was observed (Table 6, entry 6). Analogous mixtures of silyl enols and alcohols were also obtained in the reactions with alkyl ketones, which contain two or three protons in the α-positions. Thus, the hydrosilylation of acetone resulted in the formation of $(CH_3)_2CHOSiMe_2Ph$ (84%)

and $CH_3C(OSiMe_2Ph)=CH_2$ (16%) (Table 6, entry 7), and the hydrosilylation of $CH_3C(O)CH_2CH_3$ gave a mixture of $CH_3CH(OSiMe_2Ph)CH_2CH_3$ (57%), $CH_2=C(OSiMe_2Ph)CH_2CH_3$ (19%), $CH_3C(OSiMe_2Ph)=CHCH_3$ (24%) (Table 6, entry 8), which also demonstrates only a slight preference for the formation of an internal silyl enol in comparison with a terminal analogue.

In order to establish the influence of the catalyst on the ratio of products, we also performed hydrosilylation of PhC(O)Me in the presence of the ruthenium complex **67-BAF**, which contains a less electron donating phosphine PPh_3. The latter reaction gave a mixture of products with a significantly increased amount of $PhC(OSiMe_2Ph)=CH_2$ (76%) (Table 6, entry 9).

Surprisingly, complex **66-BAF** also catalyzes the hydrosilylation of ethyl acetate, which is known to be a very inert substrate (Scheme 96).[iii] The reaction proceeds at room temperature and results in the formation of 2 molecules of $EtOSiMe_2Ph$ from each molecule of $CH_3C(O)OEt$. The mechanism of this reaction remains unknown, but the formation of the expected silyl acetal intermediate $CH_3CH(OSiMe_2Ph)OEt$[iii] was not observed in the reaction mixture by NMR spectroscopy.



Scheme 96. Hydrosilylation of ethyl acetate in the presence of [CpRu(PPr$^i_3$)(NCMe)$_2$]BAF(5% mol) in $CDCl_3$

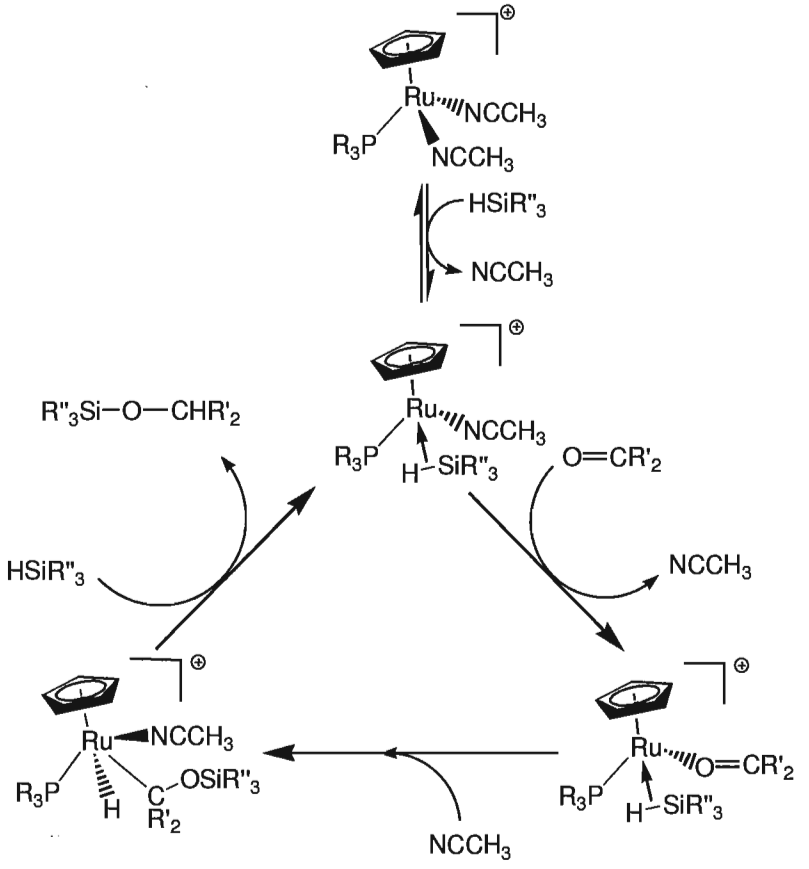
The mechanistic studies of hydrosilylation of carbonyls

To establish the mechanism of hydrosilylation, we performed stoichiomeric reactions with ruthenium complexes **66-BAF**. As mentioned before, the EXSY NMR study of complex **66-BAF** revealed a fast exchange between the coordinated and free nitrile, suggesting that NCMe dissociation is a reasonable first step. There is no coordination of carbonyl substrates to ruthenium even when the reaction is monitored in the neat carbonyl. In contrast, as previously described, the reactions of **66-BAF** with silanes easily give silane σ-complexes $[CpRu(PR_3)(NCMe)(\eta^2\text{-}HSiR_3)]BAF$. The ^1H EXSY spectrum of complex $[CpRu(PPr^i_3)(NCMe)(\eta^2\text{-}HSiMeCl_2)]BAF$ does

[iii] See corresponding chapter of the historical (Hydrosilylation of esters)

not show any exchange with free nitrile. However, we cannot completely rule out dissociation of the second molecule of acetonitrile under the catalytic conditions.

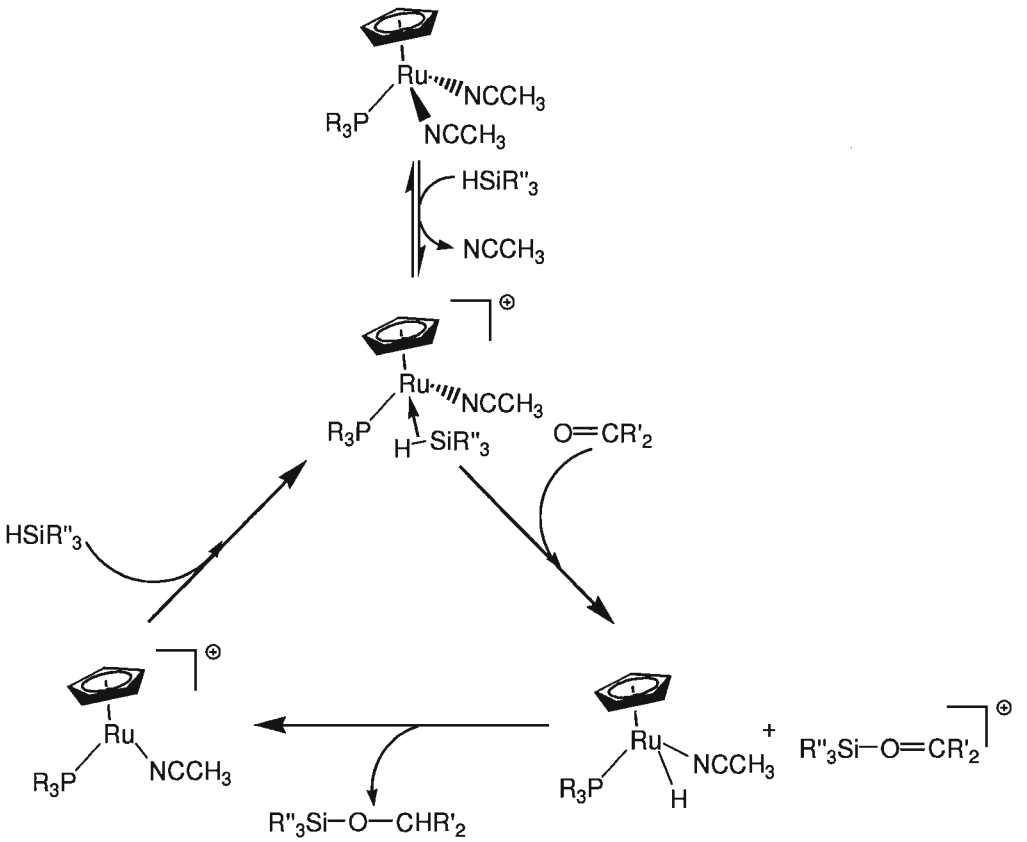
Therefore, two possible mechanisms of the hydrosilylation of carbonyls can be proposed. The first one, the classical Ojima type mechanism, includes dissociation of both nitriles from the catalyst (Scheme 97). In this case, dissociation of the first acetonitrile from the complex $[CpRu(PR_3)(NCMe)_2]^+$ preludes the coordination of silane with the formation of the previously investigated cationic silane complexes $[CpRu(PR_3)(NCMe)(\eta^2\text{-}HSiR''_3)]^+$, which could further undergo substitution of the coordinated nitrile with a carbonyl substrate. The silyl transfer to the coordinated carbonyl molecule in the resulting complex $[CpRu(PR_3)(O{=}CR'_2)(\eta^2\text{-}HSiR''_3)]^+$ could then lead to the formation of $[CpRu(PR_3)(H)(CR'_2(SiR''_3)]^+$, which could undergo hydride transfer from the ruthenium with a release of $R''_3SiO\text{-}CHR'_2$, and the catalyst can be regenerated by the reaction with $HSiR''_3$ (Scheme 97).



Scheme 97. The proposed Ojima type mechamism of hydrosilylation of carbonyls mediated by $[CpRu(PR_3)(NCMe)_2]^+$

The second possible mechanism involves dissociation of only one of acetonitrile ligands and also starts with the formation of the cationic silane σ-

complexes $[CpRu(PR_3)(NCMe)(\eta^2\text{-}HSiR''_3)]^+$, which could directly react with the carbonyl substrate by silylum ion transfer with the formation of $[CpRu(PR_3)(NCMe)(H)]$ and $[R''_3SiO{=}CR'_2]^+$ (Scheme 98). Analogously to the previous mechanism, the hydride transfer from the ruthenium complex to the silylium cation adduct with carbonyl gives $R_3SiO\text{-}CHR'_2$, and the reaction of the resulting ruthenium complex with silane finishes the catalytic cycle. This type of process is called ionic hydrosilylation.[108, 135]



Scheme 98. The proposed ionic mechanism of hydrosilylation of carbonyls mediated by $[CpRu(PR_3)(NCMe)_2]^+$

In order to distinguish between the above mechanisms, DFT COSMO calculations were performed by Prof. Vyboishchikov (Univ. of Gerona), which revealed the feasibility of formation of complex $[CpRu(PMe_3)(\eta^1\text{-}O{=}CMe_2)(\eta^2\text{-}HSiMe_3)]^+$, but the silyl migration to oxygen in this complex was not found, and the reaction of $[CpRu(PMe_3)(\eta^2\text{-}HSiMe_3)]^+$ with $O{=}CMe_2$ is highly unfavourable (Figure 16, left). On the other hand, the silyl transfer from the complex $[CpRu(PMe_3)(NCMe)(\eta^2\text{-}HSiMe_3)]^+$ to carbonyl requires $\Delta^{\ddagger}G^{\circ}_{298}$ of 18.6 kcal/mol,

which is the rate-limiting step in the ionic mechanism of hydrosilylation depicted on (Figure 16, right). The next step, the hydride transfer from [CpRu(PMe_3)(NCMe)(H)] to $[Me_3SiO{=}CMe_2]^+$, has a much lower activation barrier ($\Delta^{\ddagger}G^{\circ}_{298}$ = 4 kcal/mol), and the resulting complex $[CpRu(PMe_3)(NCMe)(\eta^1\text{-}H\text{–}CMe_2\text{–}O\text{–}SiMe_3)]^+$ easily dissociates with the formation of the final product $Me_3SiO\text{-}CHMe_2$. Therefore, the DFT calculations favoured the ionic mechanism of the Ru-catalyzed hydrosilylation. Notably, an analogous mechanism has been previously suggested for borane-catalyzed hydrosilylation,[135a] for dialkyl ether cleavage with silanes mediated by a cationic Ir complex,[135b] and for silane alcoholysis on electrophilic metal centers.[108,135a,b]

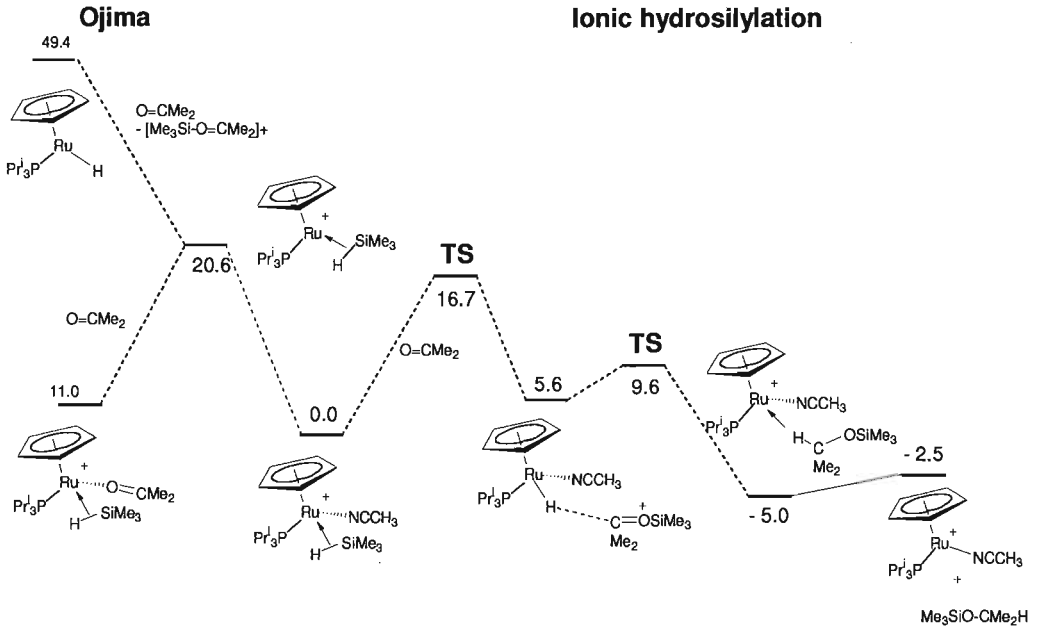
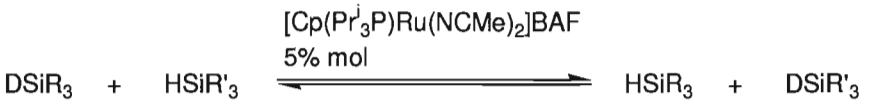


Figure 16. Ionic Hydrosilylation and Dissociative Ojima-Type Pathways Calculated by DFT (Gibbs energies are given in kcal/mol)

Additional evidence for the ionic mechanism of hydrosilylation of the Ru-catalyzed reactions could be obtained by comparing the properties of this catalytic system with the previously described systems, which operate in a similar way. The formation of the silylium cation adduct with a carbonyl molecule is the key process of the ionic hydrosilylation mechanism. Thus, the $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyls was also proposed to proceed via the intermediate formation of silylium cations $[R_3Si]^+[HB(C_6F_5)_3]^-$, which could coordinate carbonyl substrates (Figure 17, left).[135a] A typical feature of these cations is their ability to abstract hydrides from

other hydrosilanes. Therefore, the borane $B(C_6F_5)_3$ also effectively catalyzes exchange of protons between silanes, which was proven by the reaction of $HSiEt_3$ with $DSiPh_3$.[135a] As expected, the exchange of protons between D_3SiPh and $HSiMe_2Ph$ as well as between D_3SiPh and $H_2SiMePh$ was observed in the presence of 5% mol of **66-BAF** (Scheme 99).



Scheme 99. H/D exchange between silanes catalyzed by [Cp(Pr$^i_3$P)Ru(NCMe)$_2$]BAF (5% mol)

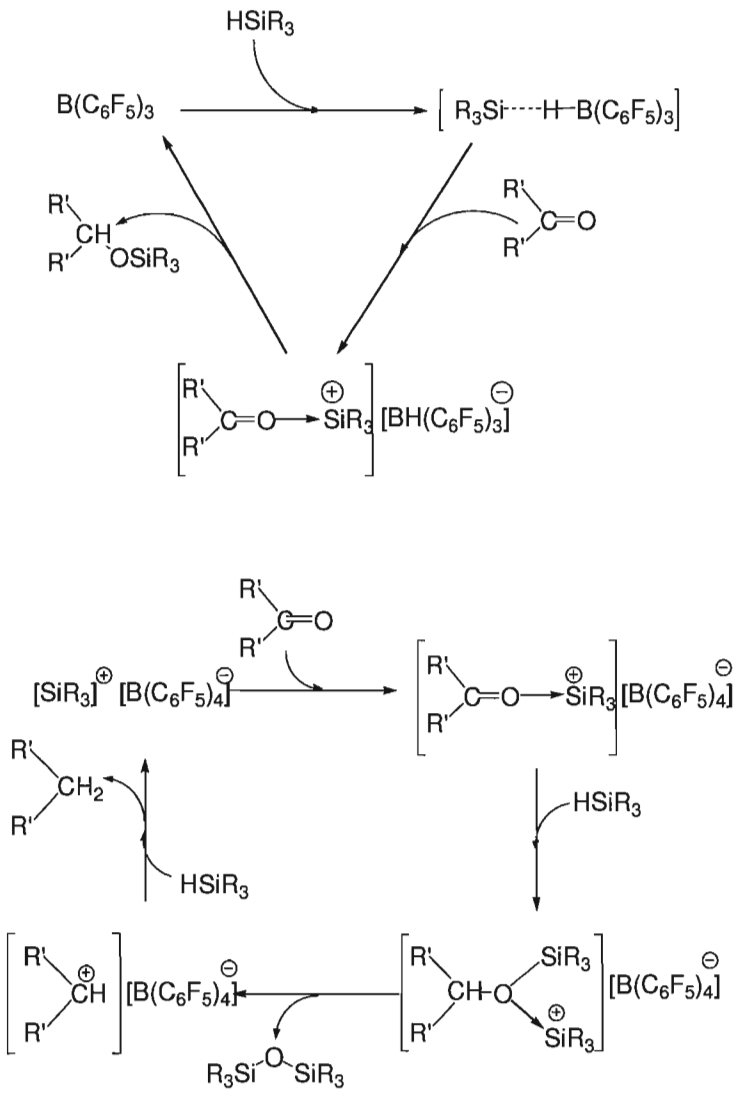
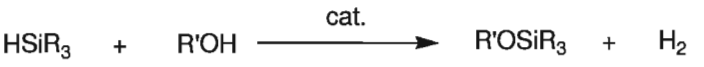


Figure 17. The proposed mechanisms of $B(C_6F_5)_3$-catalyzed (top) and $[SiR_3]^+$-catalyzed (bottom) reduction of carbonyls with silanes

The generation of highly reactive silylium cation intermediates in the reaction raises a question about the role of the ruthenium hydride complex [CpRu(PR_3)(NCMe)(H)], because the silylium cations are also known to catalyze the reduction of carbonyls.[135a] However, the reaction of carbonyls with silanes mediated by silylium cations proceeds *via* a completely different mechanism and results in deoxygenation of carbonyls (Figure 17, top).[135a] Therefore, the ruthenium complex [CpRu(PR_3)(NCMe)(H)] must be the actual participant in the catalytic cycle, playing a role similar to that of the borohydride anion $[HB(C_6F_5)_3]^-$ in the borane-catalyzed hydrosilylation of carbonyls (Figure 17, bottom).[135a]

III.2.2 Dehydrogenative coupling reactions with silanes

Introduction of a silyl group is one of the most common methods for the protection of the alcohol functionality in organic synthesis.[136] The resulting silyl ethers are stable under a wide range of conditions, and at the same time, the protecting group can be easily removed using standard procedures.[136] The silyl ethers are also very important precursors for the synthesis of different siloxane materials. Usually, the silyl ethers are prepared by the reaction of chlorosilanes with alcohols or alkoxides under acidic or basic conditions.[137] However, many complex organic compounds are not stable under these conditions. Also, chlorosilanes are very sensitive to air and can be easily hydrolyzed. Therefore, the development of new protecting procedures based on the use of more stable hydrosilanes is of high interest. In contrast to reactions with chlorosilanes, the coupling of alcohols with hydrosilanes can be performed under very mild conditions, and the only by-product of this reaction is dihydrogen, which simplifies the isolation of silyl ethers and makes this process much more atom efficient (Scheme 100).[137-138]



Scheme 100. Alcoholysis of silanes

Apart from strongly electrophilic and nucleophilic catalysts, dehydrogenative coupling of silanes and alcohols can be performed in the presence of transition metal complexes.[137-139] The cationic late transition metal compounds have proven to be very

efficient catalysts for this reaction, which was often postulated to proceed *via* intermediate formation of cationic silane σ-complexes.[104,107] Due to the proven feasibility of formation of such complexes in the reactions of the cationic complex $[CpRu(PPr^i_3)(NCMe)_2]^+$ with silanes, we also attempted to perform catalytic dehydrogenative coupling of silanes and alcohols.

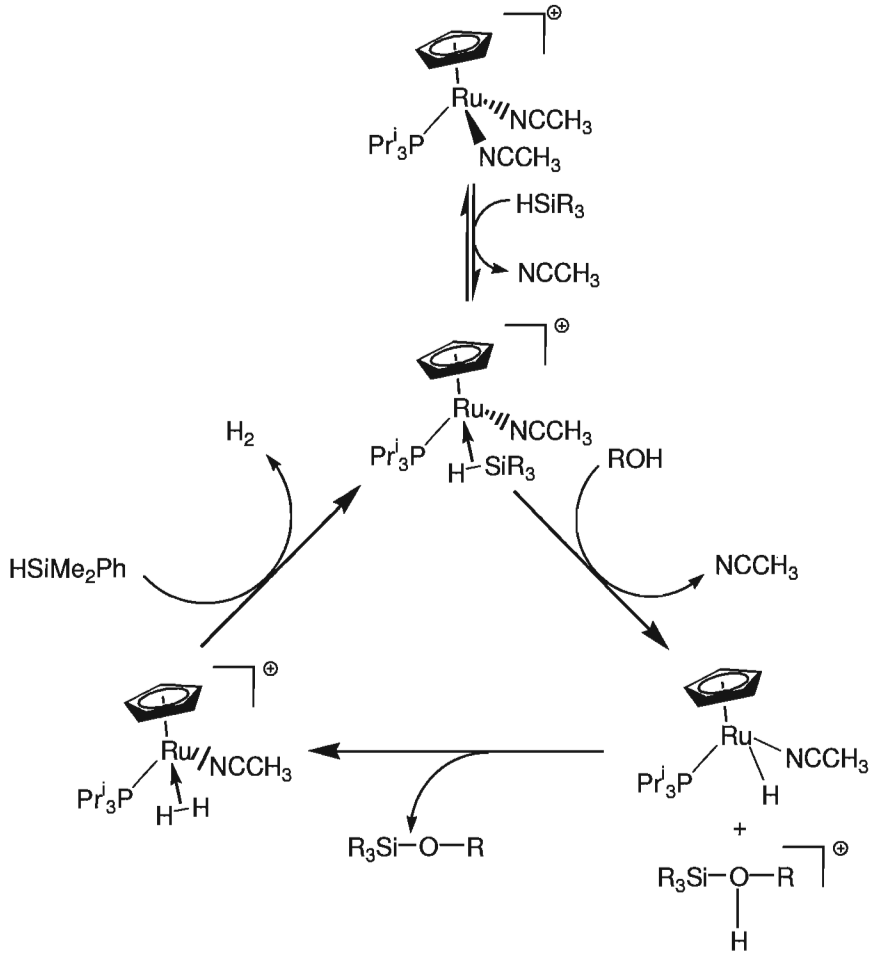
We found that complex **66-PF_6** effectively catalyzes coupling of alcohols with silanes. Importantly, this reaction can be performed with monohydrosilanes, as many of the previously described catalysts operate only with the more expensive dihydro- and trihydrosilanes.[137] Thus, the reaction of $HSiMe_2Ph$ with EtOH in the presence of 5% mol of **66-PF_6** proceeds with fast evolution of hydrogen gas within about 5 min at room temperature (Table 7, entry 1). Complex **66-PF_6** also catalyzes dehydrogenative coupling of EtOH with $HSiEt_3$, but longer reaction time is required (Table 7, entry 1).

Table 7. Dehydrogenative coupling of silanes with alcohols in the presence of $[CpRu(PPr^i_3)(NCMe)_2]^+$[a]

	Substrate	Silane	Time	Conv.[b]	Products
1	EtOH	$HSiMe_2Ph$	5 min	100%	$EtOSiMe_2Ph$
		$HSiEt_3$	50 h	100%	$EtOSiEt_3$
2	i-PrOH	$HSiMe_2Ph$	30 min	100%	$i\text{-}PrOSiMe_2Ph$
3	t-BuOH	$HSiMe_2Ph$	1 h	100%	$t\text{-}BuOSiMe_2Ph$
4	PhOH	$HSiMe_2Ph$	30 min	100%	$PhOSiMe_2Ph$

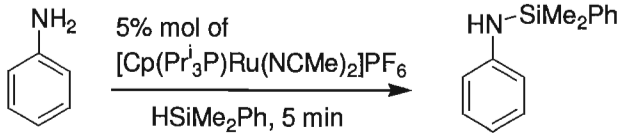
[a] In a general procedure, to a solution of alcohol and silane in chloroform was added $[CpRu(PPr^i_3)(NCMe)_2]^+$ (5% mol). [b] Based on NMR data.

The alcoholysis of $HSiMe_2Ph$ strongly depends on the nucleophilicity/steric bulk of alcohols. Thus, primary alcohols are much more reactive than secondary alcohols, and the latter are more reactive than tertiary alcohols (Table 7, entries 1-4). Such a dependence is in agreement with the proposed mechanism of this reaction, which includes the rate limiting step abstraction of the silylium ion from the cationic silane σ-complex $[CpRu(PPr^i_3)(NCMe)(\eta^2\text{-}HSiMe_2Ph]^+$ by alcohol (Scheme 101). This reaction gives the ruthenium complex $[CpRu(PPr^i_3)(NCMe)H]$ and the silyloxonium species $[Me_2PhSi\text{-}O(H)R]^+$, which could further react with the formation of $[CpRu(PPr^i_3)(NCMe)(H_2)]^+$ and $Me_2PhSi\text{-}OR$. The evolution of hydrogen from ruthenium and coordination of another molecule of silane finishes the proposed catalytic cycle (Scheme 101).



Scheme 101. The proposed mechanism of alcoholysis of silanes

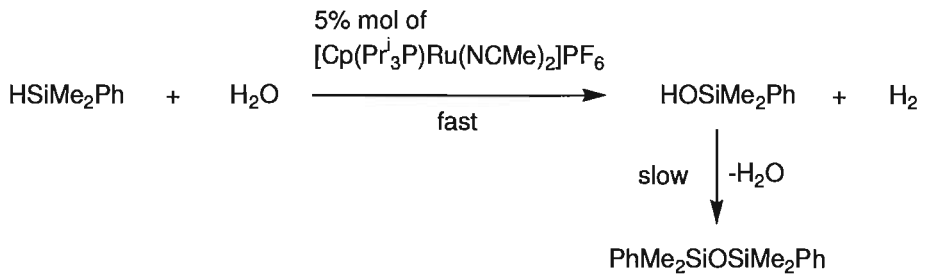
In addition to the reactions with alcohols, we also tested an amine substrate in dehydrogenative coupling with $HSiMe_2Ph$. There are only a few catalytic reactions of this type in literature,[140] and these Si-N bond formation reactions are of interest as a direct and simple synthetic route to silyl amine and silicon nitride compounds.[140a-d] The reaction between $PhNH_2$ and one equiv. of $HSiMe_2Ph$ in the presence of **66-PF$_6$** resulted in fast substitution of hydrogen in the aniline with the formation of PhHN-$SiMe_2Ph$ (Scheme 102).



Scheme 102. The reaction between $PhNH_2$ and $HSiMe_2Ph$ mediated by $[CpRu(PPr^i_3)(NCMe)_2]^+$

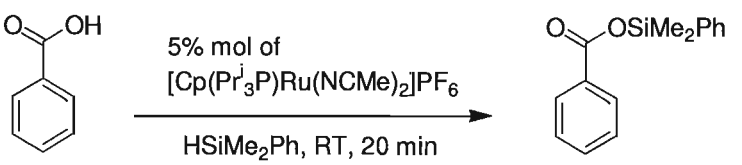
As it was mentioned before, dihydrogen is the only by-product of dehydrogenative coupling reactions. Due to the exponentially increasing interest in hydrogen as an environmentally friendly fuel,[141] significant research efforts are now being devoted to the development of efficient hydrogen sources. Therefore, the dehydrogenative coupling reactions could be considered as one of the potential sources of hydrogen, which could be generated under ambient conditions. This idea has been discussed by Abu-Omar et al.,[142] who used H_2O as the cheapest coupling partner for the reaction with silane in the presence of a rhenium catalyst.

The ruthenium complex **66-PF$_6$** also effectively catalyzes hydrolysis of $HSiMe_2Ph$ with the generation of hydrogen gas (Scheme 103). Interestingly, under standard reaction conditions, most of the silane was converted into the silanol $HOSiMe_2Ph$, which undergoes a very slow condensation into the siloxane $O(SiMe_2Ph)_2$. Therefore, this reaction can be potentially used as a very mild method for the synthesis of silanols, which are widely used for the preparation of polymeric silicon materials.



Scheme 103. Hydrolysis of $HSiMe_2Ph$

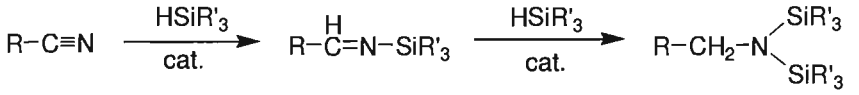
Noteworthy, the complex **66-PF$_6$** can also efficiently operate under acidic conditions. Thus, it catalyzes the dehydrogenative coupling of PhCOOH with $HSiMe_2Ph$, which results in a very selective formation of the silyl ester $PhCOOSiMe_2Ph$ (Scheme 104).



Scheme 104. Dehydrogenative coupling of $HSiMe_2Ph$ with PhCOOH

III.2.3 Hydrosilylation of nitriles

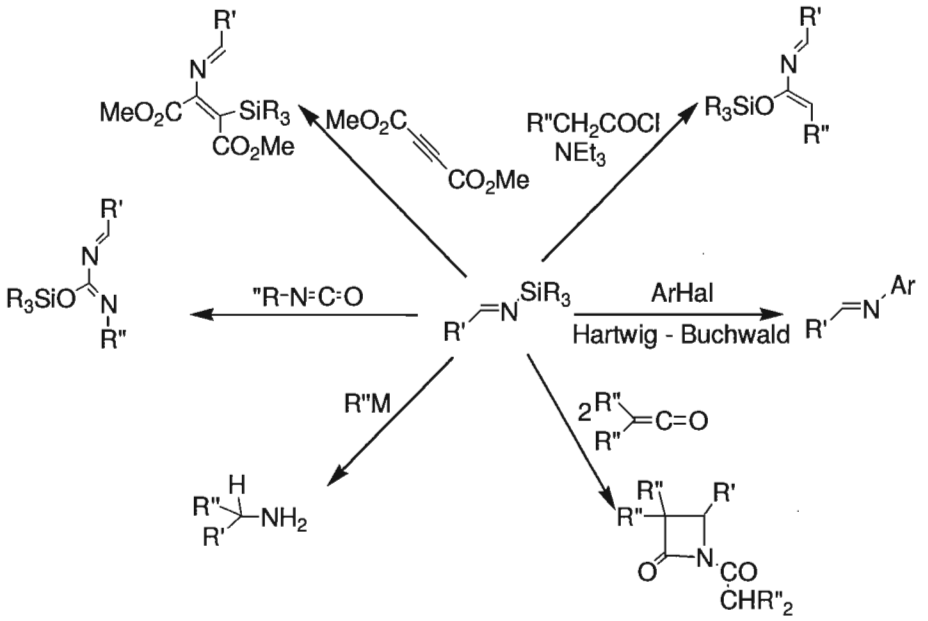
Catalytic reduction of nitriles by silanes could potentially result in the preparation of silylated imines or amines (Scheme 105), which represents an attractive alternative to the common approaches for the synthesis of these compounds.



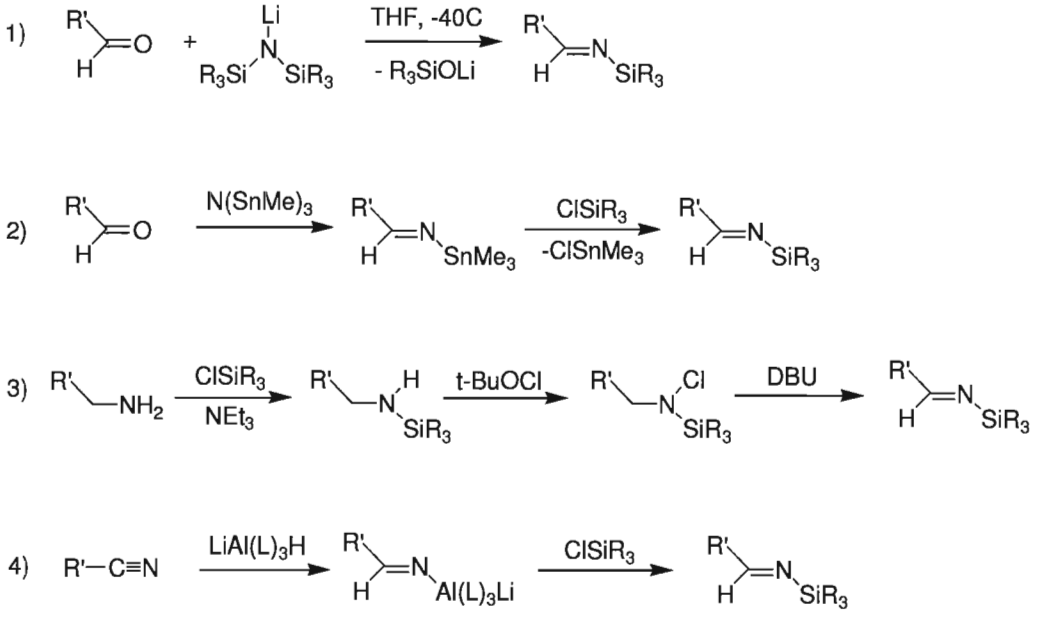
Scheme 105. Hydrosilylation of nitriles

Silylated imines are of special interest due to their important role in medicinal chemistry and organic synthesis.[20] Due to the well-known instability of imines RCH=NH, the corresponding N-silylated imines became the most common surrogates of these compounds with a large number of applications (Scheme 106).[20] Thus, the silyl imines are valuable starting materials for the synthesis of a variety of azadienes, which are the key components in the preparation of a number of heterocyclic compounds.[20] Different *N*-aryl imines can be synthesized with high yields using Buchwald-Hartwig coupling of silyl imines with aryl halides.[143] The textbook Staudinger's reaction utilizes silyl imines for the construction of a β-lactam ring, the core motif of most antibiotics, such as penicillins, cephalosporins, penems etc.[20] Silyl imines can be also easily converted into the primary amines by the reaction with organolithium or organozinc compounds, which could also be used for the synthesis of chiral amines. Countless number of other nitrogen containing compounds can be synthesized directly from silyl imines, such as 1,2-diamines, 1,2-aminols, aziridines etc.[20]

Due to the high importance of silyl imines, significant research efforts have been devoted to the development of efficient synthetic routs to these compounds (Scheme 107).[20] Thus, *N*-silyl imines can be prepared from the corresponding aldehydes by the reaction with (bis)silyl amide at low temperature or in two steps via stannyl imines.[20] The oxidation of *N*-silylamines by *tert*-butyl hypochlorite followed by the base-induced elimination of HCl is another common method.[20] Silyl imines are also often obtained from nitriles by the reaction with lithium aluminium triethoxy hydride, followed by transmetalation of the lithium salt with chlorosilane.[20] As one can see, the direct hydrosilylation of nitriles (Scheme 105) is the only method, which allows for the preparation of silyl imines in one step with the 100% atom efficiency.



Scheme 106. Selected applications of silyl imines.



Scheme 107. Synthetic approaches to silyl imines

Nitriles have been traditionally considered to be inert in hydrosilation, to the extent that nitriles are often used as solvents in many catalytic applications. Metal mediated stoichiometric H-Si addition to C≡N triple bond has been realized only very

recently.[iv] Most of the known examples of catalytic hydrosilylation lead to the reduction of nitriles with the formation of silylated amines or enamines,[30, 32-34, 89c] and only few examples of selective reduction of unfunctionalized nitriles to silylated imines have been performed at high temperature (100-200°C).[35-36]

During our studies of cationic ruthenium silane σ-complexes $CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)$, we observed formation of the hydrosilylated acetonitrile product, which gave us an idea to check the catalytic activity of the ruthenium complex in the hydrosilylation of nitriles. We doscovered that complex **66** effectively catalyzes hydrosilylation of both aromatic and aliphatic nitriles with the very selective formation of silyl imines at room temperature, a process that finds no precedents in the literature.

Table 8. Monohydrosilylation of simple nitriles in the presence of $[CpRu(PPr^i_3)(CH_3CN)_2]^+$ (5% mol, chloroform, RT)[a]

N	Substrate	Silane	Time	Conv.[b]	Products
1	CH_3CN	$HSiMe_2Ph$	20 min[c]	100%	$CH_3CH{=}NSiMe_2Ph$ (90%)
2	i-PrCN	$HSiMe_2Ph$	2 h	100%	i-PrCH=$NSiMe_2Ph$
3	t-BuCN	$HSiMe_2Ph$	24 h[d]	14%	t-BuCH=$NSiMe_2Ph$
4	PhCN	$HSiMe_2Ph$	4 h[e]	100%[f]	PhCH=$NSiMe_2Ph$

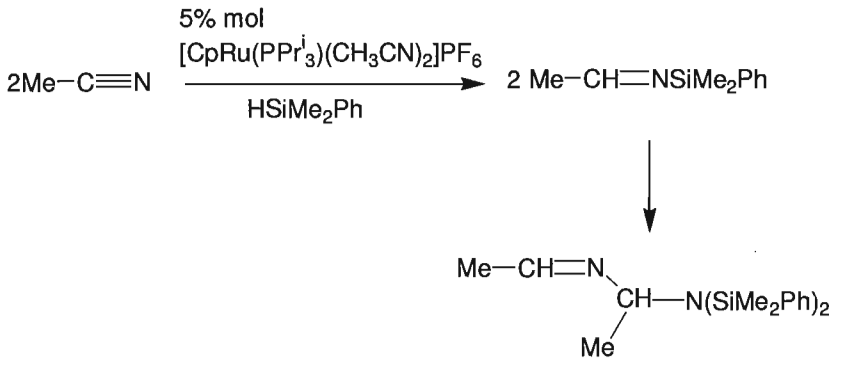
[a] In a general procedure to a solution of nitrile and silane in chloroform was added $[CpRu(PPr^i_3)(NCMe)_2]BAF$ (5% mol). [b] Based on NMR data. [c] Reaction in acetone; [d] At 50°C; [e] 1 h in acetone; [f] 95% isolated yield under solvent free conditions.

Simple aromatic or aliphatic silylated imines can be easily obtained from the corresponding nitriles (Table 8) by the reaction with $HSiMe_2Ph$. The reaction time increases with the increasing bulkiness of the nitriles (Table 8, entries 1-3). The hydrosilation of t-BuCN is still selective, but requires more severe conditions (50 °C) and longer reaction times (Table 8, entry 3). Slightly longer time is also needed for the full conversion of benzonitrile (4 h) at room temperature in chloroform, but only 1 h is required for the reaction in acetone.

In comparison with all the other substrates, acetonitrile showed very unusual behaviour in this reaction. Thus, the full conversion of acetonitrile was observed after only 20 min, and the corresponding silyl imine was the main product at this point. However, the silyl imine then slowly dimerizes with the formation of $CH_3CH{=}N\text{-}CH(CH_3)N(SiMe_2Ph)_2$, which became the dominant product after 6 h (Figure 18). The

[iv] See corresponding section of the historical

mechanism of dimerization remains unknown but we can speculate that the dimer results from the so far unknown N-Si addition across the C=N bond. Due to the loss of selectivity we were not able to isolate $CH_3CH{=}NSiMe_2Ph$ on the preparative scale, and only the corresponding dimer was obtained as the main product. In addition, the (bis)hydrosilylated nitrile and a silyl enamine were also observed as minor products in the hydrosilylation of acetonitrile.



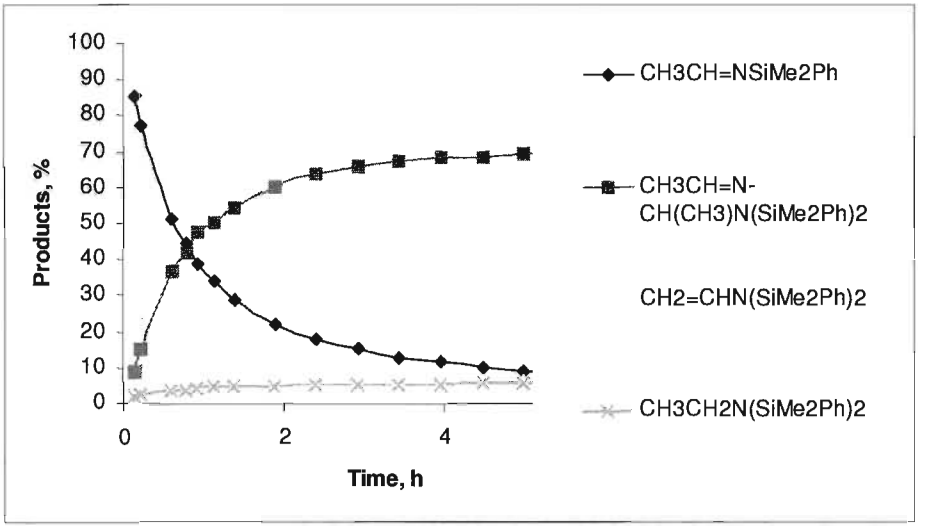


Figure 18. Hydrosilylation of acetonitrile

Changing the phosphine ligand in the ruthenium complex or using a different silane has a drastic effect on the catalytic activity. The best results were achieved for the system PPr$^i_3$/HSiMe$_2$Ph. All the other combinations for the catalytic system were much less active or completely inactive. Since the pre-catalyst is a cationic complex $[CpRu(PPr^i_3)(NCMe)_2]^+$, we also studied the influence of the counter-anion. Rewardingly, the substitution of the expensive BAF-anion for the more readily

available $[PF_6]^-$ or $[BF_4]^-$ results only in insignificant increase of reaction times without any drastic effect on the selectivity of the reaction.

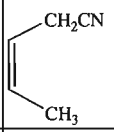
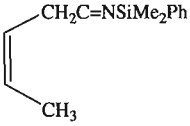
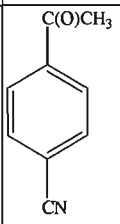
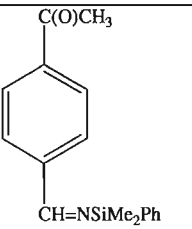
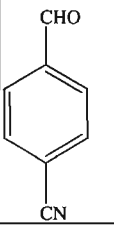
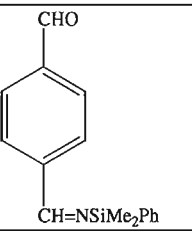
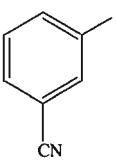
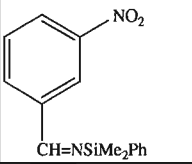
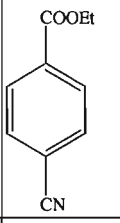
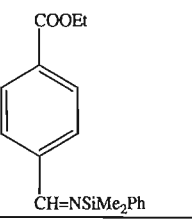
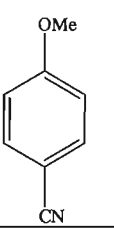
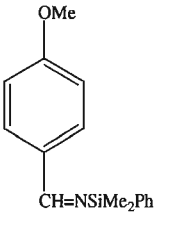
Unprecedented selectivity towards functional groups was observed in the hydrosilylation of functionalized nitriles in the presence of **66** (Table 9). The CN group in the homoallylic position is selectively reduced in the presence of C=C double bond (Table 9, entry 1). In contrast, the hydrosilylation of acrylonitrile required a much longer time and the reaction does not go to completion even after 24 h at room temperature (Table 9, entry 2), which suggests possible poisoning of the catalyst by the chelating azabutadiene product. Notably, previous reports on the hydrosilylation of acrylonitrile showed selective Si-H addition to the C=C double bond[30a, 144] with only a few examples of double hydrosilylation of the cyano group.[33b] Our attempt to hydrosilylate a non-conjugated alkynyl nitrile (Table 9, entry 3) resulted in a slow Si-H addition to the terminal C≡C triple bond, which can be explained by the high propensity of half-sandwich complexes of Ru to activate alkynes.[145] On the other hand, electron-poor aryl nitriles containing the usually reactive keto-, aldo-, nitro-, and ester functionalities in the aryl substituent are all hydrosilylated exclusively on the cyano group (Table 9, entries 4-7), even though some of the reaction times are increased significantly in comparison with the hydrosilylation of benzonitrile (Table 8, entry 4). In contrast, the hydrosilylation of the electron-rich *p*-cyanoanisole proceeds at the same rate (100% after 1 h in acetone-d_6, entry 8) as of benzonitrile. Also, the hydrosilylation of the 3-cyanopyridine proceeds selectively at the cyano group but a long reaction time is required (entry 9).

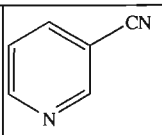
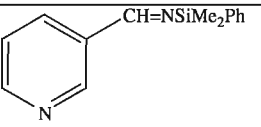
Due to the exceptional tolerance of this method to the presence of carbonyl functionality, the hydrosilylation of nitriles can be also performed in acetone as a solvent, which also significantly accelerates the reaction rate. Thus, the full conversion of benzonitrile to the silylated imine was four times faster in acetone (1 h) than in chloroform (4 h).

The hydrosilylation of liquid substrates can be carried out under solvent free conditions in the presence of the same catalyst. Importantly, significantly reduced loadings of the catalyst can be used in this case. Thus, hydrosilylation of both alkyl (i-PrCN) and aromatic (PhCN) nitriles was performed under these conditions in the presence of less than 1% mol of **66-PF$_6$**, but longer reaction times are required (24 h). In contrast to hydrosilylation of carbonyls, which required the ruthenium complex

with the BAF counter anion for the solvent free reactions, the ruthenium complex with the cheap PF_6^- counter anion can be effectively used for the hydrosilylation of nitriles. Presumably, the enhanced stability of the catalyst in this case is achieved due to the high concentration of nitrile in the reaction mixture.

Table 9. Hydrosilylation of functionalized nitriles with $HSiMe_2Ph$ in the presence of $[CpRu(PPr^i_3)(CH_3CN)_2]^+$ (5% mol, chloroform, RT)[a]

N	Substrate	Time	Conv.[b]	Products
1		2.5 h	100%	
2	CH_2=CH-CN	24 h	30%	CH_2=CH-CH=$NSiMe_2Ph$
3	HC≡$C(CH_2)_3CN$	168 h	40%	$Me_2PhSiCH$=$CH(CH_2)_3CN$
4		8 h	100%	
5		14 h	100%	
6		4 h	100%	
7		48 h[c]	100%	
8		1 h[d]	100%	

9		14 h	68%	

[a] In a general procedure, to a solution of ketone and silane in chloroform was added $[CpRu(PPr^i_3)(NCMe)_2]^+$(5% mol). [b] Based on NMR data. [c] reaction in CH_2Cl_2; [d] reaction in acetone.

Taking advantage of the low solubility of the cationic ruthenium complex in non-polar solvents, the products of hydrosilylation can be extracted with hexane or ether and the catalyst can be easily separated from the reaction mixture.[135c] Importantly, the recovered catalyst can be used again in the reaction, as illustrated in Figure 19. Slow decrease in the catalytic activity can be mostly explained by some loss of the ruthenium complex during the separation and extraction of products, which was performed with microscale quantities of the reagents.

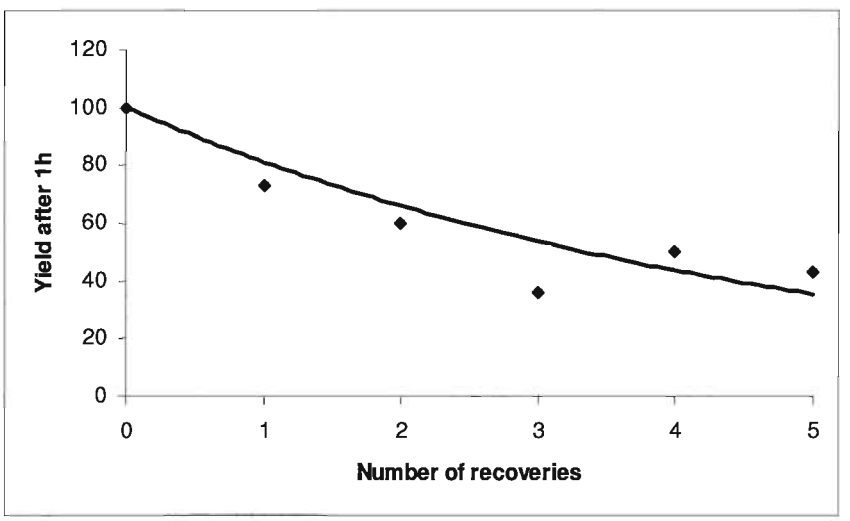


Figure 19. Hydrosilylation of PhCN with $HSiMe_2Ph$ in acetone using recovered catalyst $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (5% mol initially).

Our attempts to extend this methodology to an open flask setup were unsuccessful because of the high sensitivity of the products to air. However, a thorough exclusion of water from solvents is not required as the silane reacts fast with trace water in the presence of the ruthenium catalyst with the formation of siloxane. The reactions can be, therefore, conveniently run on the bench in closed flasks pre-flashed with inert gas. Moreover, the reactions in acetone, which was dried over molecular sieves for several days prior to reaction, were notably slower than in

commercially available acetone. This observation suggests that traces of water could accelerate the reaction, but this phenomenon is not fully understood. A similar effect was achieved after addition of catalytic amounts of 4-(dimethyamino)pyridine, which could potentially act as a nucleophile, to the reaction mixture in dry acetone.

(Bis)hydrosilylation of nitriles with the direct formation of corresponding silyl amines is also of significant interest. First of all, the silicon-nitrogen bond withstands a variety of reaction conditions, which provides an efficient protection of the otherwise very reactive primary amines.[146] At the same time, silyl amines can react with a variety of electrophiles, which can be used in the synthesis of value-added compounds. For example, this strategy can be applied to the formation of new C-N bonds.[146] Also, the (bis)hydrosilylation of nitriles could be a valuable alternative to the more common hydrogenation of nitriles to primary amines, which is often hampered by the low selectivity because imines and secondary amines are usually formed as by-products in this reaction.[19g]

Table 10. (Bis)hydrosilylation of nitriles with $HSiMe_2Ph$ in the presence of $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (5% mol, chloroform, RT)[a]

N	Substrate	Conv. (time)	Products
1	PhCN	100% (66h)	$PhCH_2N(SiMe_2Ph)_2$
2	$MeO(C_6H_4)CN$	100% (48 h)	$MeO(C_6H_4)CH_2N(SiMe_2Ph)_2$
3	*m*-$NO_2(C_6H_4)CN$	100% (48 h)	*m*-$NO_2(C_6H_4)CH{=}N(SiMe_2Ph)$
4	p-$CH_3(O)C(C_6H_4)CN$	100% (48 h)	p-$CH_2{=}C(OSiMe_2Ph)(C_6H_4)CH_2N(SiMe_2Ph)_2$ (40% in the mixture)
5	i-PrCN	100% (24 h)	$(CH_3)_2CHCH_2N(SiMe_2Ph)_2$ (43%) $(CH_3)_2C{=}CHN(SiMe_2Ph)_2$ (57%)

[a] In a general procedure to a solution of ketone and silane (2.5 equiv.) in chloroform was added $[CpRu(PPr^i_3)(NCMe)_2]BAF$ (5% mol). [b] Based on NMR data.

We found, that some simple and non-functionalized nitriles can be also reduced to disilylamines in the presence of **66-BAF** (Table 10). Thus, the bis(silyl) benzylamine was obtained in the reaction of benzonitrile with two equivalents of silane (Table 10, entry 1). Surprisingly, there was no hydrosilylation of the related imine PhMeC=NPh under the same conditions as the (bis)hydrosilylation of benzonitrile proceeds *via* intermediate formation $PhCH{=}NSiMe_2Ph$. *p*-Cyanoanisole can be also selectively (bis)hydrosilylated after 48h (Table 10, entry 2), but the reaction with the electro-poor *meta*-$NO_2(C_6H_4)CN$ stops at the imine stage (Table 10, entry 3). On the other hand, hydrosilylation of functionalized nitriles gave a mixture

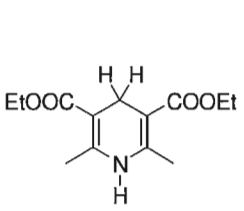
of products due to the loss of chemoselectivity upon the second stage of hydrosilylation (Table 10, e.g. entry 4). Also, (bis)hydrosilylation of an enolizable alkylnitrile was accompanied by the concomitant formation of an enamine (Table 10, entry 5).

Due to the mentioned above similarity in the mechanism of hydrosilylation of carbonyls catalyzed by the ruthenium complex **66** with borane $B(C_6F_5)_3$, we also performed hydrosilylation of nitriles in the presence of $B(C_6F_5)_3$, which has never been studied before. Thus, the hydrosilylation of acetonitrile resulted in a fast and very selective formation of $CH_3CH_2N(SiMe_2Ph)_2$, which could not be achieved with the ruthenium catalyst. On the other hand, the hydrosilylation of benzonitrile gave a mixture of the corresponding silyl imines and amines, which was converted into one product, the silyl amine $PhCH_2N(SiMe_2Ph)_2$, after the addition of a second equivalent of silane. Unfortunately, the poor selectivity towards the carbonyl functionality was observed, so that the keto-group of 4-(acyl)benzonitrile was hydrosilylated preferably.

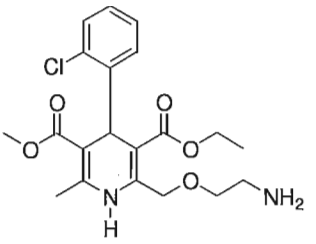
Based on our previous studies on catalytic hydrosilylation of carbonyls (Scheme 98), an analogous mechanism was proposed for the hydrosilylation of nitriles, which is based on the intermediate formation of the ruthenium hydride complex $CpRu(PPr^i_3)(NCR)H$ and a silylium cation adduct with the nitrile $[R'_3Si\text{-}NCR]^+$, followed by the hydride transfer from ruthenium.

III.2.4 Hydrosilylation of pyridines

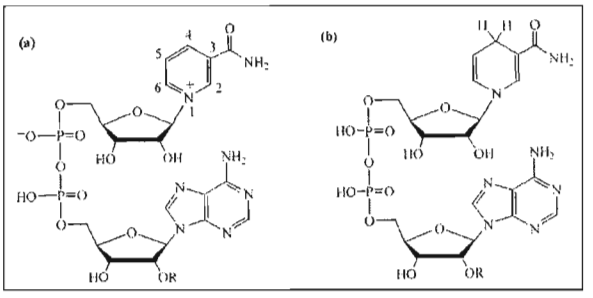
Partially reduced pyridines are an abundant class of organic compounds with numerous applications (Figure 20).[38] For example, the Hantzsch ester, a representative of this class, is widely used in organic synthesis as a very selective reducing agent.[147] The derivatives of dihydropyridine also play an important role in the medicinal chemistry as the most popular calcium channel blockers, which are aimed to reduce blood pressure.[38] Notably, dihydropyridines are the key components of metabolic oxidation in biological systems, where NAD^+ acts as the oxidizing agent, and the corresponding dihydropyridine derivative NADH is the reducing agent.[38a, b, 38d] There are also many synthetic applications of dihydropyridines, which have been previously reviewed.[38a, b, 38d]



Hantzsch ester



Amlodipine
(calcium channel blocker)



NAD^+ **NADH**

Figure 20. Selected examples of dihydropyridines

The synthesis of partially reduced pyridines is not a trivial task. However, there are a number of synthetic approaches to these compounds. One of them is based on the reduction of corresponding pyridinium salts, which is usually performed in the presence of stoichiometric or excess amounts of borohydres, thionites, Zn, Li/NH_3.[38a, b, 38d] All these methods have limitations, and the development of new synthetic strategies is of high interest. Therefore, the discovery of heterogeneous hydrosilylation of pyridine by Cook and Lyons[39] followed by the invention of homogeneous hydrosilylation by Harrod et al.[40] has received considerable attention. These methods allow for a one step preparation of N-silyl dihydro- and tetrahydopyridines. The latter compounds could potentially be very convenient and universal precursors for a large number of valuable dihydro- and tetrahydropyridine derivatives. However, the poor regioselectivity of catalytic hydrosilylation of pyridines[39-40] has so far prevented the synthetic application of this reaction.

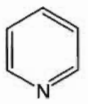
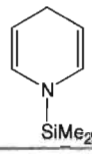
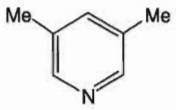
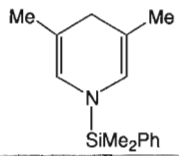
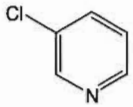
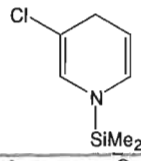
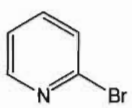
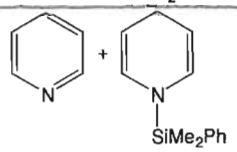
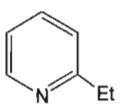
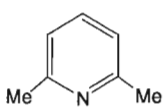
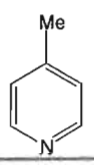
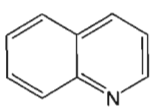
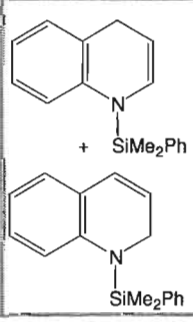
We found that complex **66-BAF** effectively catalyzes hydrosilylation of pyridine with $HSiMe_2Ph$. Importantly, this catalytic system operates even at room temperature and, in contrast to the previously reported Ti-catalyzed hydrosilylation,[40] the reaction with pyridine resulted in a very selective formation of *N*-silyl 1,4-

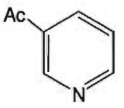
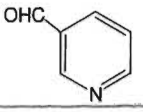
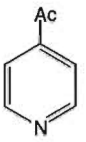
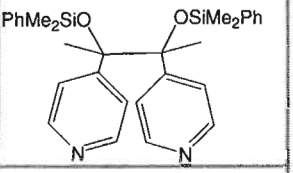
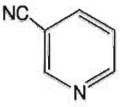
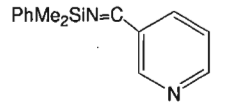
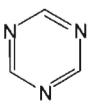
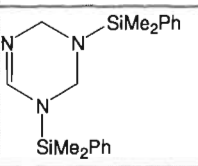
dihydropyridine (Table 11, entry 1). Such a high selectivity is of great importance because the common reduction methods often give mixtures of 1,2- and 1,4-dehydripyridines, which are difficult to separate.[38] The presence of methyl substituents in the 3- and 5-position has no effect on the course of the hydrosilylation (Table 11, entry 2), and also halogen in the 3-position is tolerated (Table 11, entry 3). Surprisingly, the hydrosilylation of 2-bromopyridine results in the formation of pyridine and the silylated 1,4-dihydropyridine with low overall conversion (Table 11, entry 4), which suggests that the substrate initially undergoes dehalogenation followed by hydrosilylation of the resulting pyridine. The steric accessibility of the nitrogen centre and the 4-position in pyridines has a drastic impact on the reaction, and the pyridines with substituents in the 2-, 4- and 6-positions cannot be converted into corresponding dihydropyridines by this method (Table 11, entries 5-7). There is a high preference of 1,4-hydrosilylation by this system over the common 1,2-reduction. Thus, 4-methylpyridine, which would favour 1,2-hydrosilylation due to the steric factor, remained inert under the catalytic conditions (Table 11, entry 7).

Importantly, such a challenging substrate as quinoline was successfully converted into a mixture of 1,4- and 1,2-hydrosilylated products, but only moderate overall yield was achieved (Table 11, entry 8). The latter reaction can be also performed under solvent-free conditions to give a better yield (70%) with the reduced loading of the catalyst (0.5% mol). Hydrosilylation of pyridine under solvent free condition is also a very convenient method for the preparation of *N*-silyl 1,4-dihydropyridine, because it requires only 0.2% of the catalyst and proceeds with a better yield of the product (96%).

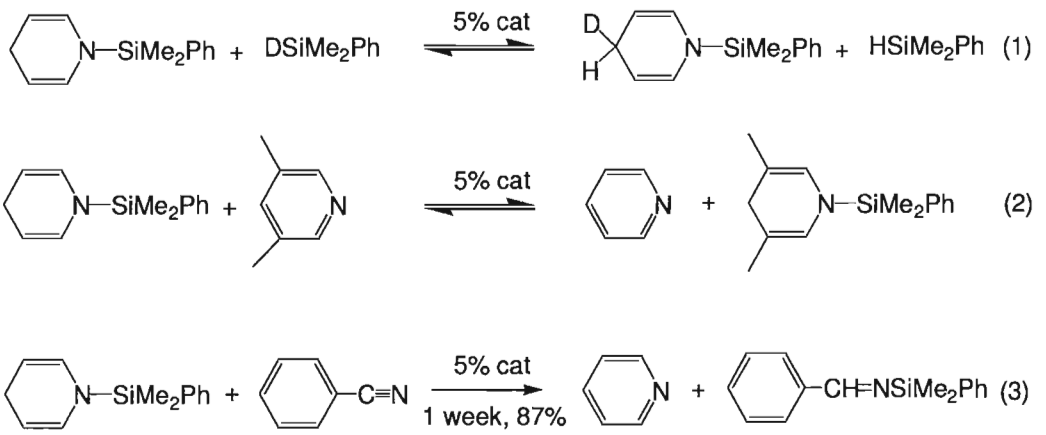
We also checked the selectivity of this reaction towards different functional groups. Thus, the hydrosilylation of the 3-acyl and 3-formyl pyridine resulted in the formation of a mixture of products in both cases (Table 11, entries 9 and 10). Surprisingly, the 4-acylpyridine cleanly gave a pinacole derivative, which could be a result of a radical reaction (Table 11, entry 11). As mentioned before, the cyano group is hydrosilylated preferably, so that the 3-(silyliminoformyl)pyridine is formed in high yield (Table 11, entry 12). The hydrosilylation of triazine resulted in the formation of a mixture of mono- and (bis)hydrosilylated triazine, which can be converted into one product, *N*-silyl-1,2,3,4-tetrahydroderivative, by the reaction with a second equivalent of silane (Table 11, entry 13).

Table 11. Hydrosilylation of pyridines with $HSiMe_2Ph$ in the presence of $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (5% mol, CH_2Cl_2, RT)[a]

N	Substrate	Time	Conversion[b]	Products
1		30 min	86%[c]	
2		3 h	82%	
3		15 min	100%	
4		3 h	47%	
5		3 h	0%	NR
6		24 h	0%	NR
7		24 h	0%	NR
8		30 min	50%[d]	

9		30 min	100%[e]	Mixture of partially reduced pyridines
10		30 min	100%[e]	Mixture of partially reduced pyridines
11		15 h	50%	
12		14 h	68%	
13		3.5 h	98%[e]	

[a] In a general procedure, to a solution of heteroaromatic substrate and silane in dichloromethane was added [CpRu(PPr$^i_3$)(NCMe)$_2$]BAF (5% mol). [b] Based on NMR data. [c] 92% isolated yield under solvent-free conditions; [d] 70% under solvent-free conditions; [e] 2 equiv. of $HSiMe_2Ph$ was added.

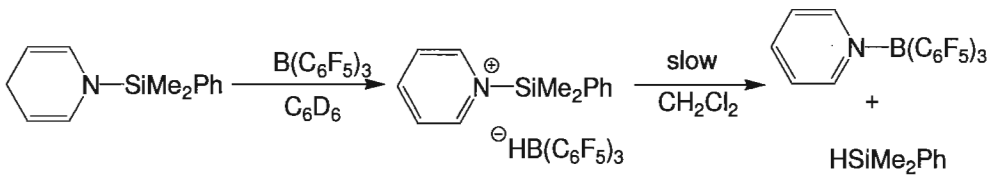


Scheme 108. Reversibility of hydrosilylation of pyridine

Surprisingly, we found that the hydrosilylation of pyridine is reversible. Thus, in the presence of catalyst **66-BAF**, the *N*-silyl 1,4-dihydropyridine can be used for hydrosilylation of benzonitrile to give the pyridine and the imine $PhHC{=}NSiMe_2Ph$ (Scheme 108, eq. 1). Also, an equilibrium mixture of 1,4-hydrosilylated pyridines

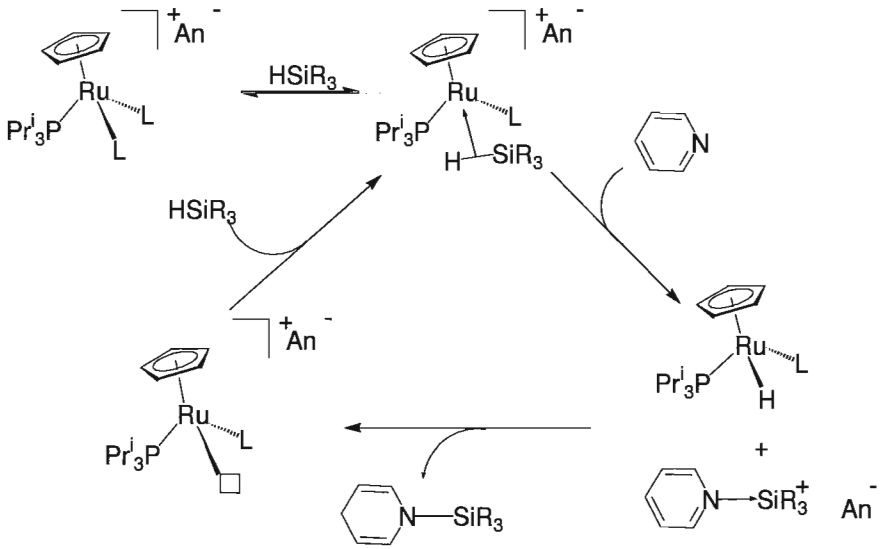
forms in the presence of 3,5-lutidine (Scheme 108, eq. 2). The treatment of *N*-silyl 1,4-dihydropyridine with $DSiMe_2Ph$ in the presence of **66-BAF** resulted in scrambling of deuterium between free silane and the 4-position of *N*-silyl 1,4-dihydropyridine (Scheme 108, eq. 3). Notably, these reactions are very rare examples of a reversible hydrosilylation.

Interestigly, dehydrosilylation of *N*-silyl 1,4-dihydropyridine can be also achieved by addition of $B(C_6F_5)_3$ in benzene, which abstracts hydride from the 4-position with precipitation of the pyridinium salt $[C_5H_5N^*SiMe_2Ph]HB(C_6F_5)_3$ (Scheme 109). The latter decomposes slowly (24 h) in dichloromethane with the formation of $C_5H_5N^*B(C_6F_5)_3$ and $HSiMe_2Ph$ (Scheme 109).



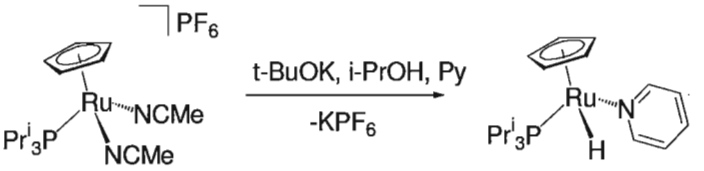
Scheme 109. The reaction of N-silyl dihydropyridine with $B(C_6F_5)_3$

We previously suggested an ionic hydrosilylation mechanism for hydrosilylation of carbonyls and nitriles catalyzed by $[CpRu(PPr^i_3)(L)_2]^+$, which includes the formation of cationic silane σ-complexes $[CpRu(PPr^i_3)(L)(\eta^2\text{-}HSiR_3)]^+$, nucleophilic abstraction of a silylium ion by the substrate followed by hydride transfer from the ruthenium hydride $CpRu(PPr^i_3)(L)H$. An analogous mechanism can be proposed for the hydrosilylation of pyridines (Scheme 110).



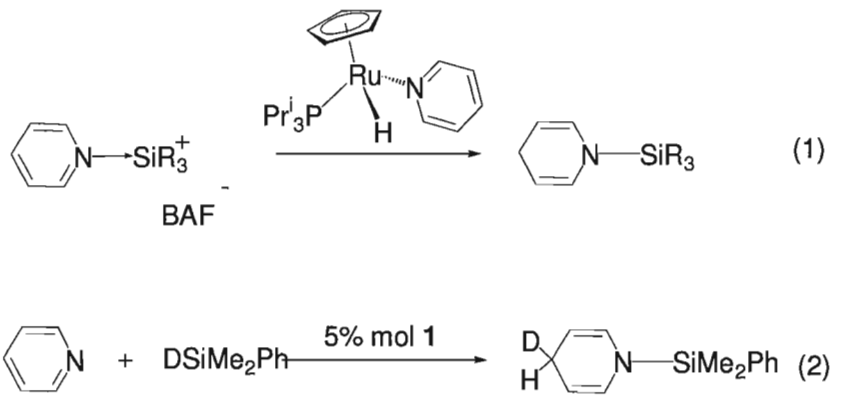
Scheme 110. The proposed mechanism of hydrosilylation of pyridines

Previously, we were able to prove the formation of silane σ-complexes $[CpRu(PPr^i_3)(L)(\eta^2\text{-}HSiR_3)]^+$ as intermediates in the hydrosilylation reactions. In order to check the feasibility of the hydride transfer step, we prepared a neutral pyridine-stabilised hydride complex $[CpRu(PPr^i_3)(Py)H]$ by the reaction of **66-PF$_6$** with *t*-BuOK in *i*-PrOH in the presence of excess pyridine (Scheme 111). The complex $[CpRu(PPr^i_3)(Py)H]$ was characterized by NMR. Its isolation in analytically pure form was compromised by low thermal stability in the absence of excess pyridine.



Scheme 111. The synthesis of CpRu(PPr$^i_3$)(Py)H

As expected, the reaction of $[CpRu(PPr^i_3)(Py)H]$ with the readily available pyridinium salt $[(Et_3Si)(Py)]BAF$ yields the 1,4-hydrosilylated pyridine (Scheme 112, eq. 1). Furthermore, the suggested mechanism is in agreement with the results of catalytic hydrosilylation of pyridine with the deuterated silane $DSiMe_2Ph$: the deuterium atoms were observed exclusively in the 4-position of the product (Scheme 112, eq. 2). The latter observation rules out the formation 1,4-hydrosilylated products from the kinetic products of 1,2-addition, which was previously proposed in the Ti-catalyzed hydrosilylation of pyridines by Harrod et al.[40]



Scheme 112. Hydrosilylation of pyridine with $DSiMe_2Ph$ and the reaction of $[(Et_3Si)(Py)]BAF$ with CpRu(PPr$^i_3$)(Py)H

We believe that the hydride from the ruthenium hydride complex $CpRu(PPr^i_3)(L)H$ is predominantly transferred to the pyridinium cation in a single step (a 2e process). However, we cannot exclude the possibility of a sequence of one electron processes (Scheme 112, eq. 2). Thus, Norton et al. showed that both pathways are feasible for the closely related system $RO_2C\text{-}Pyr^+/Cp(dppe)RuH$.[148] It was also shown, that the single electron transfer (SET) mechanism could be predominant for substrates bearing substituents in the 4-position, which could explain the formation of a pinacole derivative in the hydrosilylation of 4-acylpyridine (Table 11, entry 11).

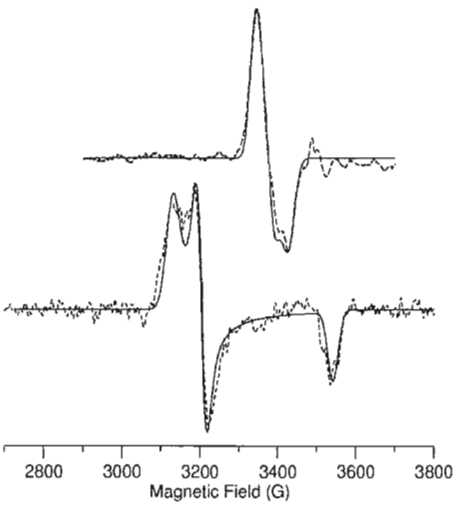
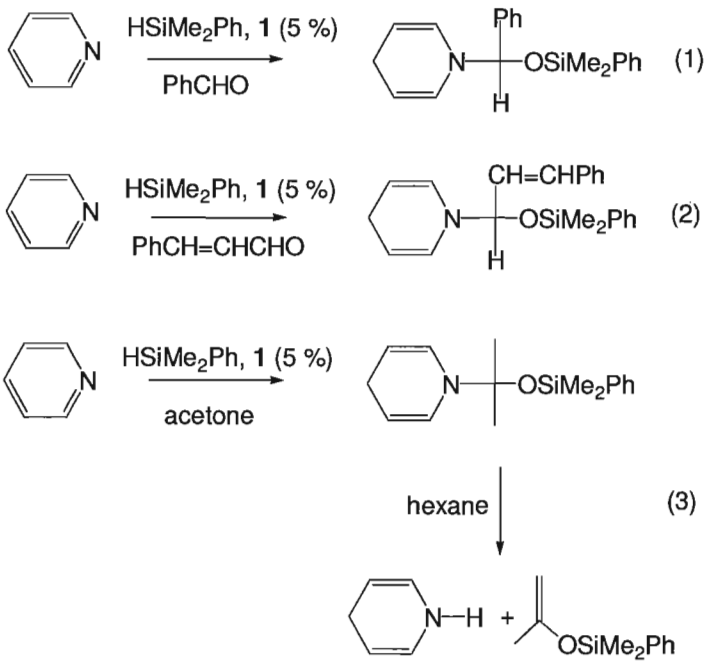


Figure 21. EPR spectra of different reaction mixtures. Top: $[CpRu(PPr^i_3)(CH_3CN)_3]BAF$, pyridine and $HSiMe_2Ph$ in CH_2Cl_2; T = 80 K. Bottom: $[CpRu(PPr^i_3)(CH_3CN)_3]PF_6$, pyridine and $HSiMe_2Ph$ in CH_2Cl_2; T = 120 K. Dashed lines: experimental data, Solid lines: simulations

We indeed observed weak EPR signals of paramagnetic species in the EPR spectrum [v] of a frozen reaction mixture of pyridine, $HSiMe_2Ph$, and complex $[CpRu(PPr^i_3)(CH_3CN)_2]^+$ (20%). The nature of paramagnetic compounds depends on the nature of the counter ion in the ruthenium catalyst. Thus, experimental and simulated EPR spectrum of the complex with BAF^- and PF_6^- as the counter ions are depicted on Figure 21. The top spectrum, which was obtained with BAF as the counter ion, was simulated with g_{xx}=2.089, g_{yy}=2.066 and g_{zz}=2.035. The bottom spectrum, which was obtained with the counter ion PF_6^-, was reproduced with g_{xx}=2.230, g_{yy}=2.178 and g_{zz}=1.970. The latter g-values are quite typical for low-spin

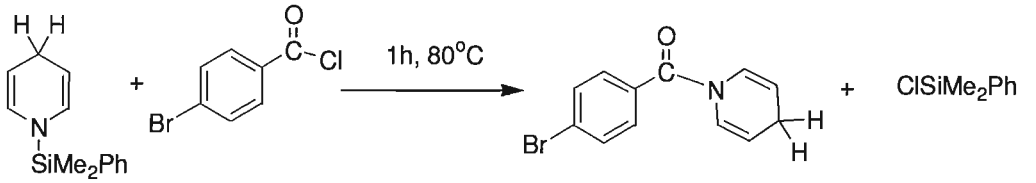
[v] I thank Prof. Art van der Est (Brock University) for the recording and interpretation of the EPR spectrum

Ru(III) half-sandwich complexes.[149] Much smaller g-anisotropy was observed in the top spectrum, which is not compatible with a Ru-centred low spin Ru(III) complex.[150] However, the average g-value of 2.062 is still significantly larger than what would be expected for a purely organic radical. Therefore, the unpaired electron in this paramagnetic species is, probably, delocalized between a ligand and the Ru atom.[151]



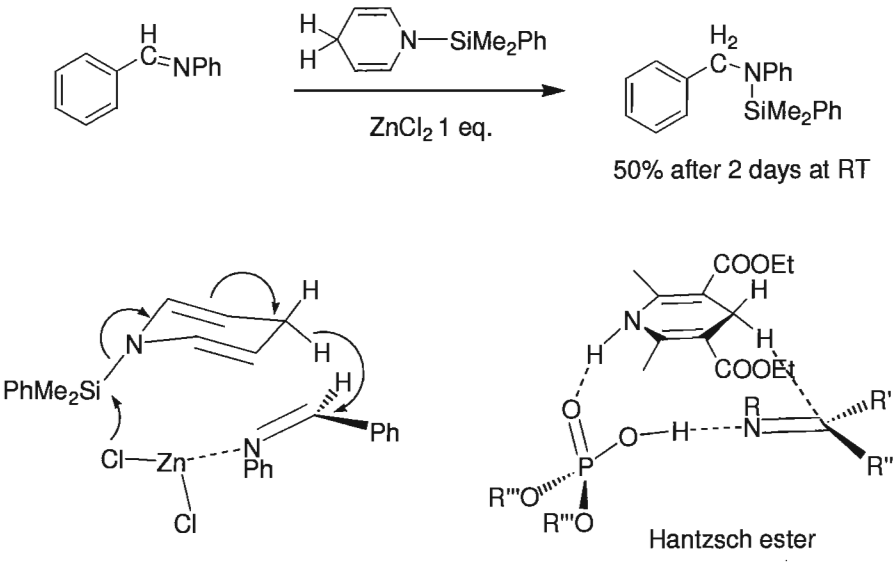
Scheme 113. Hydrosilylation of pyridines in the presence of carbonyls

In order to check further the compatibility of pyridine hydrosilylation with the presence of a carbonyl function, we performed the hydrosilylation of a 1:1 mixture of pyridine and aldehydes. Unexpectedly, we observed a mixture of *N*-silyl 1,4-dihydropyridine and the product of its formal N-Si addition across the C=O bond (Scheme 113, eq. 1 and 2). Moreover, the hydrosilylation of pyridine in acetone as solvent resulted in exclusive formation of the product of N-Si addition across the C=O bond (Scheme 113, eq. 3). However, the extraction of the product with hexane resulted in a formal dehydroamination reaction with the formation of 1,4-dihydropyridine and a silylated enol (Scheme 113, eq. 3).



Scheme 114. The reaction of N-silyl dihydropyridine with acid chloride

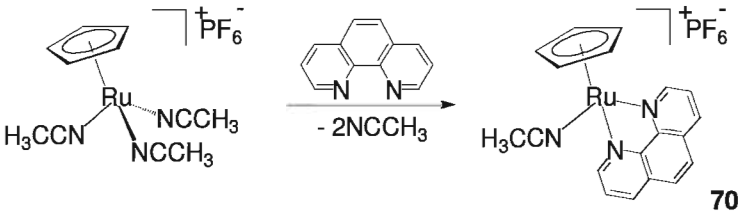
To investigate the chemical properties of silylated dihydropyridines, we attempted the reactions of these compounds with several common substrates. Thus, we attemted to use *N*-silyl 1,4-dihydropyridine for the reduction of acyl chloride, 4-$Br(C_6H_4)C(O)Cl$, to corresponding aldehyde. However, the reaction resulted in the formation of $ClSiMe_2Ph$ and the corresponding amide (Scheme 114), which remained stable even at 100°C. In contrast, the *N*-silyl 1,4-dihydropyridine did not react with ethylacetate, even at high temperatures (up 100 to °C) and in the presence of catalyst **66-BAF** (5 % mol). Also, *N*-silyl 1,4-dihydropyridine did not react with aldimines, even when complex **66-BAF** was used as an activator. However, we found that *N*-silyl 1,4-dihydropyridine slowly (50% after 2 days by NMR) hydrosilylates the aldimine PhN=CHPh in ether in the presence of an equivalent of $ZnCl_2$ (Scheme 115). Interestingly, there was no reaction between *N*-silyl 1,4-dihydropyridine and $ZnCl_2$. No reaction was also observed between $HSiMe_2Ph$ and PhN=CHPh in the presence of $ZnCl_2$ under these conditions. Based on these results, we can propose that $ZnCl_2$ in this reaction effectively plays the same role as a phosphoric acid in the reduction of imines by 1,4-dihydropyrides,[147a] forming a cyclic transition state (Scheme 115, bottom). This hypothesis can be also supported by the fact that the previously reported $ZnCl_2$-mediated hydrosilylations required very high temperatures (150-200 °C).[152]



Scheme 115. Hydrosilylation of imines with N-silyl dihydropyridine

III.2.5 Partial reduction of phenanthroline with silanes

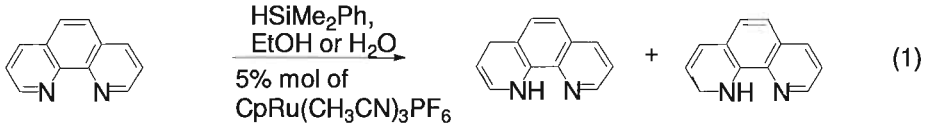
As mentioned before, the quinoline does undergo hydrosilylation (Table 11, entry 8). On the other hand, its chelating analogue, phenanthroline, poisons the catalyst **66-PF$_6$** by forming a very stable complex [Cp(Pr^i_3P)Ru(κ^2-phen)]PF_6 . In order to free up a reaction site in the catalyst, we attempted the hydrosilylation of phenanthroline in the presence of $[CpRu(NCCH_3)_3]^+$, which contains three labile acetonitrile ligands, and one of them would remain bound to ruthenium after the reaction of this complex with phenanthroline (Scheme 116). However, the hydrosilylation of dry phenanthroline proceeded with very small overall conversion even in the presence of this ruthenium complex.

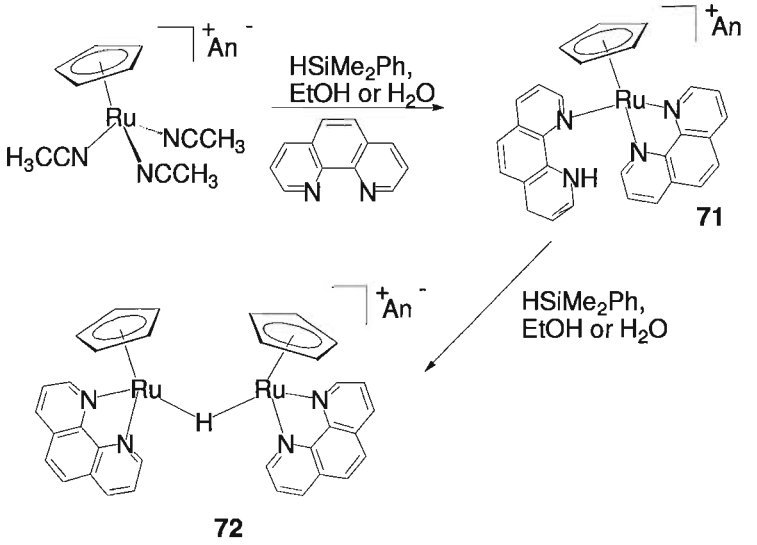


Scheme 116. The reaction of $[CpRu(NCCH_3)_3]PF_6$ with phenanthroline

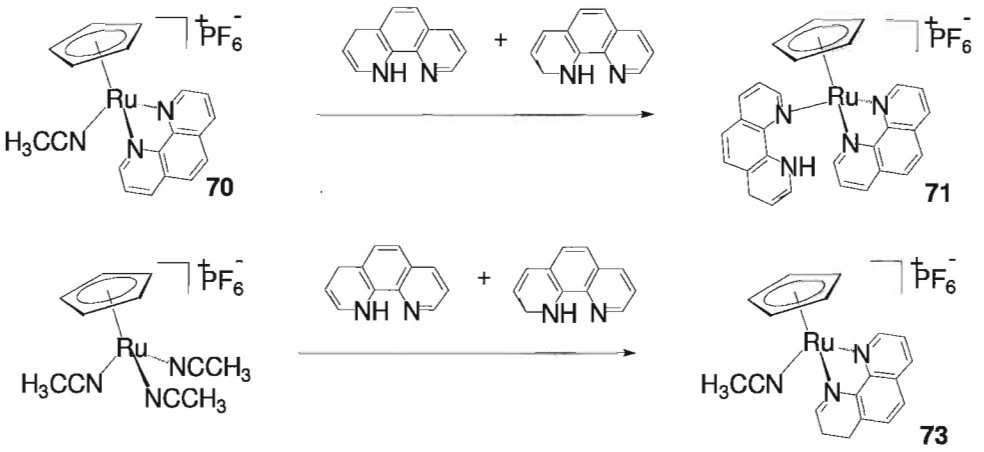
Accidentally, we found that adventitious water, which is often present in phenanthroline, gives a rise to a different catalytic process. Thus, in the presence of

water the compound **70** formed *in situ* catalyzes the reduction of phenanthroline by excess $HSiMe_2Ph$ to 1,4-dihydrophenanthroline (Scheme 117, eq. 1). This reaction can be also carried out in the presence of alcohol as the proton source. The whole process is accompanied by intensive evolution of dihydrogen, which is a result of concomitant silane hydrolysis (alcoholysis). However, our independent experiments showed that phenanthroline cannot be reduced by gaseous hydrogen under these conditions in the absence of silane. Importantly, the reduction of phenanthroline can be also performed with other silanes, e.g. the reducing mixture $HSiEt_3$/EtOH can be used with the same efficiency.





Scheme 117. The reactions of $[CpRu(NCCH_3)_3]PF_6$ with phenanthroline



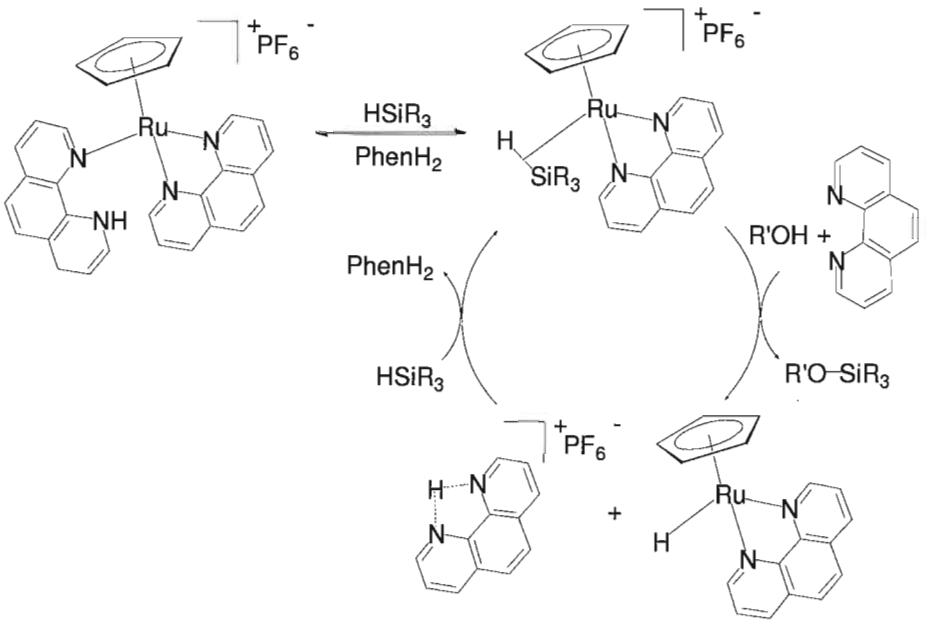
Scheme 118. The reactions of dihydriphenanthrolines with cationic ruhenium complexes

The ruthenium complex $[Cp(\kappa^2\text{-phen})Ru(\kappa^1\text{-phenH}_2)]PF_6$ (**71**) (Scheme 117) with a partially reduced phenanthroline ligand is the predominant Ru species in the reaction mixture during the catalysis (as evidenced by NMR spectroscopy) (Scheme 117). The complex **71** was also obtained independently by the reaction of **70** with a mixture of dihydrophenanthrolines (Scheme 118), which was isolated after the reduction of phenanthroline by $HSiEt_3$/EtOH in the presence of $[CpRu(NCCH_3)_3]^+$. Interestingly, the reaction of the same mixture of 1,4- and 1,2-dihydrophenanthrolines with $[CpRu(NCCH_3)_3]PF_6$ resulted in isomerization of the starting dihydrophenanthrolines with the formation of a stable ruthenium complex **73** with coordinated chelate 3,4-dihydrophenanthroline (Scheme 118).

At the end of catalytic reduction of phenanthroline, **71** slowly converts into the hydride-bridged dimer $[\{Cp(\kappa^2\text{-phen})Ru\}_2(\mu\text{-H})]PF_6$ (**72**) (Scheme 117). The latter complex does not catalyze the reaction, but its formation gives some evidence for the intermediacy of a neutral ruthenium hydride Cp(phen)RuH. Unfortunately, all our attempts at preparing the compound Cp(phen)RuH have been unsuccessful so far.

According to the proposed catalytic cycle of phenanthroline reduction, the reaction starts with the displacement of a labile ligand L in $[Cp(\kappa^2\text{-phen})RuL]^+$ ($L=NCCH_3$, $phenH_2$) by silane to give a silane σ-complex (Scheme 119). Possibly, the latter complex is too bulky and cannot react with phenanthroline directly. Alternatively, it could react with smaller nucleophile, such as water or alcohol, to furnish the hydride Cp(phen)RuH and the protonated silanol $[PhSiMe_2SiOH_2]^+$, which is then deprotonated by phenanthroline to give $[phen\text{-}H]^+$. The hydride transfer from

Cp(phen)RuH to the 4-position of $[phenH]^+$ results in the formation of the 2H-reduced phenanthroline, which coordinates to ruthenium to give a latent form of the catalyst, the observed complex $[Cp(\kappa^2\text{-phen})Ru(\kappa^1\text{-phenH}_2)]^+$.

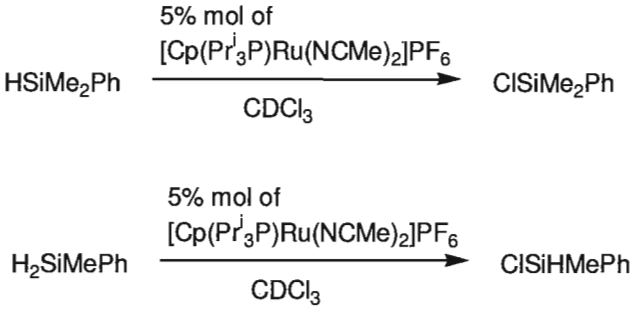


Scheme 119. The proposed mechanism for reduction of phenanthroline

III.2.6 Reduction of alkyl chlorides

Alkyl and aryl halides are very abundant compounds with a large number of applications as solvents, reagents, insecticides etc.[7] Fast accumulation of these compounds could result in a severe damage to the environment, as many of the commonly used chlorinated and fluorinated compounds display very slow biodegradation.[7] Therefore, the development of efficient methods for the treatment of these robust materials is highly important. Hydrosilanes have proven to be very efficient reducing reagents for the reduction of alkyl and aryl halides, which is usually performed in the presence of radical initiators.[7] However, the radical reactions are usually difficult to control, whereas the potentially more selective transition metal catalyzed reduction of alkyl and aryl halides with silanes is much less developed.

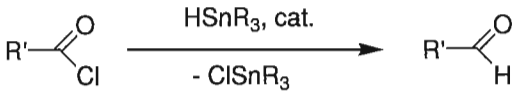
We found that slow catalytic dehalogenation of $CDCl_3$ with $HSiMe_2Ph$ takes place in the presence of the ruthenium complex **66** in chloroform. Unfortunately, no reaction between PhCl or CH_2Cl_2 and $HSiMe_2Ph$ was observed under the same conditions. However, the reactions of the cheap $CHCl_3$ with silanes could be potentially used for the synthesis of chlorosilanes, which are valuable starting materials in silicon chemistry. There are several methods for the chlorination of hydrosilanes,[153] but most of them have selectivity problems in case of polyhydrosilanes, which usually give mixtures of chlorosilanes. Complex **66-PF_6** slowly catalyzes the monochlorination of $H_2SiMePh$ with the formation of ClSiHMePh in 73% yield after 4 days at room temperature (Scheme 120). Analogous reaction with H_3SiPh did not happen due to the decomposition of the catalyst.



Scheme 120. Chlorination of silanes with $CDCl_3$.

III.2.7 Reduction of acid chlorides

Reduction of acid chlorides into corresponding aldehydes is one of the fundamental reactions in organic chemistry. In addition to the standard methods based on the use of alumo- and borohydrides,[77] the reduction of acid chlorides is often performed by organotin compounds, which are toxic and unstable (Scheme 121).[79] Therefore, the development of analogous procedures based on the use of hydrosilanes is of significant interest. As mentioned in the historical, there is only a handful of examples of such transformation, and the development of new catalytic systems is required for the establishment of the scope of this method.

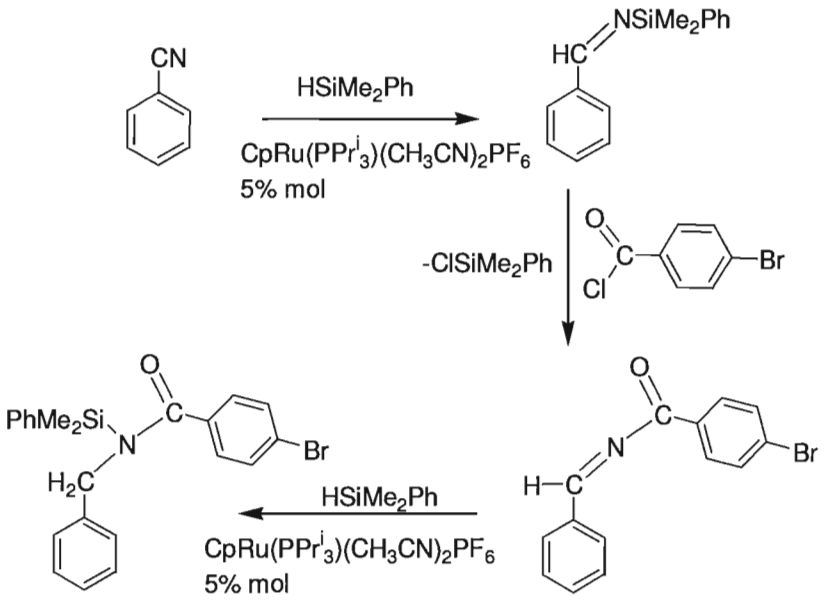


Scheme 121. Reduction of acid chlorides with organotin compounds

Inspired by the reduction of chloroform with $HSiMe_2Ph$ in the presence of **66-PF_6**, we attempted to reduce the more reactive C-Cl bond of acid chlorides. Rewardingly, the reaction between PhC(O)Cl and $HSiMe_2Ph$ gave benzaldehyde quite selectively. As previously described, complex **66-PF_6** catalyzes the hydrosilylation of carbonyls, and the formation of benzaldehyde in the reaction with PhC(O)Cl was indicative of the preferable reduction of acid chloride over benzaldehyde under these conditions. However, only 10% conversion of PhC(O)Cl was achieved, and further improvement of the catalytic system was required. Presumably, such a low yield comes from the low stability of the ruthenium catalyst under these conditions. In order to increase the yield of this reaction, acetonitrile was added to the reaction mixture, which was aimed to stabilize the catalyst. Under these conditions, the full conversion of PhC(O)Cl into PhCHO was observed after 24 h in chloroform (50% conv. after 4h).

Interestingly, the reduction of PhC(O)Cl dominates over the hydrosilylation of the C≡N bond of nitrile, which in our previous studies was found to be the most reactive functionality. Thus, the reaction of $HSiMe_2Ph$ with PhC≡N mediated by **66-PF_6** proceeds only in the absence of acid chloride derivatives with the selective formation of silyl imine $PhCH{=}NSiMe_2Ph$. Upon the addition of PhC(O)Cl, the latter silyl imine could be converted into the *N*-acylimine PhC(O)N=CHPh, which could be further reduced into the *N*-silyl amide $PhC(O)N(SiMe_2Ph)\text{-}CH_2Ph$ by the reaction with $HSiMe_2Ph$ in the presence of the same catalyst **66-PF_6** (Scheme 122). Notably,

the complex **66-PF_6** does no catalyze the hydrosilylation of imine PhCH=NPh under similar conditions, and the reduction of activated N-acylimines or related compounds with silanes mediated by **66-PF_6** could be an interesting topic for the future work.

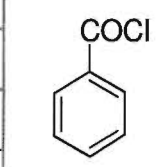
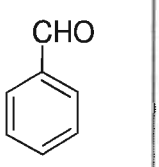


Scheme 122. The hydrosilylation of benzonitrile and N-acylimine with $HSiMe_2Ph$ in the presence of $[Cp(Pr^i_3P)Ru(NCMe)_2]PF_6$

The choice of acetonitrile as an additive for the stabilization of the catalyst is explained by the low price of this compound, which is also widely used as a common solvent. However, the hydrosilylation of acetonitrile proceeds as a minor reaction during the reduction of acid chlorides. As a result, a small impurity of the amide $RC(O)NHCH_2CH_3$ is usually observed in the reaction, which is formed analogously to the previously discussed reactions (Scheme 122). Therefore, the use of a more inert nitrile, such as t-BuCN (10% mol), is recommended for the more selective reduction of acid chlorides with a higher yield of the aldehyde.

In order to establish the effect of solvent, the reduction of benzoyl chloride was also studied in acetone and acetonitrile (Table 12). The best result was achieved in acetone, where the reaction proceeds within just 3 h at room temperature (Table 12, entry 3). On the other hand, a greater stabilization of the catalyst was achieved in acetonitrile, but the reaction was much slower (Table 12, entry 4).

Table 12. Reduction of benzoyl chloride with $HSiMe_2Ph$ in different solvents.[a]

N	Substrate	Solvent	Time	Conversion[c]	Product
1		$CDCl_3$	24 h	100%	
2		Acetone[b]	24 h	10%	
3		Acetone	3 h	100%	
4		CD_3CN[b]	24 h	100%	

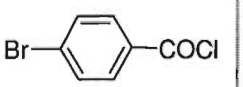
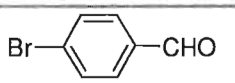
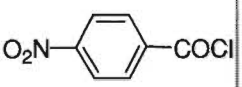
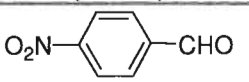
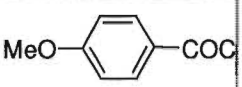
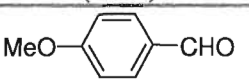
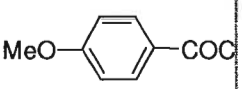
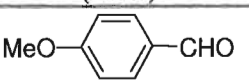
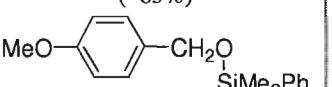
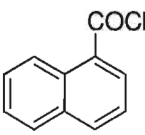
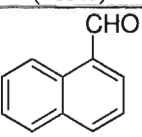
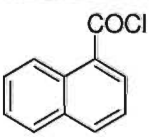
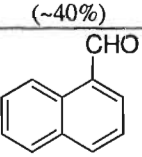
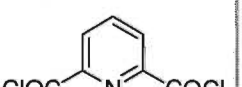
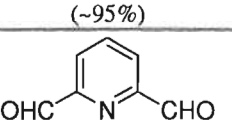
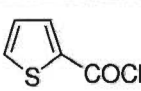
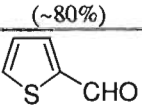
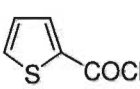
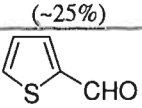
[a] In a general procedure, to a solution of benzoyl chloride was added 1.5 equiv. of $HSiMe_2Ph$, 2 equiv. of CH_3CN and 5% mol of 1. [b] CH_3CN was not added. [c] Based on ^1H NMR data.

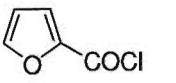
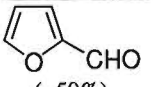
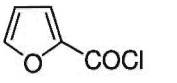
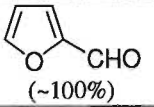
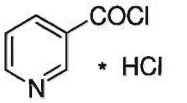
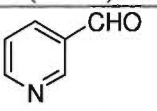
To establish the scope and limitations of the reaction, catalytic reduction of different acid chlorides was performed. Thus, the reduction of aromatic acid chloride with a bromine substituent in *para*-position proceeds smoothly in acetone within 5 h with the selective formation of the corresponding aldehyde (Table 13, entry 1). Also, the electron withdrawing nitro-group in the aromatic substrate does not affect the course of the reaction (Table 13, entry 2). In contrast to electron poor substrates, the reduction of aromatic acid chloride with the electron donating methoxy-group resulted in the formation of a mixture of compounds, which contained only 10% of the target aldehyde (Table 13, entry 3). The formation of a complex mixture of products can be explained by concomitant hydrosilylation of acetonitrile followed by previously discussed reactions with acyl chlorides. Presumably, hydrosilylation of acetonitrile proceeds at comparable rate with the reduction of acyl chlorides in this case. Therefore, we attempted the reduction of 4-$MeO(C_6H_4)COCl$ in the presence of more inert t-BuCN (10% mol) instead of acetonitrile. Under these conditions, the reaction proceeds much more selectively (Table 13, entry 4). However, slow hydrosilylation of the resulting aldehyde slightly reduce the overall yield. The reaction with a polycyclic representative, naphthoyl chloride, also gave a mixture of compounds with about 40% of the corresponding aldehyde (Table 13, entry 5). As in the previous case, highly selective reduction of acyl chloride was achieved by applying t-BuCN as a stabilizing additive (Table 13, entry 6).

Heteroaromatic acid chlorides can be reduced with a variable success. Thus, the full conversion of 2,6-pyridinedicarbonyl chloride with 2 equiv. of $HSiMe_2Ph$ into a mixture of corresponding mono- and (bis)aldopyridines was observed after 1 h; the 2,6-(bis)aldopyridine became the dominant product (~80%) after 3 h at room

temperature (Table 13, entry 7). On the other hand, the reduction of acid chloride derivatives of furan and thiophene resulted in a much less selective formation of the corresponding aldehydes, and an attempt to reduce the pyridinium salt of 3-pyridinecarbonyl chloride gave a mixture of compounds with only traces of 3-aldopyridine (Table 13, entries 8, 10, 12). As usual, switching to more inert t-BuCN additive resulted in a very selective formation of the corresponding aldehydes in the reduction of acyl chloride derivatives of furan and thiophene (Table 13, entries 9, 11).

Table 13. Reduction of acid chlorides with $HSiMe_2Ph$ mediated by $[Cp(Pr^i_3P)Ru(NCMe)_2]PF_6$.[a]

N	Substrate	Additive	Conv. (Time)[b]	Products[b]
1		CH_3CN (2 eq.)	100% (5 h)	 (~100%[h])
2		CH_3CN 2(eq.)	90% (5 h)	 (~95%)
3		CH_3CN (2 eq.)	100% (6 h)	 (~10%)
4		t-BuCN (10% mol)	>90% (24 h)	 (~85%)  (~15%)
5		CH_3CN (2 eq.)	100% (19 h)	 (~40%)
6		t-BuCN (10% mol)	100% (20 h)	 (~95%)
7		CH_3CN (2 eq.)	100% [e] (3 h)	 (~80%)
8		CH_3CN (2 eq.)	70% (2 h)	 (~25%)
9		t-BuCN (10% mol)	>97% (24 h)	 (~100%)

10		CH_3CN (2 eq.)	84% (22 h)	 (~50%)
11		t-BuCN (10% mol)	100% (24 h)	 (~100%)
12		CH_3CN (2 eq.)	100% [e],[f] (24 h))	 (traces)
13	CH_3COCl	CH_3CN (2 eq.)	100% (2 h)	CH_3CHO (~50%)
14	CH_3COCl	t-BuCN (10% mol)	>90% (2 h)	CH_3CHO (~80%) CH_2=CHOSiMe_2Ph (~20%)
15	CH_3CH_2COCl	CH_3CN (2 eq.)	100% (1 h)	CH_3CH_2CHO (~70%)
16	$ClCH_2COCl$	CH_3CN (2 eq.)	100% (1 h)	$ClCH_2CHO$ (~90%)
17	$ClCH_2CH_2COCl$	CH_3CN (2 eq.)	90%[g] (24 h)	$ClCH_2CH_2CHO$ (~70%)
18	PhCH=CHCOCl	CH_3CN (2 eq.)	70% (18 h)	PhCH=CHCHO (18%) $PhCH_2CH$=CHOSiMe_2Ph (82%)
19	EtOOC-COCl	CH_3CN (2 eq.)	100%[g] (20 h)	EtOOCCHO (~65%)
20	ClOC-COCl	CH_3CN (2 eq.)	75%[f]	Mixture

[a] In a general procedure to a solution of acid chloride in acetone-d_6 was added ~1.5 equiv. of $HSiMe_2Ph$, 2 equiv. of CH_3CN, and 5% mol of $[Cp(Pr^i_3P)Ru(NCMe)_2]PF_6$. [b] Conversions and yields are based on ^1H NMR data. [e] 2.5 equiv. of $HSiMe_2Ph$ was added. [f] Conversion of silane is given. [g] Reaction was carried out in $CDCl_3$. [h] 80% isolated yield.

The reactivity of alkyl acid chloride derivatives was also examined. Full conversion of $CH_3C(O)Cl$ was observed after 4 h at room temperature in chloroform, but a mixture of products was obtained, which contained about 40% of CH_3CHO (Table 13, entry 13). A similar composition of the products was also obtained in other solvents, such as acetonitrile and chloroform. In contrast, the reduction of related substrates $CH_3CH_2C(O)Cl$, $ClCH_2C(O)Cl$, and $ClCH_2CH_2C(O)Cl$ resulted in a much more selective formation of the corresponding aldehydes (70-90%) (Table 13, entries 15-17). Presumably, the presence of electron accepting chlorine close to the acyl chloride group in the molecule promotes the reduction. Thus, the reduction of α-

substituted acyl chloride derivative proceeds much cleaner and faster than β-substituted analogue (Table 13, entries 16, 17). Our attempt to increase the selectivity of the reduction of CH_3COCl in the presence of t-BuCN resulted in the formation of a mixture of CH_3CHO and CH_2=$CHOSiMe_2Ph$ (Table 13, entry 14). In principal, the latter compound can be easily converted into the target aldehyde by a simple acidic work-up.

Conjugated acid chlorides, such as PhCH=CHC(O)Cl, were reduced by this method into a mixture of the corresponding aldehyde (18%) and a product of formal 1,4-addition of silane to the aldehyde (82%) (Table 13, entry 18). Interestingly, almost no hydrosilylation of PhCH=CHCHO was observed in the absence of acid chloride under similar conditions, which indicates that the product of 1,4-addition of silane in the reaction with PhCH=CHC(O)Cl was obtained not *via* direct addition of silane to aldehyde, but the mechanism of this reaction remains unclear.

Importantly, the acid chloride substrate with an ester group, EtO(O)CC(O)Cl, can be reduced into EtO(O)CC(O)H rather selectively (Table 13, entry 19). On the other hand, the reaction with the analogous compound Cl(O)CC(O)Cl did not produce any aldehyde (Table 13, entry 20).

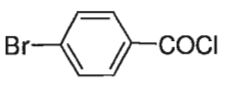
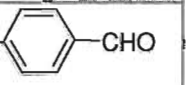
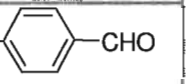
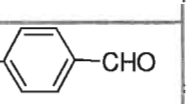
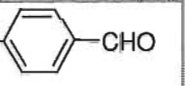
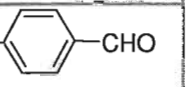
The reduction of acid chlorides with silane mediated by **66-PF_6** allowed us to perform reactions, which were previously not achievable by other similar methods. Thus, the only catalytic reduction method reported previously, the Pd-catalyzed reduction with PMHS,[83] can be used only for the synthesis of electron rich aromatic aldehydes, and this method was not applicable for the reduction of alkyl acid chlorides and electron poor benzoyl chlorides. In contrast, our ruthenium catalyst shows the best results with electron poor benzoyl chlorides (Table 13, entries 1,2). Also, good to excellent yields of the corresponding alkyl aldehydes can be obtained by this method (Table 13, entries 13-17). Therefore, the Ru-catalyzed reduction of acid chlorides is a valuable addition to the existing synthetic repertoire.

To further establish the selectivity of the reaction, the reduction of 4-bromobenzoyl chloride with silane was also performed in the presence of other potentially reactive compounds, such alkenes, alkynes, esters etc (Table 14). Thus, the presence of hexene-1 or ethyl ester does not influence the course of reduction of 4-$Br(C_6H_4)C(O)Cl$ with $HSiMe_2Ph$ (Table 14, entries 1,2). On the other hand, the hydrosilylation of an internal triple bond C≡C of alkyne proceeds as fast as the reduction of acid chloride, and a mixture of $EtCH=C(SiMe_2Ph)Et$ (50%) and 4-

$Br(C_6H_4)CHO$ (50%) was observed for the reaction in the presence of hexyne-3 (Table 14, entry 3). In contrast, no hydrosilylation of the terminal triple bond of PhC≡CH was observed. Unfortunately, the latter compound poisons the catalyst, and the reduction of 4-bromobenzoyl chloride stops at 54% conversion only (Table 14, entry 4).

Acid chlorides can be easily hydrolyzed, which makes the carboxylic acids very common contaminants for these compounds. Therefore, we also studied the reduction of 4-$Br(C_6H_4)C(O)Cl$ in the presence of PhCOOH. A fast dehydrogenative coupling of PhCOOH and $HSiMe_2Ph$ was observed within 10 min with the formation of $PhCOOSiMe_2Ph$. No significant decomposition of the catalyst was observed and the reduction of 4-bromobenzoyl chloride with a second equiv. of $HSiMe_2Ph$ then proceeds as usual (Table 14, entry 5).

Table 14. The reduction of 4-bromobenzoyl chloride with $HSiMe_2Ph$ in the presence of alkenes, alkynes, etsters, and acids[a]

N	Substrate 1	Substrate 2	Conv.	Products
1		$CH_3(CH_2)_3CH=CH_2$	Sub.1: ~100% Sub. 2: 0%	
2		AcOEt	Sub.1: ~90% Sub. 2: 0%	
3		EtC≡CEt	Sub.1: ~50% Sub. 2: ~50%	 $EtCH=C(SiMe_2Ph)Et$
4		PhC≡CH	Sub.1: ~50% Sub. 2: ~5%	
5		PhCOOH	Sub.1: ~100%[b] Sub. 2: ~100%	 $PhCOOSiMe_2Ph$

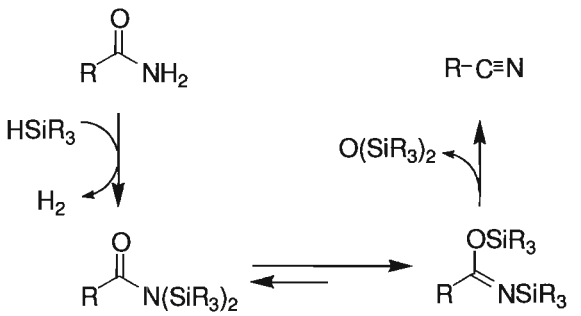
[a] In a general procedure, to a solution of acid chloride in acetone-d_6 was added 1.5 equiv. of $HSiMe_2Ph$, 2 equiv. of CH_3CN, and 5% mol of $[Cp(Pr^i_3P)Ru(NCMe)_2]PF_6$; [b] 2.5 equiv. of silane was added.

In order to check the practicability of this reduction method, the reaction with a representative acid chloride was performed on a larger scale. Thus, the reduction 4-$Br(C_6H_4)C(O)Cl$ (1g) with $HSiMe_2Ph$ in the presence of **66-PF_6** (5% mol) and t-BuCN (10% mol) as stabilizer afforded the corresponding aldehyde in 80% isolated yield after recrystallization of the product from a hexane solution. Importantly, most of the catalyst can be easily separated from the products by washing with hexane and

then used again in the reaction. There is a slow decomposition of the ruthenium complex during the reaction, but the catalyst can be used for at least 5 times without significant decrease in activity.

III.2.8 Reduction of primary amides

Hydrosilylation of amides with the formation of corresponding silyl amines is a valuable alternative to the reduction of these compounds using aluminium hydrides or boranes. Due to the difficulty of hydrogenation of amides,[55] significant research efforts have been devoted to the development of effective synthetic procedures for the hydrosilylation of these challenging substrates.[vi] Significant recent progress has been achieved in the hydrosilylation of tertiary and secondary amides.[vi] On the other hand, the majority of these methods cannot be applied for the reduction of primary amides, and only a few available procedures allow for the hydrosilylation of primary amides with unsatisfactory yields.[vi]



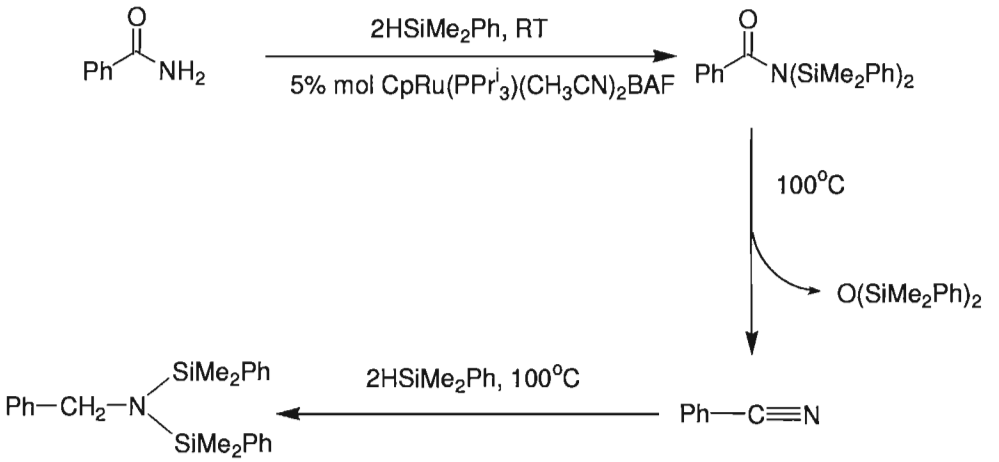
Scheme 123. Dehydration of amides with silanes

It is known that (bis)silylated amides exist in solutions as an equilibrium mixture of N,N- and N,O-(bis)silyl derivatives (Scheme 123).[67, 70-71] The latter could undergo elimination of siloxane at high temperature with the formation of corresponding nitriles. Based on this reaction sequence, the research groups of Nagashima and Beller have recently developed alternative procedures to the standard dehydration methods for the synthesis of a variety of nitriles from primary amides. [67, 70-71] However, further hydrosilylation of nitriles by these methods has not been reported. As previously discussed, complex **66-BAF** effectively catalyses the

[vi] See corresponding section of historical for the recent examples

hydrosilylation of nitriles. Therefore, we attempted hydrosilylation of primary amides into the corresponding silyl amines.

We found that complex **66-BAF** catalyzes dehydrogenative coupling of $PhC(O)NH_2$ with $HSiMe_2Ph$ in PhCl with the formation of corresponding (bis)silyl amide $PhC(O)N(SiMe_2Ph)_2$ (Scheme 124). The latter undergoes siloxane elimination at 100°C with the formation of PhCN, which can be further reduced into $PhCH_2N(SiMe_2Ph)_2$ by the reaction with two equivalents of $HSiMe_2Ph$ at this temperature. Notably, this reaction can be only productively carried out in PhCl, and our initial attempts to use chloroform as a solvent were unsuccessful due to the concomitant chlorination of $HSiMe_2Ph$ under these conditions. Also, the reduction of $PhC(O)NH_2$ into the silyl amine can be only performed in the presence of the ruthenium complex with the inert BAF counter anion, and the reaction in the presence of **66-PF_6** stopped after dehydrogenative coupling of the amide with silane.



Scheme 124. Reduction of benzamide with $HSiMe_2Ph$ in the presence of $CpRu(PPr^i_3)(CH_3CN)_2BAF$

Analogous reaction with $CH_3C(O)NH_2$ resulted only in dehydrogenative coupling of $HSiMe_2Ph$ with the amide without further dehydration into CH_3CN. However, 94% conversion of the starting $CH_3C(O)NH_2$ with the formation of $CH_3CH_2N(SiMe_2Ph)_2$ was achieved after 3 days at 100°C in toluene (Table 15, entry 2). Unfortunately, the reactivity of other tested amides is much lower, and the reactions do not proceed further after dehydrogenative coupling with silane (Table 15, entries 3,4).

Table 15. Reduction of primary amides with $HSiMe_2Ph$ in the presence of $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (5% mol, toluene, 100°C)

N	Substrate	Time	Conv	Products
1	$PhC(O)NH_2$[a]	2 days	100%	$PhCH_2N(SiMe_2Ph)_2$
2	$CH_3C(O)NH_2$	3 days	94%	$CH_3CH_2N(SiMe_2Ph)_2$
3	$CH_2=C(Me)C(O)NH_2$	3 days	100%	$CH_2=C(Me)C(O)N(SiMe_2Ph)_2$
4	$CF_3C(O)NH_2$	2 days	100%	$CF_3C(O)N(SiMe_2Ph)_2$

[a] reaction in PhCl

In order to check the selectivity of reduction, we performed competitive hydrosilylation of $PhC(O)NH_2$ in the presence of $PhC(O)CH_3$ and AcOEt. However, the hydrosilylation of both additional substrates was observed. Thus, $PhC(O)CH_3$ was converted into $PhC(OSiMe_2Ph)=CH_2$, and AcOEt was reduced into the silyl ether $EtOSiMe_2Ph$ under standard reaction conditions at 100°C.

So far we have been able to perform succesful reduction of only two substrates with $HSiMe_2Ph$ in the presence of **66-BAF**, and this method was found to be less general and selective than originally expected.

III.3 *Tris(1-pyrazolyl)borato cationic silane complexes of ruthenium*

Our initial studies of electron deficient cationic silane σ-complexes were based on the synthesis and investigation of cationic half-sandwich ruthenium complexes of type $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$. Thus, we succeeded in the preparation of a series of cationic silane σ-complexes and were able to study the effect of substituents at silicon as well as phosphine ligands on the extent of Si-H bond activation. Moreover, the above complexes were proposed to be intermediates in a number of catalytic reactions with hydrosilanes. So far we have investigated the influence of phosphine ligands and silanes on the stability and catalytic activity of ruthenium complexes. Later, we also became interested in the effect of the Cp-ligand on the properties of the silane σ-complexes. Based on our previous results on the comparative studies of Cp- and Cp*-substituted silyl complexes, we expected even more dramatic changes in the behaviour of the silane complexes by switching to the isolobal compounds supported by the hydrotris(1-pyrazolyl)borato (Tp) ligand (Figure 22).[154]

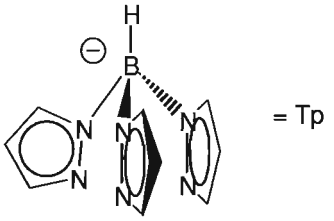


Figure 22. Hydrotris(1-pyrazolyl)borato (Tp) ligand

The ancillary ligands Cp, Cp* and Tp are very common in organometallic chemistry since all of them provide a relatively inert backbone for a large number of transition metal complexes.[155] These ligands are isoelectronic and isolobal, occupy three coordination sites on the metal and bear a net negative charge. Therefore, the metal complexes with these ligands have similar structures (half-sandwich complexes). However, there are also several significant differences in the properties of these ligands. Thus, the Tp ligand is considerably bulkier (cone angle of 180°) than Cp (100°) and even Cp* (146°).[156] Also, the Tp is a ligand of a lower field strength in comparison with both Cp and Cp*.[157] There is also a difference in the bonding type to

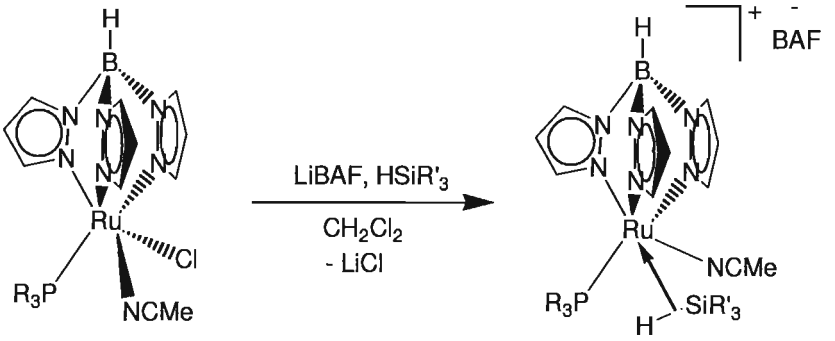
the metal centre since the Tp ligand is bound with σ-donating pyrazolyl rings and the Cp' ligands are bound in a π-fashion. Finally the Tp ligand is hard, whereas the Cp-ligand is soft. Because of these notable differences, the chemical and thermal properties of the corresponding transition metal complexes could vary significantly with the type of the ancillary ligand.

In order to establish the effect of the Tp ligand on the properties of cationic silane σ-complexes, we attempted the preparation of complexes $[TpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$, which would resemble the previously studied ruthenium compounds with the Cp-ligand. Our initial strategy for the synthesis of target compounds was based on our synthetic approach to the Cp-analogues and consisted in substitution of one of the labile acetonitrile ligands in $[TpRu(PR_3)(CH_3CN)_2]BAF$ with silane. Unexpectedly, absolutely no reaction between $[TpRu(PPr^i_2Me)(CH_3CN)_2]BAF$ and H_3SiPh was observed even in the presence of excess silane. The complex $[TpRu(PPr^i_2Me)(CH_3CN)_2]BAF$ remains inert even when dissolved in the neat $HSiMeCl_2$.

The unusual inertness of complex $[TpRu(PPr^i_2Me_3)(CH_3CN)_2]BAF$ was explained by a control experiment with the deuterated acetonitrile. There was no exchange between the coordinated and free acetonitrile even when the complex $[TpRu(PPr^i_2Me)(CH_3CN)_2]BAF$ was dissolved in pure CD_3CN. In contrast to complexes $[CpRu(PR_3)(CH_3CN)_2]BAF$, where the acetonitrile ligands can be easily substituted and undergo fast exchange with free acetonitrile, the nitrile ligands in the analogous complex $[TpRu(PPh_3)(CH_3CN)_2]BAF$ are strongly bound to the metal centre, which completely rules out the possibility of their substitution with silane under ambient conditions. Obviously, such a behaviour is the consequence of increased hardness of the Tp-ligand, which makes the ruthenium centre more prone to bind hard ligands, such as nitrile.

Our alternative synthetic route to complexes $[TpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ was based on the reaction of the readily available complex $TpRu(PR_3)(CH_3CN)Cl$ with LiBAF in the presence of silane (Scheme 125). The abstraction of the chlorine ligand in complex $TpRu(PR_3)(CH_3CN)Cl$ with LiBAF allows for generation of a free coordination site, which can be occupied by a silane molecule. Using these methods, we were able to synthesize several target cationic silane σ-complexes $[TpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ ($PR_3 = PPh_3$ (**74**), PPr^i_2Me

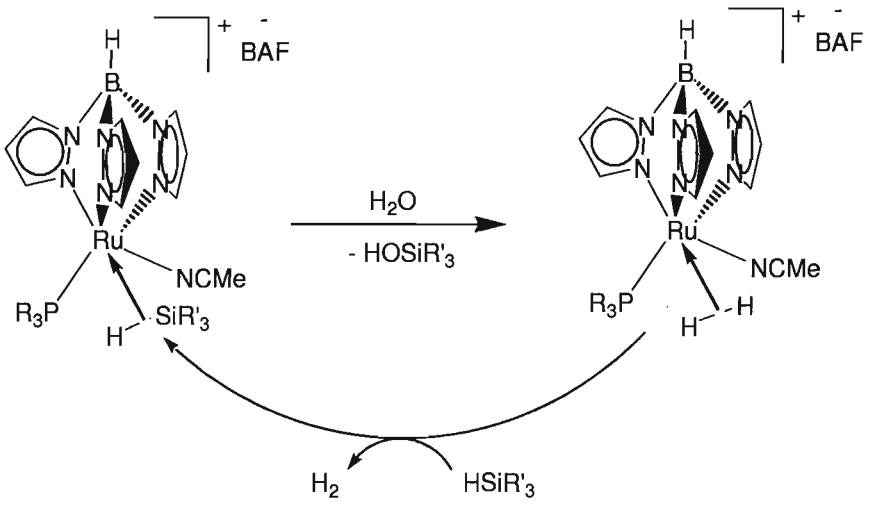
(**75**); SiR'$_3$ = SiH_2Ph (**d**), SiHMePh (**e**)) which were characterized by NMR spectroscopy.



Scheme 125. The synthesis of [TpRu(PR$_3$)(CH$_3$CN)(η^2-HSiR'$_3$)]BAF

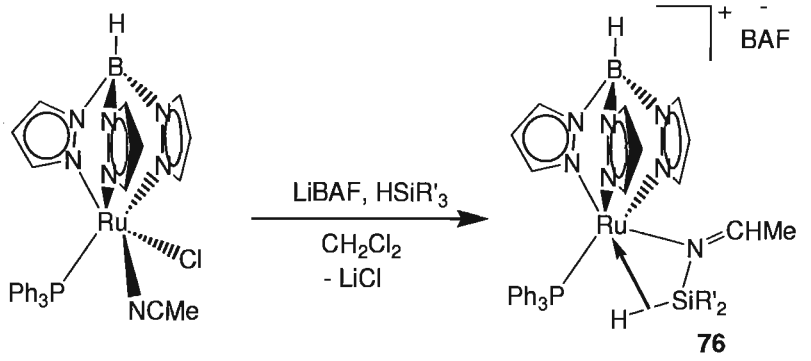
The complexes [TpRu(PR$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF exhibit a characteristic upfield-shifted signal of coordinated Si-*H* bond in ^{1}H NMR, which appears as a doublet of triplets flanked with silicon satellites at -11.83 ppm for **74d** or at -12.25 ppm for **75d**. The *J*(Si-H) in the complex **74d** (86 Hz) is slightly larger than in the analogous compound **75d** (82 Hz), which can be easily explained by the higher electron donating ability of the alkyl phosphine PPr$^i_2$Me, and, as a result, a better oxidative addition of the Si-H bond in the latter complex. Importantly, both values of *J*(Si-H) are significantly larger than in the analogous Cp-complexes. This result is in agreement with the fact that the much bulkier and less electron donating Tp-ligand reduces the extent of back-donation on the (Si-H)* antibonding orbital in comparison with the Cp-ligand, and, therefore, stabilizes an earlier stage of oxidative addition of silane.

The 1D EXSY NMR experiments confirmed the presence of a fast exchange between the coordinated and free silane in the complex [TpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF, which was also observed in the Cp-complexes. Notably, the synthesized complexes [TpRu(PR$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF often contained small impurities of the ruthenium dihydrogen complexes [TpRu(PR$_3$)(CH$_3$CN)(H$_2$)]BAF, which were formed as a result of hydrolysis of the corresponding silane σ-complexes with adventitious water (Scheme 126). However, in the presence of excess silane, the compounds [TpRu(PR$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF can be obtained quite selectively (Scheme 126).



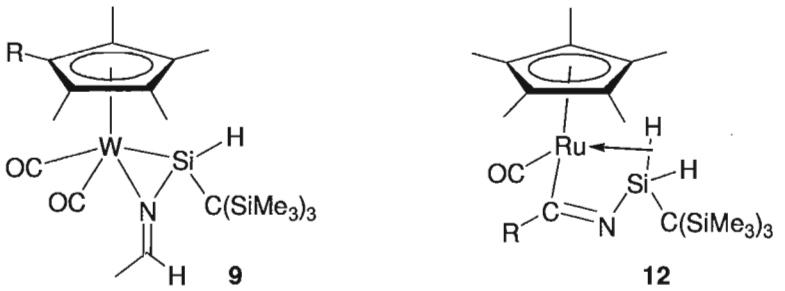
Scheme 126. Hydrolysis of [TpRu(PR$_3$)(CH$_3$CN)(η^2-HSiR'$_3$)]BAF

To our surprise, some initial preparations of the cationic silane σ-complexes [TpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiR'$_3$)]BAF were poorly reproducible and we observed a quite selective formation of complexes of a completely different type, which also contained the σ-coordinated Si-H bonds. Analysis of the NMR data allowed us to assign the agostic structure of these compounds which contained the coordinated to the ruthenium centre monohydrosilylated acetonitrile ligand TpRu(PPh$_3$){(η^2-HSiR'$_2$)N=CHCH$_3$}BAF (**76**) (SiR'$_2$ = SiHPh (d), SiMePh (e)) (Scheme 127). These complexes are of significant interest, as they can be viewed as potential intermediates in the catalytic hydrosilylation of nitriles. As previously mentioned, we have developed a highly efficient method for the hydrosilylation of nitriles in the presence of complex [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]$^+$, but we were unable to observe the agostic derivatives.



Scheme 127. The synthesis of TpRu(PR$_3$)((η^2-HSiR'$_2$)N=CHCH$_3$)BAF

There are only few reports on stoichiometric hydrosilylation of nitriles by transition metal complexes,[24, 26-27] and new examples are of high importance for the development of more efficient catalytic procedures and better understanding of this process. Notably, the silylimino β agostic complexes have never been reported and the compounds $TpRu(PPh_3)\{(\eta^2\text{-}HSiR_2)N{=}CHCH_3\}BAF$ are the first examples of this type. Their closest analogues, the iminosilyl tungsten complex **9** (Scheme 128) and iminoacyl ruthenium complex **12** (Scheme 128), were reported only recently by Tobita et al.[26-27]



Scheme 128. Iminoacyl tungsten and ruthenium complexes

The agostic complexes **76** were obtained as mixtures of diastereomers. Notably, the ratio of different isomers strongly depends on the nature of silane in the agostic complex. Thus, only 14% of the second diastereomer was observed in the complex $TpRu(PPh_3)((\eta^2\text{-}H_2PhSi)N{=}CHCH_3)BAF$. On the other hand, the ratio of two diastereomers of the complex $TpRu(PPh_3)((\eta^2\text{-}HMePhSi)N{=}CHCH_3)BAF$ was close to 2:3, which can be explained by a smaller difference in the size of the Me and Ph groups on silicon in the latter example in comparison of with the difference between H and Ph in the complex $TpRu(PPh_3)((\eta^2\text{-}H_2PhSi)N{=}CHCH_3)BAF$.

In ^1H NMR, the agostic complexes **76** exhibit characteristic quartets (coupled to the CH_3-group) of the iminium protons N=C*H*, which were observed at 8.10 ppm (**76d**) or at 8.27 ppm (**76e**, the major diastereomer) and 8.72 ppm (**76e**, the minor diastereomer). The protons of the coordinated Si-*H* bonds resonate at -9.95 ppm (**76d**) or at -10.51 ppm (**76e**, major diastereomer) and -10.67 ppm (**76e**, minor diastereomer). The *J*(Si-H)s of more than 90 Hz in the above agostic complexes (Table 16) are indicative of an early stage of oxidative addition of the Si-H bond to the metal centre and are the largest among all previously discussed ruthenium complexes.

Table 16. The observed *J*(Si-H) values in cationic ruthenium Tp-complexes

Complex	*J*(Si-H), Hz
[TpRu(PR_3)(CH_3CN)(η^2-$HSiR'_3$)]BAF	
PR_3 = PPh_3; SiR'_3 = SiH_2Ph	86
PR_3 = PPr^i_2Me; SiR'_3 = SiH_2Ph	82
TpRu(PR_3)((η^2-$HSiR'_2$)N=$CHCH_3$)BAF	
PR_3 = PPh_3; SiR'_2 = SiHPh	92
PR_3 = PPh_3; SiR'_2 = SiMePh	95 and 99[a]

[a] major and minor diastereomers

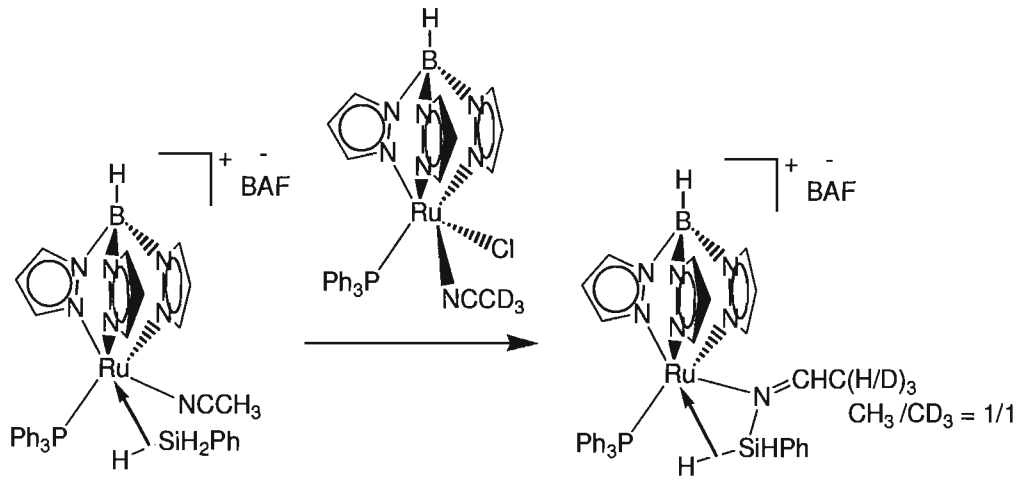
As mentioned before, the synthesis of the cationic ruthenium β-agostic or σ-complexes by the reaction of TpRu(PR_3)(CH_3CN)Cl with LiBAF in the presence of silane was not reproducible. The reactions were usually accompanied by the formation of small amounts of the (bis)acetonitrile complex [TpRu(PR_3)(CH_3CN)$_2$]BAF, but either a rather selective formation of β-agostic or σ-complexes or a slow conversion of the initially produced σ-complexes into the β-agostic analogues was usually observed. We found that the reason behind these results was the amount of LiBAF used in the reaction. The use of excess LiBAF results, quite expectably, in the formation of silane σ-complexes **74**. On the other hand, a slight deficiency in LiBAF leads to the formation of the β-agostic complexes **76**.

It is tempting to propose that the β-agostic ruthenium compounds **76** are produced as a result of intramolecular hydrosilylation of the coordinated acetonitrile in the corresponding σ-complexes **74**. However, the σ-complexes are remarkably stable in solutions for long periods of time without formation of significant amounts of β-agostic compounds when prepared using the excess of LiBAF. The coordinated silane in σ-complexes also does not react with external acetonitrile molecules, and only a simple substitution takes place in the reaction of [TpRu(PPh_3)(CH_3CN)(η^2-$HSiH_2Ph$)]BAF and CH_3CN with the formation of [TpRu(PPh_3)(CH_3CN)$_2$]BAF and free silane.

The lack of LiBAF allows for the presence of residual TpRu(PR_3)(CH_3CN)Cl in the reaction mixture, which was assumed to be the key substance in the formation of β-agostic complexes. Indeed, we found that addition of catalytic amounts of TpRu(PPh_3)(CH_3CN)Cl to a solution of silane σ-complex **74d** resulted in fast formation of the β-agostic complex **76d**.

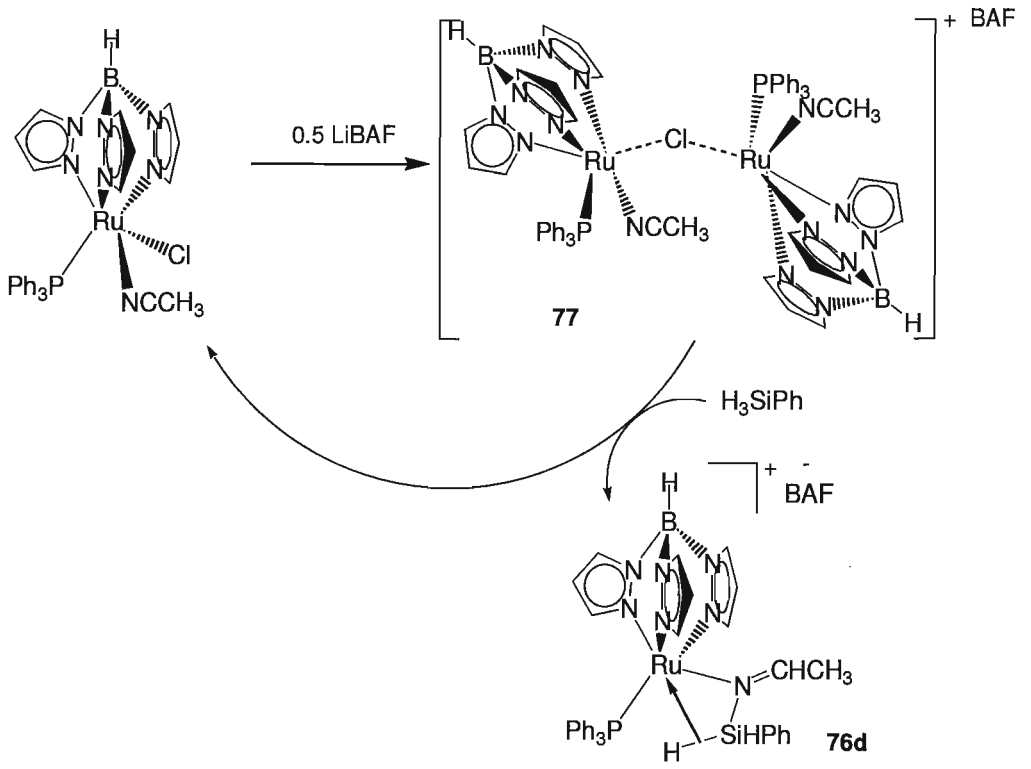
In order to establish the effect of $TpRu(PPh_3)(CH_3CN)Cl$ on the formation of agostic complexes, we carried out the reaction of $TpRu(PPh_3)(CH_3CN)Cl$ with a 20 fold excess of H_3SiPh. However, only very slow conversion (5% after 1 day) of the ruthenium complex was observed, with the product being $TpRu(PPh_3)H_2SiR_2Ph$.

In contrast to the highly electophilic cationic (bis)acetonitrile complex $[TpRu(PPh_3)(CH_3CN)_2]BAF$, which does not undergo an exchange of free and coordinated acetonitriles, a slow exchange between the free and coordinated acetonitrile molecules was observed in complex $TpRu(PPh_3)(CH_3CN)Cl$. Thus, the full conversion of $TpRu(PPh_3)(CH_3CN)Cl$ into the deuterated analogue $TpRu(PPh_3)(CD_3CN)Cl$ was observed within 1 day at room temperature in CD_3CN. Interestingly, the reaction of the silane σ-complex **74d** with an equimolar amount of $TpRu(PPh_3)(CD_3CN)Cl$ resulted in immediate formation of the corresponding β-agostic complex, which contained 50% of hydrosilylated CD_3CN.



Scheme 129. The reaction of $[TpRu(PPh_3)(CH_3CN)(\eta^2\text{-}HSiH_2Ph)]BAF$ with deuterated $TpRu(PPh_3)(CD_3CN)Cl$

Based on the above results, we proposed an intermediate formation of the cationic chlorine bridged ruthenium dimer $[\{TpRu(PPh_3)(CH_3CN)\}_2Cl]BAF$ (**77**), which could further react with the silane to give the β-agostic complex. And indeed, the feasibility of this process was proven by generation of the dimer complex in the reaction of $TpRu(PPh_3)(CH_3CN)Cl$ with 0.5 equiv. of LiBAF. As expected, the treatment of compound **77** with H_3SiPh resulted in the formation of the β-agostic complex **76d** and the starting ruthenium chloride $TpRu(PPh_3)(CH_3CN)Cl$ (Scheme 130).

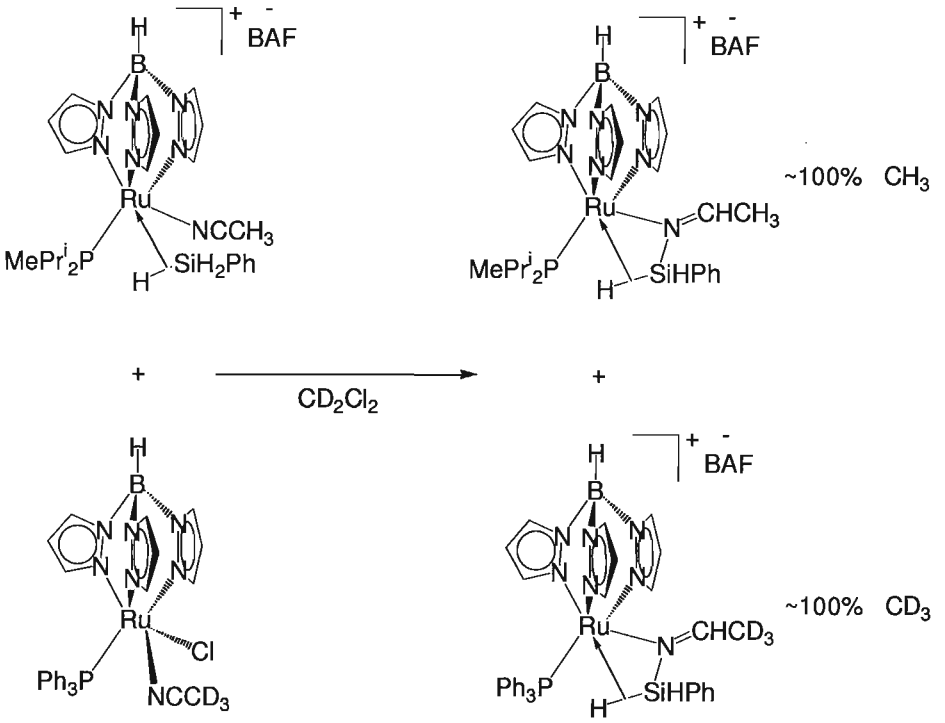


Scheme 130. The proposed route for the formation of agostic ruthenium complexes

In order to get a deeper insight into these processes, we performed a series of additional control experiments. In the reaction of neutral chlorides and silane σ-complexes, which contained different phosphine ligands, a mixture of the corresponding agostic complexes was obtained. Thus, the reaction of [TpRu(PPr$^i_2$Me)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF with an equimolar amount of TpRu(PPh$_3$)(CH$_3$CN)Cl gave a mixture of β-agostic complexes TpRu(PR$_3$)((η^2-HSiHPh)N=CHCH$_3$)BAF with the predominant formation of the product with the PPh$_3$ ligand (PPh$_3$ complex : PPr$^i_2$Me complex = 6:1). Similarly, the reaction of [TpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF with TpRu(PPr$^i_2$Me)(CH$_3$CN)Cl gave a mixture of β-agostic complexes in the ratio of 8:1 (PPh$_3$ complex: PPr$^i_2$Me complex). Therefore, both of the above reactions favoured the formation of a β-agostic complex with the less electron donating phosphine. The possible rationale for this is that the weaker phosphine donor makes the coordinated nitrile more deficient and more subject to the attack of silane.

However, the above experiments do not provide conclusive information on the possible exchange of nitriles between the complexes. Therefore, we carried out a

reaction between [TpRu(PPr$^i_2$Me)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF and the deuterated ruthenium chloride TpRu(PPh$_3$)(CD$_3$CN)Cl, which resulted in the formation of the corresponding β-agostic complexes. The resulting agostic complexes contained the hydrosilylated acetonitrile ligands originating from the starting ruthenium complex, i.e. corresponding to the phosphine ligand (Scheme 131). Thus, we could assume the absence of a nitrile exchange between the starting σ-complex and the ruthenium chloride. In other words, the acetonitrile ligands remain bound to the same metal centres throughout the reaction.

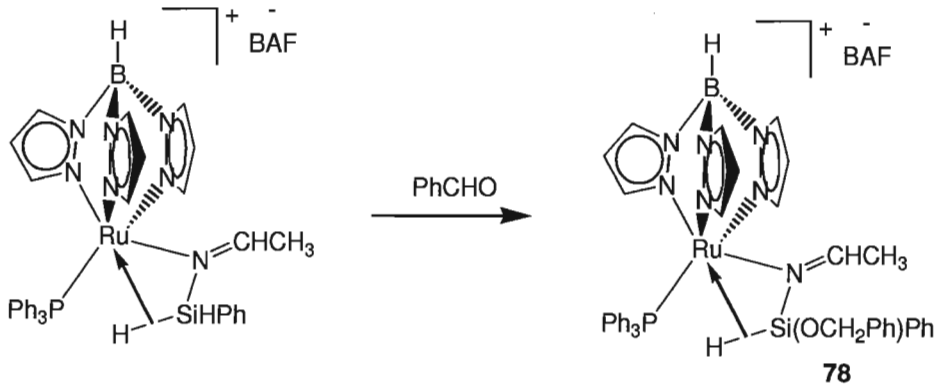


Scheme 131. The reaction of TpRu(PPh$_3$)(CD$_3$CN)Cl with [TpRu(PPr$^i_2$Me)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF (only agostic products are shown)

As mentioned before, the agostic complexes **76** can be viewed as intermediates in the hydrosilylation reactions. Therefore, the reactivity studies of these compounds were also performed. Upon the addition of acetonitrile, the complex **76d** slowly converted into the (bis)acetonitrile complex [TpRu(PPh$_3$)(CH$_3$CN)$_2$]BAF. Unfortunately, the high inertness of the latter does not allow for performing a catalytic hydrosilylation since the acetonitrile ligands in this compound are tightly bound to the ruthenium centre.

Interestingly, the reaction of the agostic complex **76d** with PhCHO resulted in a slow insertion (100% conv. after 4 h at RT) of benzaldehyde into one of the Si-H

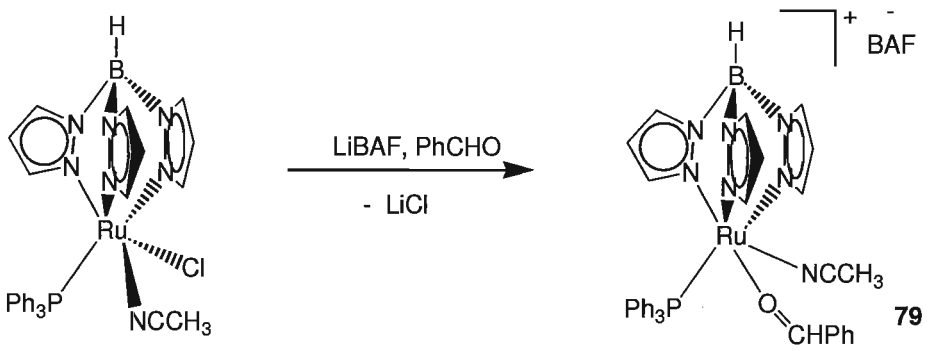
bonds of the ruthenium complex. Similarly to the starting agostic complex, only one major diastereomer of the product was obtained (as evidenced by NMR data), which could be a result of direct insertion of benzaldehyde into the terminal Si-H bond.



Scheme 132. The reaction of $TpRu(PPh_3)((\eta^2\text{-}HSiHPh)N{=}CHCH_3)BAF$ with PhCHO

In ^1H NMR, the product of benzaldehyde insertion, $TpRu(PPh_3)(\{\eta^2\text{-}HSi(OCH_2Ph)Ph\}N{=}CHCH_3)BAF$ (**78**), exhibits a characteristic up-field chemical shift of the coordinated Si-*H* at -10.40 ppm, which appears as a doublet (J(P-H) = 11.3 Hz) flanked with ^{29}Si satellites. The observed J(Si-H) of 112 Hz in this compound is significantly larger than in the starting agostic complex (J(Si-H) = 92 Hz), which can be explained by the increased contribution of the 3s orbitals of Si into the Si-H bond due to the presence of an electron withdrawing OCH_2Ph substituent on silicon in the product, according to the Bent's rule.[102]

The insertion of benzaldehyde into the Si-H bond in the presence of an excess of PhCHO (~2 equiv.) is accompanied by the substitution of *N*-silyl imine ligand in the β-agostic compound with the formation of the (bis)benzaldehyde ruthenium complex $[TpRu(PPh_3)(O{=}CHPh)_2]BAF$ (~30%). Thus, we attempted the preparation of an analogous (mono)benzaldehyde complex $[TpRu(PPh_3)(O{=}CHPh)(CH_3CN)]BAF$ (**79**), which could be tested in the reactions with silanes. The complex **79** was obtained with 100% yield by the reaction of $TpRu(PPh_3)(CH_3CN)Cl$ with LiBAF in the presence of PhCHO.



Scheme 133. The synthesis of [TpRu(PPh$_3$)(O=CHPh)(CH$_3$CN)]BAF

The NMR data of complex **79** suggest the coordination of benzaldehyde in the η^1-fashion, which was concluded from the absence of a ^{31}P coupling of the O=*CH* group in ^{1}H and ^{13}C NMR. Unfortunately, the reaction of complex **79** with H_3SiPh was not selective and resulted in a slow formation of a mixture complexes, such as TpRu(PPh$_3$)((η^2-HSiHPh)N=CHCH$_3$)BAF, TpRu(PPh$_3$)({η^2-HSi(OCH$_2$Ph)Ph}N=CHCH$_3$)BAF, [TpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF, and [TpRu(PPh$_3$)(CH$_3$CN)(H$_2$)]BAF. Analogously, the reaction of [TpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiH$_2$Ph)]BAF with PhCHO also resulted in a mixture of complexes. Interestingly, the addition of a 10 fold excess of silane and benzaldehyde to this mixture resulted in the conversion of H_3SiPh into oligomers of the phenylhydrosiloxane (-O-SiHPh-)$_n$, which is indicative of some deoxygenation of benzaldehyde in the reaction. Similarly, the polyphenylhydrosiloxane was also produced in the catalytic reaction of H_3SiPh with cyclohexanone in the presence of the *in situ* generated σ-complex **74d**. However, the carbonyl substrates in both cases were converted into a mixture unidentified of products. Presumably, the starting cationic σ-complex **74d** gives rise to the formation of highly reactive silylium cations, which are known to catalyze the deoxygenation of carbonyls.[135a]

Noteworthy, the complex **74d** catalyzes the dehydrogenative coupling of EtOH with H_3SiPh with the formation of a mixture of alkoxy silanes $H_{3-n}Si(OEt)_nPh$, and no deoxygenation was observed in this case. Instead, the redistribution of substituents in the alkoxy silanes was observed, which resulted in regeneration of H_3SiPh and formation of $Si(OEt)_3Ph$.

III.4 *Hydridosilyl complexes of iron*

III.4.1 Neutral dihydrosilyl iron complexes

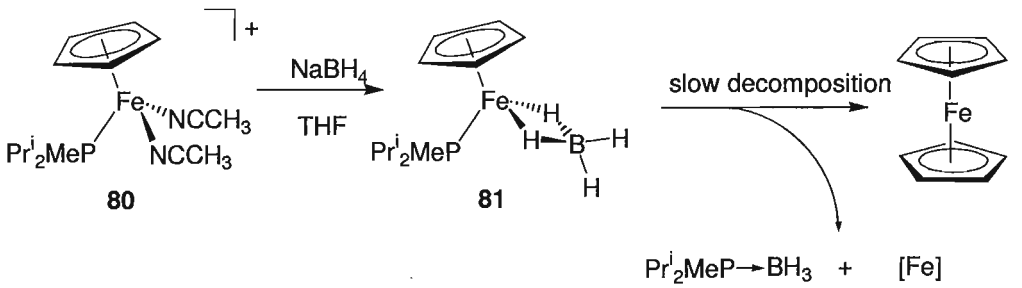
Late transition metal complexes are among the most effective and widely used catalysts for a large number of transformations.[158] The majority of these catalysts are based on precious metals, which are very expensive and toxic.[158] Therefore, the development of cheaper and environmentally benign catalytic systems has recently received considerable attention. The iron based catalytic systems is one of the most desirable alternative to the existing precious metal catalysts. The abundant and non-toxic iron is often considered as a "cheap metal for a noble task".[158a] It has been recently applied for many catalytic transformations, including some hydrosilylation reactions.[158b] However, little is known about hydridosilyl complexes of iron, which could be potential intermediates of these reactions.[12f, g] Most of the known Fe(II) complexes are classical silyl derivatives, whereas the formally Fe(III) and even Fe(I) compounds are usually formulated as silane σ complexes.[12a, 159] The situation with the potential oxidation state IV is more complex. Thus, the bis(imino)pyridine compound $[N_3]Fe(\eta^2\text{-}H_3SiPh)_2$ is a very rare example of a bis(silane) σ-complex (formally Fe(0) complex).[160] On the other hand, the adduct of $[PhB(CH_2{}^iPr_2P)_3]FeH$ with $H_2SiMePh$ was formulated as an unusual Fe(II) derivative with the η^3-coordinated $H_2SiMePh$.[161]

As mentioned before, the η^2-silane complex $[Cp(OC)(Et_3P)Fe(\eta^2\text{-}HSiEt_3)]^+$ was obtained by the addition of $HSiEt_3$ to the Fe(II) cation $[Cp(OC)(Et_3P)Fe]^+$.[106] An analogous η^2-silane structure was also suggested for the compound $(R'Ph_2P)_3FeH_3SiR_3$.[162] The only classical Fe(IV) structures were reported for the complexes $(arene)FeH_2(SiX_3)_2$ (X=F, Cl), which was confirmed by the X-ray structure analysis.[163] Interestingly, the related half-sandwiches $Cp(OC)FeH(SiX_3)_2$ have been recently shown to have very unusual highly delocalized Si···H···Si bonding.[164] Taking into account that electron donating ligands could stabilize a Fe(IV) center, we attempted the synthesis of a new class of iron dihydride silyl complexes $Cp(R_3P)FeH_2(SiR_3)$ and investigation of their properties.

The synthesis of hydrido silyl complexes $CpFe(PMePr^i{}_2)H_2(SiR_3)$.

We found that the reaction of the cationic iron complex $[CpFe(PMePr^i{}_2)(NCCH_3)_2]PF_6$ (**80-PF$_6$**) with excess $NaBH_4$ in THF at 0°C results in

the formation of a neutral, highly unstable complex $CpFe(PMePr^i_2)(BH_4)$ (**81**) (Scheme 134). Almost immediate conversion of the starting compound into the borohydride complex can be visually observed by the instantaneous color change from red to dark green upon addition of $NaBH_4$. Complex **81** slowly decomposes even at low temperature with the formation of ferrocene and insoluble iron species, which precipitate from hexane solutions in the form of a brown powder. Therefore, only freshly prepared complex **81** was used for all the further reactions with this compound. Notably, the borohydride complexes of iron are quite rare, and their preparation and investigation is of interest especially because of the different possible binding modes of $[BH_4]$ to iron in these complexes.[165] More importantly, the borohydride complexes of iron can be used as valuable starting materials for the synthesis of a variety of derivatives, which could contribute to the development of the organometallic iron chemistry. The application of **81** for the synthesis of the target hydridosilyl iron complexes will be discussed below.

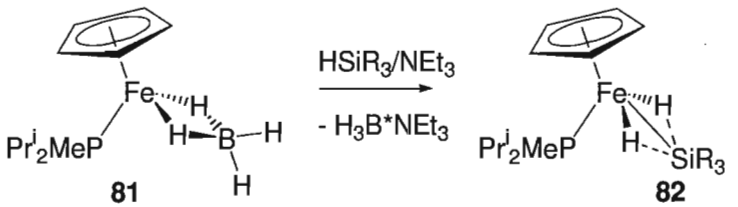


Scheme 134. The synthesis of $Cp(Pr^i_2MeP)Fe(BH_4)$

The NMR signals of the complex **81** are very broad and difficult to analyze because of the presence of paramagnetic iron impurities that could be formed during the decomposition of the iron borohydride complex (Scheme 134). However, there are distinct broad signals in the ^1H NMR spectrum, which correspond to the Cp, Pr^i_2MeP and BH_4 fragments of the complex. The bridging hydrides of the BH_4 ligand resonance at -20 ppm in ^1H NMR, which was integrated as 2 protons. Such an upfield chemical shift is quite common for transition metal borohydride complexes.[165] The ^{11}B NMR experiment revealed the presence of two signals with different intensities. The major broad singlet at 65.8 ppm was assigned to the iron borohydride complex, and the less intense multiplet at 28.6 corresponds to one of the decomposition products, the adduct $Pr^i_2MeP{*}BH_3$. The presence of $Pr^i_2MeP{*}BH_3$ was also confirmed

by ^{31}P NMR, which revealed a characteristic quartet at 28.6 ppm with the J(B-P) of 55 Hz.

The treatment of the freshly prepared iron borohydride complex with silanes in the presence of NEt_3 affords new hydridosilyl iron complexes. The addition of NEt_3 to the reaction mixture was aimed to abstract and trap the BH_3 fragment from the starting borohydride complex in a form of a Lewis acid-base adduct Et_3N*BH_3. A representative series of iron complexes $CpFe(PMePr^i_2)H_2(SiR_3)$ (**82**) with different silyl groups (SiR_3 = $SiCl_3$ (**a**), $SiCl_2Me$ (**b**), $SiClMe_2$ (**c**), SiH_2Ph (**d**), SiHMePh (**e**), $SiMe_2Ph$ (**f**)) was obtained by this method, which allowed us to investigate the effect of substituents at silicon on the properties of these new compounds.



Scheme 135. The synthesis of $CpFe(PMePr^i_2)H_2(SiR_3)$

The compounds **82** were isolated in the form of yellow oils or crystals and studied by spectroscopic methods. All of the synthesized hydrido silyl iron complexes exhibit very characteristic upfield chemical shifts of the iron bound hydrides in ^1H NMR at -15.75 – (-14.60) ppm, which usually appear as doublets (due to coupling to ^{31}P) with ^{29}Si satellites (Table 17). The large values of J(P-H) and relatively small coupling constants J(Si-H) could be indicative of the presence of strong Ru-H bonds (Table 17). The J(P-H) values do not change significantly within the groups of chlorosilyl or alkylarylsilyl ligands, which could be explained by the advanced silane oxidative addition in all of the above hydrosilyl complexes. Unfortunately, the observed coupling constant J(Si-H) did not clear up the picture about the bonding modes of the silyl ligands in the iron complexes. All hydrosilyl complexes exhibit the J(Si-H) of around 20 Hz, which does not allow us to make a reliable conclusion about the presence of a direct Si-H interaction in these complexes. The J(Si-H) of 20 Hz is generally considered as a borderline between classical and non-classical hydrido silyl complexes.[12c, 100] In principal, the structure of the hydrido silyl iron compounds can be described as a classical dihydrosilyl complex $CpFe(PMePr^i_2)H_2(SiR_3)$. On the other hand, the NMR data could be also compatible with the presence of a fast degenerate

exchange between two forms of silane hydride complexes, characterized by two coupling constants, the J^1(Si-H) of 40 Hz and the J^3(Si-H) close to 0 Hz, leading to the average J(Si-H) of 20 Hz.[12c, 109, 166] Therefore, additional studies, such as X-Ray structure analyses or DFT calculations, were required to elucidate the actual structure.

Table 17. Selected spectroscopic parameters of $CpFe(PMePr^i_2)H_2(SiR_3)$

	SiR_3					
	$SiMe_2Ph$ (f)	**$SiHMePh$ (e)**	**SiH_2Ph (d)**	**$SiMe_2Cl$ (c)**	**$SiMeCl_2$ (b)**	**$SiCl_3$ (a)**
δ Fe*H*, ppm	-15.75	-15.34 -15.52[a]	-15.24	-15.70	-15.06	-14.60
J(P-H) Hz	52.8	53.0 54.0[a]	52.1	50.5	50.6	50.6
J(Si-H) Hz	21.1	21.2 17.0[a]	19.8	21.8	19.2	18.9

[a] second diastereomer

Fortunately, the X-ray quality crystals of complexes **82a** and **82b** were obtained from concentrated ether solutions at -30°C (Figure 23, 21). The structural parameters of the silyl ligand in complex **82b** are scattered due to the rotational disorder of $SiMeCl_2$ group. Surprisingly, the X-ray structure analysis of **82a** revealed the presence of simultaneous interaction of the silicon atom with both hydrides. The hydrido silyl complex **82a** has an extremely short Fe-Si bond of 2.168(1) Å. This bond distance is considerably shorter than the Fe-Si contacts in the related classical compounds $(\eta^6\text{-PhMe})FeH_2(SiCl_3)_2$ (2.220(2) Å)[163c] and $CpFe(CO)(H)(SiCl_3)_2$ (2.252(3) Å).[167] Moreover, it is very close to the Fe=Si double bond in the silylene complex $Cp^*Fe(=SiMes_2)(SiMes_3)(CO)$ (2.154(1) Å).[168] Interestingly, analogous situation has been observed for the complex $[PhB(CH_2PPr^i_2)_3]FeH(\eta^3\text{-}H_2SiMePh)$, in which the presence of a very short Fe-Si bond of 2.1280(7) Å was explained by the simultaneous coordination of two Si-H bonds to the iron centre.[161] For the same reason, relatively short Ru-Si and Ru-B distances were previously observed in η^3-silane and η^3-borane ruthenium complexes.[169] The presence of Si-H interactions in complex **82a** would certainly influence the structural parameters of the silyl ligand. And indeed, two sets of Si-Cl bonds can be observed. The Si-Cl bonds, which are situated trans to the hydrides, are noticeably longer than the remaining Si-Cl bond (2.1125(9) vs. 2.0835(14) Å). For comparison, all the Si-Cl bonds are relatively short and almost identical in the related classical complexes $(\eta^6\text{-PhMe})FeH_2(SiCl_3)_2$ and

$CpFe(CO)(H)(SiCl_3)_2$ (2.072 – 2.079(2) Å and 2.048 – 2.061(4) Å). [163c,167] In addition, the Si-H distance of 1.88(3) Å was observed, which is considerably smaller than the formal upper limit of 2.0 Å for the complexes with significant Si-H interactions.[100]

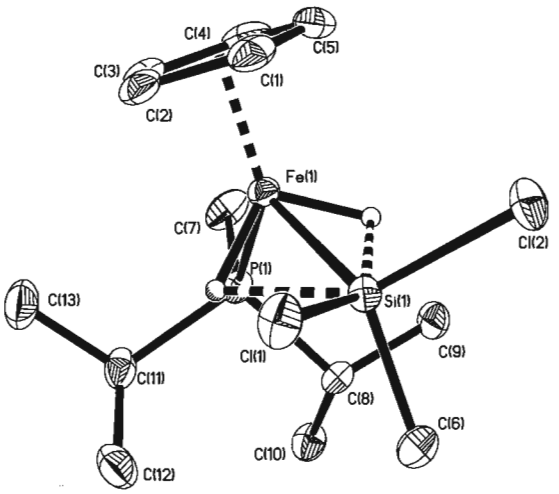


Figure 23. Molecular structure of $CpFe(PMePr^i_2)(\eta^3\text{-}H_2SiMeCl_2)$ (H atoms, except Si-H, are omitted for clarity)

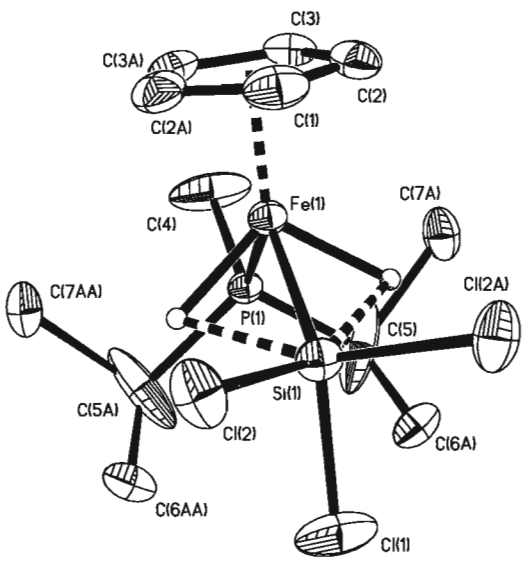
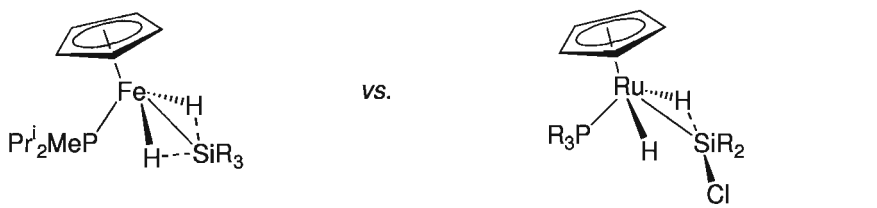


Figure 24. Molecular structure of $CpFe(PMePr^i_2)(\eta^3\text{-}H_2SiCl_3)$ (H atoms, except Si-H, are omitted for clarity)

Also, a very short Ru-H bond of 1.35(3) Å was revealed. However, the Si-H and Ru-H bond distances cannot be reliable parameters due to the large inaccuracy in the location of hydrides by the X-ray crystal analysis.

Any remaining doubts on the possible structure of the hydrido silyl complexes **82** were eliminated after the DFT calculations, which were performed by Prof. Vyboishchikov. First of all, the DFT calculations revealed unusual features of the silane H^aSiMe_3 addition to $CpFe(PMe_3)H^b$ (Appendix, Figure 26). This process starts with the formation of the η^1-silane σ-complex $CpFe(PMe_3)H^b(\eta^1\text{-}H^aSiMe_3)$, which has a long Fe-Si separation, but similar Fe-H^a and Si-H^a bonds of 1.692 Å and 1.641 Å, respectively. Once the Fe-Si distance reaches the value of 2.65 Å, the Si-H^a starts to elongate (1.930 Å), and the interaction of the Si atom with the iron bound proton starts to build up (a negative $J(Si\text{-}H^b)$ of -0.7 Hz was found at this point).

Two simultaneous and equivalent Si-H interactions were found in the optimized structure of $CpFe(PMe_3)H_2SiMe_3$, which has the Si-H distances of 2 Å. The DFT calculations also revealed several unusual features of these interactions. First of all, the orientation of the silyl group does not influence the extent of Si-H interactions, which was proven by calculation of three silyl rotamers for each complex $CpFe(PMe_3)H_2(SiMe_{3-n}Cl_n)$ (n = 0-4). This fact is very unusual, because the interligand hypervalent interactions (IHI) in the related ruthenium hydrido silyl complexes $CpRu(PR_3)H_2(SiMe_2Cl)$ require the presence of an accepting group *trans* to the hydride, which also means that silicon interacts with only one of the ruthenium bound hydrides at a time (Figure 25). As mentioned before, the orientation of the silyl group in the latter case is so crucial that, in contrast to complex $CpRu(PPh_3)H_2(SiMe_2Cl)$, the analogous compound $Cp^*Ru(PPh_3)H_2(SiMe_2Cl)$ does not exhibit any IHI due to unfavourable steric interactions between the bulkier Cp* ring and the $SiMe_2Cl$ group.[13a]



Two simultaneous Si-H interactions, no dependence on the orientation of silyl ligand

Only one Si-H interaction (IHI), the chloride substituent is trans to the interacting hydride

Figure 25. Comparison of interligand interaction in $Cp(PR_3)MH_2(SiR_3)$, M = Fe, Ru.

The second remarkable feature of complexes $CpFe(PMe_3)H_2(SiMe_{3-n}Cl_n)$ is that the extent of calculated multicentral bonding does not depend on the nature of substituents at silicon. Indeed, the experimental coupling constants J(Si-H) in complexes **82** are all close to 20 Hz and change only slightly. It has been previously discussed that the observed silicon coupling constant in hydridosilyl complexes is actually a sum of a one bond (direct Si-H) and a two-bond (H-M-Si) interactions: $J^{obs}(Si\text{-}H) = |{}^1J(Si\text{-}H) + {}^2J(Si\text{-}H)|$, where the value of ${}^1J$(Si-H) is negative and the value of ${}^2J$(Si-H) is positive.[12c] In this case, the calculated J(Si-H) could provide a valuable information on the overall sign of the coupling constant, which will allow one to compare the contribution of a one bond and a two-bond Si-H interactions to the overall J(Si-H). The calculated values of J(Si-H) in complexes $CpFe(PMe_3)H_2(SiR_3)$ are all negative, which additionally suggests the presence of a significant direct Si-H bond.

Catalytic activity of hydrido silyl complexes $CpFe(PMePr^i_2)H_2(SiR_3)$

After the structural studies of the hydrido silyl complexes $CpFe(PMePr^i_2)H_2(SiR_3)$, we also tested the catalytic activity of these complexes in the hydrosilylation of benzaldehyde. Unfortunately, no reaction between silanes and PhCHO was observed in the presence of catalytic amounts of complexes $CpFe(PMePr^i_2)H_2(SiR_3)$ at room temperature, but the reactions proceed at a slightly elevated temperature. Thus, the hydrosilylation of benzaldehyde with H_3SiPh can be performed at 50°C with the formation of a mixture of $HSi(OCH_2Ph)_2Ph$ (84%) and $Si(OCH_2Ph)_3Ph$ (16%) (Table 18). The ratio of products can be changed by addition of another equivalent of benzaldehyde, which gave a mixture of $HSi(OCH_2Ph)_2Ph$ (44%) and $Si(OCH_2Ph)_3Ph$ (56%) after 2 h at 50°C. Similarly, the complex $Cp(PMePr^i_2)FeH_2(SiHMePh)$ catalyzes hydrosilylation of PhCHO with $H_2SiMePh$ at 50°C with the formation of a mixture of $HSi(OCH_2Ph)MePh$ (81%) and $Si(OCH_2Ph)_2MePh$ (19%), which can be converted into pure $Si(OCH_2Ph)_2MePh$ after addition of another equivalent of benzaldehyde. There were no reactions between PhCHO and $HSiMe_2Ph$, $HSiMe_2Cl$ or $HSiMeCl_2$ in the presence of catalytic amounts of the corresponding iron hydridosilyl complexes under the same reaction conditions (Table 18).

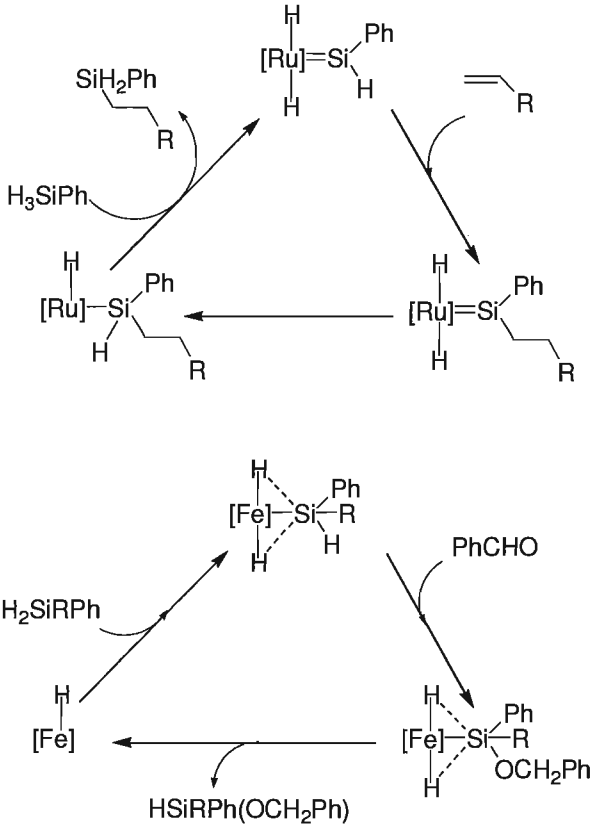
Table 18. Hydrosilylation of PhCHO in the presence of $CpFe(PMePr^i_2)H_2(SiR_3)$[a]

Substrate	Silane	SiR_3 in catalyst	Time	Conv.[b]	Products
PhCHO	H_3SiPh	SiH_2Ph	12h	100%	$HSi(OCH_2Ph)_2Ph$ (84%) $Si(OCH_2Ph)_3Ph$ (16%)
PhCHO	$H_2SiMePh$	SiHMe	12h	100%	$HSi(OCH_2Ph)MePh$ (81%) $Si(OCH_2Ph)_2MePh$ (19%)
PhCHO	$HSiMe_2Ph$	$SiMe_2Ph$	48h	0%	-
PhCHO	$HSiMe_2Cl$	$SiMe_2Cl$	48h	0%	-
PhCHO	$HSiMeCl_2$	$SiMeCl_2$	48h	0%	-

[a] In a general procedure to a solution of benzaldehyde and silane in benzene was added 5% mol of the Fe-catalyst and the reaction mixture was heated at 50°C. [b] Based on ^1H NMR data.

So far the hydrosilylation of benzaldehyde can be performed only with trihydro- or dihydrosilanes, which can be explained by steric factors, because monohydrosilanes are considerably bulkier. Therefore, the formation of silanes $Si(OCH_2Ph)_3Ph$ and $Si(OCH_2Ph)_2MePh$ in the above reactions is difficult to explain by the hydrosilylation of PhCHO with the corresponding monohydrosilanes $HSi(OCH_2Ph)_2Ph$ and $HSi(OCH_2Ph)MePh$. Possibly, these silanes are formed *via* different process, e.g. redistribution reaction at silicon.

The lack of reactivity of monohydrosilanes can be alternatively explained by a special mechanism of hydrosilylation, which requires only trihydro- or dihydrosilanes. Such a mechanism was originally discovered by Glaser and Tilley[10] for the hydrosilylation of alkenes catalyzed by the cationic ruthenium silylene complex $[Cp^*Ru(PPr^i_3)H_2(=SiHPh)]^+$ and later extended by Gade, Hoffman and co-workers[11] to the case of carbonyl hydrosilylation. An unusual feature of the Glaser-Tilley mechanism is that the alkene substrate inserts directly into the Si-H bond of the ruthenium catalyst (Scheme 136, top). The resulting complex then undergoes silane elimination followed by reaction with H_3SiPh, which regenerates the catalyst. An analogous mechanism can be proposed for the hydrosilylation of benzaldehyde catalyzed by hydridosilyl iron complexes (Scheme 136, bottom). The benzaldehyde could insert into the Si-H bond of the silyl ligand, followed by elimination of alkoxysilane with the subsequent regeneration of the catalyst by the reaction with a second equivalent of dihydro- or trihyrosilane. Notably, the feasibility of carbonyl insertion into the terminal bond Si-H of the silyl ligand in $Cp(CO)_2FeSiR_2H$ has been recently shown by Ueno et al.[170]



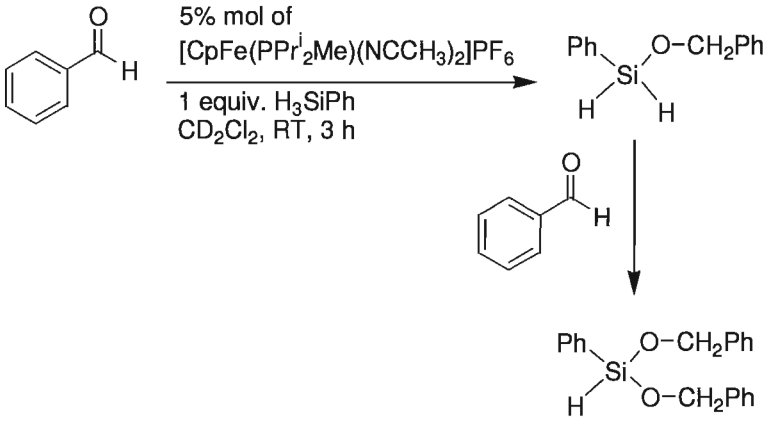
Scheme 136. The proposed mechanisms of Ru (Glazer-Tilley) and Fe catalyzed hydrosilylation.

The formation of complex $CpFe(PMePr^i_2)H_2(SiMePh(OCH_2Ph))$ (**83**) was observed in the reaction of PhCHO with $CpFe(PMePr^i_2)H_2(SiHMePh)$ even at room temperature. However, the full conversion of the starting complex was achieved only after several days at 50°C. Complex **83** is also present in the reaction mixture as a major iron species during the catalytic cycle, and the fast formation of this complex under catalytic conditions can be explained by the much higher concentration of benzaldehyde. In contrast, complex $CpFe(PMePr^i_2)H_2(SiH_2Ph)$ is the main iron compound during the catalytic hydrosilylation of benzaldehyde with H_3SiPh.

III.4.1 Hydrosilylation of carbonyls in the presence of $[CpFe(PMePr^i_2)(NCCH_3)_2]^+$

We found that cationic iron complex $[CpFe(PMePr^i_2)(NCCH_3)_2]PF_6$ (**80-PF$_6$**) catalyzes hydrosilylation of benzaldehyde with H_3SiPh at room temperature. Full conversion of benzaldehyde was observed within 3 h under these conditions (Scheme

137). Surprisingly, this reaction results in a very selective formation of (bis)benzoxysilane $HPhSi(OCH_2Ph)_2$. In contrast, most of the previously described catalytic reactions between H_3SiPh and PhCHO gave complex mixtures of mono-, bis-, and trisubstituted phenyl silanes of the general formula $H_{3-n}PhSi(OCH_2Ph)_n$ (n = 1-3). This selectivity can be explained by the high reactivity of the silane $H_2PhSi(OCH_2Ph)$, which, because of its higher Lewis acidity in comparison with H_3SiPh, could further react with a second equivalent of benzaldehyde faster than the starting silane. On the other hand, the (bis)substituted silane $HPhSi(OCH_2Ph)_2$ is probably too bulky to react further with benzaldehyde at a comparable rate. The reduction of benzaldehyde is highly sensitive to the type of silane. Thus, this reaction cannot be performed with dihydro- and monohydrosilanes, such as $H_2SiMePh$ and $HSiMe_2Ph$.



Scheme 137. Hydrosilylation of benzaldehyde in the presence of $[CpFe(PMePr^i_2)(NCCH_3)_2]PF_6$

Unfortunately, complex **80-PF_6** does not catalyze hydrosilylation of ketones under standard conditions. However, the reaction between H_3SiPh and excess acetone proceeds smoothly in the presence of 5% mol of **80-PF_6**. Thus, almost 80% conversion of the phenyl silane H_3SiPh in acetone-d_6 as the solvent happened after 2 h at room temperature (Table 19, entry 1). Full conversion of the starting silane was observed next day with the formation of a mixture of $PhHSi(OCH(CD_3)_2)_2$ (83%) and $PhH_2Si(OCH(CD_3)_2)$ (17%). Surprisingly, the addition of pyridine to the reaction mixture significantly accelerates this reaction. Thus, almost instantaneous reaction between H_3SiPh and acetone solvent was observed in the presence of 1 equiv. of pyridine and as small as 0.5% mol of **80-PF_6** (Table 19, entry 2). In addition, the

hydrosilylation of acetone can be also performed with the dihydrosilane $H_2SiMePh$, which was fully consumed after only 30 min at room temperature in the presence of 1 equiv. of pyridine and 5% mol of **80-PF$_6$** (Table 19, entry 3). However, no reaction was observed between equimolar quantities of acetone and H_3SiPh in the presence of **80-PF$_6$** (5% mol) and pyridine (10% mol) in $CDCl_3$, THF, and CD_3CN.

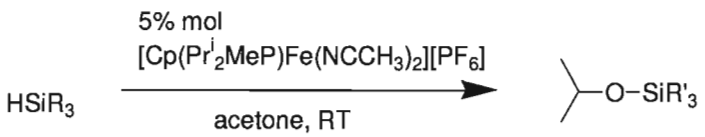


Table 19. Hydrosilylation of acetone in the presence of [CpFe(PMePr$^i_2$)(NCCH$_3$)$_2$]PF$_6$

N	Silane	Conditions	Conv.[b]
1	H_3SiPh	5% [Fe], RT, 2 h	80%
		24 h	100%
2	H_3SiPh	0.5% [Fe], 100% Py, acetone, RT, 5 min	100%
3	$H_2SiMePh$	5% [Fe], 100% Py, acetone, RT, 30 min	100%

[a] In a general procedure to a solution of silane in acetone was added [CpFe(PMePr$^i_2$)(NCCH$_3$)$_2$]PF$_6$.

[b] Based on ^{1}H NMR data.

Due to the lack of catalytic activity of complex **80-PF$_6$** in common solvents, we turned our attention to the solvent-free hydrosilylation reactions. Unfortunately, there was no reaction between H_3SiPh and PhC(O)Me in the presence of 5% mol of **80-PF$_6$** under solvent-free conditions. Presumably, the catalyst could be easily deactivated by silane under these conditions with the formation of a fluorosilane and a mixture of iron complexes. As mentioned before, these decomposition reactions are quite common for the cationic transition metal complexes PF_6^- or BF_4^- counter anions.

To overcome this problem, we synthesized the cationic iron complex [CpFe(PMePr$^i_2$)(NCCH$_3$)$_2$]BAF (**80-BAF**), which contained the more inert BAF counter anion. As for the previously described analogous ruthenium compound, the iron complex was obtained by the reaction of **80-PF$_6$** with LiBAF in dichloromethane. Rewardingly, this iron complex with a more inert counter anion was found to catalyze the hydrosilylation of PhC(O)Me with H_3SiPh under solvent free conditions. Full conversion of PhC(O)Me was observed after 18 h after addition of just 0.5% mol of **80-BAF** to an equimolar mixture of PhC(O)Me and H_3SiPh at room temperature (Table 20, entry 1). The hydrosilylation of cyclohexanone proceeds even faster (3 h) under similar reaction conditions (Table 20, entry 3). Surprisingly, even such a challenging bulky substrate as diisopropyl ketone can be successfully hydrosilylated,

but longer reaction time is required (3 days at RT) (Table 20, entry 4). Notably, this method can be used only for liquid ketones, because the cationic iron complex **80-BAF** is not soluble in H_3SiPh. However, the reactions with solid carbonyl substrates can be still performed in concentrated solutions. Thus, the hydrosilylation of benzophenone proceeds at room temperature in the presence of 1 equiv. of PhCl, which allows one to dissolve both the iron complex and the starting ketone (Table 20, entry 5). The carbonyl substrate with a nitro-group did not react with silane under these conditions (Table 20, entry 6). Also, no reaction was observed between the acetophenone and monohydrosilane $HSiMe_2Ph$ (Table 20, entry 2).

Table 20. Hydrosilylation of carbonyls under solvent-free conditions mediated by $[CpFe(PMePr^i_2)(NCCH_3)_2]BAF$ (0.5% mol)[a]

N	Substrate	Silane	Conditions	Conv.[b]
1	PhC(O)Me	H_3SiPh	RT, 18h	100%
2	PhC(O)Me	$HSiMe_2Ph$	RT, 1 day	0%
3	$C_5H_{10}CO$	H_3SiPh	RT, 3h	100%
4	$(i\text{-}Pr)_2CO$	H_3SiPh	RT, 3 days	100%
5	Ph_2CO	H_3SiPh	1 equiv. PhCl, RT, 19h	95%
6	*para*-$O_2N(C_6H_4)C(O)Me$	H_3SiPh	3 equiv. PhCl, RT, 1 day	0%

[a] In a general procedure, to a mixture of ketone and silane was added $[CpFe(PMePr^i_2)(NCCH_3)_2]BAF$ (~0.5% mol). [b] Based on NMR data.

The mechanism of the above hydrosilylation reactions remains unclear. By analogy with Ru-catalyzed reactions, we initially proposed the formation cationic silane σ-complexes $[CpFe(PMePr^i_2)(\eta^2\text{-}HSiR_3)(NCCH_3)]^+$ as potential intermediates. However, there was no reaction between **80-BAF** and an excess of H_3SiPh in the absence of carbonyl substrate (as evidenced by NMR spectroscopy). On the other hand, the significant broadening of benzaldehyde signals in ^1H NMR was observed in the presence of **80-BAF**, which could be indicative of an exchange process with the benzaldehyde at room temperature. Analogous broadening of pyridine signals in ^1H NMR was also observed in the pyridine assisted hydrosilylation reactions. The low temperature NMR experiments did not clear up the picture, as there was no change in the shape of the signals upon changing the temperature.

Based on these data, the hydrosilylation reactions catalyzed by cationic iron complex $[CpFe(PMePr^i_2)(NCCH_3)_2]^+$ are likely to start with the activation of the

carbonyl substrate followed by a reaction with silane. However, no reliable conclusions on the mechanism can be drawn at this moment.

In addition to carbonyls, we also attempted the hydrosilylation of other substrates, such as 1-hexene, benzoyl chloride or acetonitrile, in the presence of catalytic amounts of **80-PF_6**. However, these substrates did not react under standard conditions.

IV. Conclusions and Future Work

As part of our broad research programme devoted to investigation of non-classical silane complexes, we prepared a series of new half-sandwich silane complexes of ruthenium and iron. Our main goal was to study the structures of these compounds, focusing on the extent of Si-H bond activation, as well as their catalytic activity in hydrosilylation reactions.

In the iron complexes $CpFe(PPr^i_2Me)H_2(SiR'_3)$, we discovered the presence of two simultaneous and equivalent Si···H interactions, which was confirmed by X-ray analyses and DFT calculations. This type of silicate coordination of $[H_2(SiR'_3)]^-$ is unprecedented. [161,164] Remarkably, the extent of Si···H interactions in these complexes does not depend on the substitution at Si and the orientation of the silyl group. Some of the iron complexes $CpFe(PPr^i_2Me)H_2(SiR'_3)$ (SiR'_3 = SiH_2Ph, SiHMePh) showed moderate catalytic activity in hydrosilylation of benzaldehyde at 50°C. However, this reaction could be interesting for the future mechanistic studies, as the hydrosilylation could proceed *via* insertion of the carbonyl substrate into the terminal Si-*H* bond of the silyl ligand in the iron complexes $CpFe(PPr^i_2Me)H_2(Si\mathit{H}R'_3)$. The cationic iron complex $[CpFe(PPr^i_2Me)(NCCH_3)_2]^+$ showed superior catalytic activity in the hydrosilylation of carbonyls. Moreover, this complex is one of the first examples of iron catalysts which could effectively operate at room temperature.[158b, 171] Slow decomposition of the cationic iron complex was usually observed during the catalysis, and further efforts should be devoted to the development of more stable catalysts, such as $[TpFe(PPr^i_2Me)(NCCH_3)_2]^+$, $[Cp^*Fe(PPr^i_2Me)(NCCH_3)_2]^+$ or iron complexes supported by inert pincer ligands.

We found, that the ruthenium silane σ-complexes $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiR_3)$, in addition to the presence of coordinated σ-Si-H bond, also exhibit the rare secondary RuCl···SiCl interactions, which were for the first time discovered by Nikonov et al. in analogous half-sandwich complexes $Cp^*Ru(PPr^i_3)Cl(\eta^2\text{-}HSiR_3)$.[13b] The presence of significant Si-H interaction was confirmed by the observation of relatively large values of *J*(Si-H), which increase with decreasing acidity of the silane. Short RuCl···SiCl contacts were revealed by X-ray studies of these complexes. By comparing the corresponding parameters for Cp- and Cp*-complexes, we found that the less donating but sterically unhindered Cp ring promotes a less advanced oxidative

addition of the Si-H bond, which we ascribe to the reduced back-donation from ruthenium. The latter effect is, however, mitigated by the stronger additional RuCl···SiCl interactions, which help to compensate the electron deficiency of the silicon centre. So far, the secondary MCl···SiCl interactions have been only observed in ruthenium silane σ-complexes. However, analogous structural features could be also expected in other transition metal complexes, for example in the putative iron complex $CpFe(PR_3)Cl(\eta^2\text{-}HSiR'_3)$.

We also succeeded in the preparation of neutral agostic silylamido complexes $CpRu(PPr^i_3)(N(\eta^2\text{-}HSiMe_2)R)$ (R= Ar or Bu^t), which are the first examples of late transition metal compounds of this type. Our preliminary studies revealed catalytic activity of these compounds in the isomerization of hexene-1. Further mechanistic studies should be directed at the study of potential intermediates of this process, a thinkable candidate of which could be a hydrido silanimine ruthenium complex. The latter species were previously postulated/observed in nalogous reactions of agostic silylamido complexes of molybdenum.[25]

One of the major objectives of our work was the investigation of cationic silane complexes, which are barely studied in comparison with their neutral analogues. We obtained a series of ruthenium complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$, which were characterized by NMR spectroscopy. The NMR data allowed for the first systematic investigation of the effect of ancillary ligands and substituents at silicon on the extent of Si-H bond activation in the cationic silane σ-complexes. Due to the reduced back-donation from the electron-deficient cationic Ru-centre, the *J*(Si-H) values in the above complexes do not change significantly upon variation of substituents at Si. As expected, the analogous complexes with bulkier and less electron donating Tp-ligand $[TpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]BAF$ exhibit much larger *J*(Si-H).

We also reported the preparation of the first examples of cationic silylimino β-agostic complexes $[TpRu(PPh_3)\{(\eta^2\text{-}HSiR_2)N{=}CHCH_3\}]BAF$. The latter complexes also represent a rare example of potential intermediate in the monohydrosilylation of acetonitrile. The *J*(Si-H) of more than 90 Hz in these compounds are the largest among all non-classical silane complexes, which were obtained in the present work.

The above cationic silane σ-complexes $[CpRu(PR_3)(CH_3CN)(\eta^2\text{-}HSiR'_3)]^+$ were proposed as key intermediates in the ionic mechanism of hydrosilylation

reactions mediated by the ruthenium complex $[CpRu(PR_3)(NCCH_3)_2]^+$. The latter complex was found to be a versatile catalyst for a variety of reactions with hydrosilanes. Thus, good catalytic activity of this complex was observed in the hydrosilylation of carbonyls. Also, fast dehydrogenative coupling of silanes with alcohols, amines and acids was observed in the presence of this catalyst.

We reported the first chemoselective preparation of silylimines by monohydrosilylation of nitriles at room temperature in the presence of a variety of common functional groups. (Bis)hydrosilylation of the some nitriles can be also achieved with the same catalyst, but longer reaction times are required. Given the additional features that the catalyst is recyclable, easily assembled from commercial materials, works on bench and the overall process is easy to scale-up, such a catalytic activity is unprecedented.

Catalytic hydrosilylation of pyridines also proceeds at room temperature with the very selective formation of *N*-silyl 1,4-dihydropyridines, which has never been reported before in literature. Moreover, we found that the hydrosilylation of pyridines is a rare example of a reversible hydrosilylation reaction. According to our preliminary studies, the *N*-silyl 1,4-dihydropyridine can be potentially applied as a reducing reagent analogously to the widely used Hantzsch ester.

We also performed the reduction of acyl chlorides to corresponding aldehydes by $HSiMe_2Ph$ with a wide range of substrates, including both aromatic and aliphatic acyl chlorides, which was not previously achievable by other similar methods.

For the nearest future work, the new, potentially more active catalysts $[Cp^*Ru(PR_3)(NCCH_3)_2]^+$, supported by the more electron donating Cp* ligand, should be studied. Also, other unsaturated substrates, such as imines or alkynes, can be tested in hydrosilylation reactions. For example, we observed the hydrosilylation of activated N-acylimine with silane mediated by $[CpRu(PPr^i_3)(NCMe)_2]PF_6$. Also, fast hydrosilylation of 3-hexyne was observed during our competing experiments for the reduction of acyl chlorides.

V. Experimental section

V.1 *General methods and instrumentation*

Unless stated otherwise, all manipulations were performed using standard inert atmosphere (N_2 gas) Schlenk techniques or in a glove-box. Diethyl ether, hexanes, acetonitrile, and dichloromethane, were dried by Grubbs-type solvent purification system. Acetone was dried over molecular sieves (3A). Deuterated solvents C_6D_6 and PhMe-d_8, were dried by distillation from K/Na alloy; $CDCl_3$, CD_2Cl_2, and CD_3CN were dried by distillation from CaH_2; acetone-d_6 was dried over molecular sieves (3A). All organic substrates for catalytic transformations (benzaldehyde, benzoic acid, ethyl acetate, all ketones, nitriles, alcohols, acyl chlorides, amines and pyridines) were purchased from Sigma-Aldrich and used without further purification. All silanes were purchased from Gelest and used without further purification. Elemental analyses were performed in "ANALEST" laboratories (University of Toronto). Correct elemental analysis for [CpRu(PPr^i_3)(CH_3CN)(η^2-$HSiMeCl_2$)]BAF was not obtained because this compound is highly sensitive to air. NMR spectra were obtained with a Bruker DPX-300 (^{1}H 300MHz, ^{13}C 75.5 MHz, ^{29}Si 59.6 MHz, ^{31}P 121.5 MHz) and Bruker DPX-600 (^{1}H 600MHz, ^{13}C 151 MHz, ^{29}Si 119.2 MHz, ^{31}P 243 MHz) instruments at room temperature, unless specified otherwise. IR data were obtained on Perkin-Elmer 1600 FT-IR spectrometer. EPR spectra were collected on a Bruker Elexsys E580 spectrometer operating in cw mode.

V.2 *Cyclopentadienyl cationic ruthenium silane σ-complexes*

V.2.1 The syntheses of starting ruthenium complexes

Preparation of Cp_2Ru

The synthesis of Cp_2Ru was performed analogously to previously reported procedure under air atmosphere.[172] To a solution of $RuCl_3$*nH_2O (5.08 g, 22.5 mmol for n = 0) in absolute ethanol (100 mL) was added freshly distilled CpH (50 mL, 662 mmol). To the resulting black solution was added Zn dust by small portions (7*1.0 g, 85.6 mmol). Heat and gas evolution was observed after addition of first portions of zinc to the reaction mixture. The color of the reaction mixture changed from black to blue and then to grey. The reaction mixture was stirred for 1 h at room temperature after

addition of the last portion of zinc dust. The resulting mixture was filtered using a glass filter and grey precipitate was washed with toluene (3*25 mL). The filtrate was evaporated and the residue was dried under vacuum. The resulting dark oil was dissolved in toluene and passed through a plug of silica gel (100*15 mm). The yellow solution was then evaporated to afford Cp_2Ru as a light yellow crystalline solid. Yield 3.35 g (64%).

Preparation of $[CpRu(C_{10}H_8)]PF_6$

The synthesis of $[CpRu(C_{10}H_8)]PF_6$ was performed analogously to the previously reported procedure.[172] Aluminum powder (0.13 g, 48 mmol) and ether (20 mL) was added to a thick glass ampoule. The resulting mixture was stirred at room temperature for 24 h. The ether was then evaporated and the aluminum powder was dried under vacuum at 150°C for several minutes. The ampoule was then cooled down to room temperature and naphthalene (9 g, 70 mmol) was added in a flow of nitrogen followed by addition of ruthenocene (1.6 g, 6.9 mmol) and dry $AlCl_3$ (1.06 g, 7.9 mmol). The resulting solid mixture was dried under vacuum and then refilled with nitrogen. To the solid mixture was added decalin (100 mL). The reaction mixture was heated to 70°C followed by addition $TiCl_4$ (0.39 ml, 3.56 mmol) at this temperature. The resulting dark mixture was heated at 140°C for three days with stirring. The following steps of product isolation were performed under air atmosphere. The final blue solution with dark oil on the sides of the ampoule was then cooled down to 0°C and a solution of 9 mL of HCl and 9 mL of 30% H_2O_2 in 100 mL of water was slowly added (Caution: Gas and heat evolution was observed). The dark red water layer was separated from the organic phase, and the organic part was washed with water. To the combined water portions was added $NaPF_6$ (2 g). The product was then extracted with CH_2Cl_2 (4*100 mL). The combined dichloromethane fractions were dried over $MgSO_4$ and filtered. The solvent was then removed by evaporation and the product was dried under vacuum to afford $[CpRu(C_{10}H_8)]PF_6$ as an orange powder. Yield 1.6 g (58%).

Preparation of $[CpRu(CH_3CN)_3]PF_6$

The synthesis of $[CpRu(CH_3CN)_3]PF_6$ was performed analogously to the previously reported procedure.[172] Complex $[CpRu(C_{10}H_8)]PF_6$ (1.6 g, 4.2 mmol) was dissolved in 30 mL of acetomitrile and the resulting solution was stirred for 1 day at room temperature. To the solution was then added hexane (20 mL) and the resulted mixture

was stirred for 15 min. The upper hexane layer was then removed with a syringe. The remaining solution was stirred for additional 2 days and the extraction with hexane was repeated. The resulting solution was concentrated to 10 mL followed by addition of ether (40 mL) on top of the solution, which resulted in the formation of two layers. The mixture was then placed into a fridge and stored at -30°C for a week, which resulted in precipitation of the product in a form of red-orange crystals. The crystals were separated by decantation (the mother liquor can be saved for further crystallization) and dried under vacuum. Yield 1.1 g (67%).

Preparation of $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$

The synthesis of $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ was performed analogously to the previously reported procedures.[173] To a solution of $[CpRu(CH_3CN)_3]PF_6$ (0.38 g, 0.9 mmol) in acetonitrile (50 mL) was added PPr^i_3 (0.14 g, 0.9 mmol). The resulting solution was stirred at room temperature for 1 day. The solvent was then evaporated and the residue was washed with Et_2O (2*20 mL). The yellow solid was then dried under vacuum, which gave the product of sufficient purity. However, the ruthenium complex can be recrystallized from CH_3CN/Et_2O (1:6) solution at -30 °C. Yield 0.48 g (98%).

^1H ($CDCl_3$): δ 4.54 (s, 5, C_5H_5), 2.43 (s, 6, CH_3CN), 2.33 (dsept, J(H-H) =7.2 Hz, J(P-H) = 7.5 Hz, 2, $P(CH(CH_3)_2)_2$), 1.22 (dd, J(H-H) =7.2 Hz, J(P-H)=13.2 Hz, 6, $P(CH(CH_3)_2)$). ^{31}P ($CDCl_3$): δ 56.0. ^{13}C ($CDCl_3$): δ 128.1 (2C, CH_3CN), 74.9 (5C, Cp), 26.6 (d, J(P-C) = 18.7 Hz, 3C, $P(CH(CH_3)_2)_2$), 19.7 (s, 6C, $P(CH(CH_3)_2)$), 4.0 (s, 2C, CH_3CN). IR(Nujol): ν(CN)=2276 cm^{-1}.

Preparation of $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$

To a solution of $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.45 g, 0.81 mmol) in CH_2Cl_2 was added LiBAF*Et_2O (0.62 g, 0.81 mmol). The reaction mixture was stirred overnight at ambient temperature. The solvent was then removed in vacuum and the product was extracted with ether (3*50 mL). Complex $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ was obtained as yellow powder after removal of ether in vacuum. Yield 0.79 g (90%). (In some cases the product could contain complex $[CpRu(CH_3CN)_3]BAF$ as an impurity, which can be easily converted into $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ by addition of equimolar amount of PPr^i_3).

Preparation of [CpRu(PPh$_3$)(CH$_3$CN)$_2$]BAF

To a solution of [CpRu(PPh$_3$)(CH$_3$CN)$_2$]PF$_6$[173] (0.17 g, 0.26 mmol) in CH_2Cl_2 was added LiBAF*Et$_2$O (0.20 g, 0.26 mmol). The reaction mixture was stirred overnight at ambient temperature. Solvent was then removed in vacuum and the product was extracted with ether (3*50 mL). Complex [CpRu(PPh$_3$)(CH$_3$CN)$_2$]BAF was obtained as a yellow powder after removal of ether in vacuum. Yield 0.27 g (87%).

V.2.2 The synthesis of cationic silane σ-complexes

Preparation of [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiCl$_3$)]BAF

To a yellow solution of [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF (10 mg, 9.2 μmol) in $CDCl_3$ was added $HSiCl_3$ (5.5 μL, 55.2 μmol). Yield 100% (according to NMR spectra). After 15 min at room temperature all the volatiles were removed in vacuum affording the product as yellow oil. Complex [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiCl$_3$)]BAF can be also prepared as a crystalline solid by slow crystallization at -30°C from the solution of [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF in $HSiCl_3/CH_2Cl_2$/hexane (1/1/3). Yield 89%.

^{1}H NMR ($CDCl_3$): δ 5.12 (s, 5, Cp), 2.41 (s, 3, C*H*$_3$CN), 2.41 (m, 3, C*H*(CH$_3$)$_2$), 1.4–1.2 (m, 18, CH(C*H*$_3$)$_2$), -8.66 (d+sat, *J*(P-H) = 20.3 Hz, *J*(Si-H) = 53.3 Hz, 1, Si*H*). ^{31}P NMR ($CDCl_3$): δ 69.2 (s). ^{13}C NMR ($CDCl_3$): δ 128.6 (s, CH$_3$*C*N), 89.2 (s, Cp), 29.3 (d, J(P-C) = 24.1 Hz, *C*H(CH$_3$)$_2$), 19.4 (br s, CH(*C*H$_3$)$_2$), 4.25 (s, *C*H$_3$CN). ^{1}H-^{29}Si HSQC: δ 29.5. IR (neat): υ (Ru-H) = 1985 cm^{-1}. Anal. Calcd. for $C_{40}H_{30}BCl_3F_{20}NPRuSi$: C, 40.65; H, 2.56; N, 1.19. Found: C, 40.34; H, 2.57; N, 1.20.

Preparation of [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiMeCl$_2$)]BAF

Complex [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF (15 mg, 13.8 μmol) was dissolved in $HSiMeCl_2$ (0.5 mL, 6.1 mmol). All the volatiles were then removed in vacuum and the residue was dissolved in $CDCl_3$. Yield 100% (according to NMR spectra). Complex [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiMeCl$_2$)]BAF can be also prepared as a crystalline solid by slow crystallization at -30°C from the solution of [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF in $HSiMeCl_2$: hexane (1:3). Yield 85%.

^{1}H NMR ($CDCl_3$): δ 5.27 (s, 5, Cp),), 2.37 (s, 3, C*H*$_3$CN), 2.36 (m, 3, C*H*(CH$_3$)$_2$), 1.35–1.30 (dd, *J*(P-H) = 14.7 Hz, *J*(H-H) = 7.3 Hz, 9, CH(C*H*$_3$)$_2$), 1.25 (s, 3, Si*Me*), 1.24-1.19 (dd, *J*(P-H) = 14.7 Hz, *J*(H-H) = 7.3 Hz, 9, CH(C*H*$_3$)$_2$) -9.19 (d+sat, *J*(P-H)

= 22.0 Hz, *J*(Si-H) = 44.7 Hz, 1, Si*H*). ^{31}P NMR ($CDCl_3$): δ 69.2 (s). ^{13}C NMR ($CDCl_3$): δ 87.4 (s, Cp), 29.7 (s, Si*Me*), 29.1 (d, J(P-C) = 24.1 Hz, *C*H(CH_3)$_2$), 19.3 (br s, CH(*C*H_3)$_2$), 4.19 (s, *C*H_3CN). ^{1}H-^{29}Si HSQC: δ 58.0. IR (neat): υ (Ru-H) = 1987 cm^{-1}. Anal. Calcd. for $C_{41}H_{33}BCl_2F_{20}NPRuSi$: C, 42.40; H, 2.86; N, 1.21. Found: C, 41.74; H, 3.04; N, 1.10.

Preparation of [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiMe$_2$Cl)]BAF

Complex [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF was dissolved in $HSiMe_2Cl$ (0.6 mL). The resulting yellow solution was then transferred into NMR tube, containing D_2O in a sealed capillary. The resulting equilibrium mixtrute contained 78% of complex [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiMe$_2$Cl)]BAF along with the starting (bis)acetonitrile complex. Complex [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-HSiMe$_2$Cl)]BAF can be also prepared as a crystalline solid by slow crystallization at -30°C from the solution of [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF in $HSiMe_2Cl$/hexane (1/3). Yield 80%.

^{1}H NMR ($HSiMe_2Cl$, D_2O insert): δ 5.52 (s, 5, Cp), 2.73 (m, 3, C*H*(CH_3)$_2$), 2.67 (s, 3, C*H*$_3$CN), 1.72 – 1.57 (m, 18, CH(C*H*$_3$)$_2$), 1.39 and 1.29 (s, 3, Si*Me*), -9.20 (d+sat, *J*(P-H) = 23.2 Hz, *J*(Si-H) = 45.1 Hz, 1, Si*H*). ^{31}P NMR ($HSiMe_2Cl$, D_2O insert): δ 69.4 (s). ^{1}H-^{13}C HSQC ($HSiMe_2Cl$, D_2O): δ 85.5 (Cp), 28.8 (*C*H(CH_3)$_2$), 19.5 (CH(*C*H_3)$_2$), 13.3 and 12.0 (Si*Me*), 4.2 (*C*H_3CN). ^{1}H-^{29}Si HSQC ($HSiMe_2Cl$, D_2O insert): δ 54.7. Anal. Calcd. for $C_{42}H_{36}BClF_{20}NPRuSi$: C, 44.21; H, 3.18; N, 1.23. Found: C, 43.80; H, 3.31; N, 1.17.

Preparation of [CpRu(PPr$^i_3$)(CH$_3$CN)(η^2-H$_3$SiPh)]BAF

To a yellow solution of [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]BAF (20 mg, 18.4 μmol) in $CDCl_3$ (0.6 mL) was added H_3SiPh (22.6 μL, 0.18 mmol). Yield 100% (according to NMR spectra). The product was obtained in a form of yellow oil after evaporation of all the volatiles in vacuum.

^{1}H NMR ($CDCl_3$): δ 7.70-7.65 (m, 2, Ph), 7.45-7.40 (m, 3, Ph), 5.35 (dd, *J*(H-H) = 8.8 Hz, *J*(H-H) = 2.7 Hz, 1, Si*H*), 5.04 (s, 5, Cp), 4.87 (br d, *J*(H-H) = 8.7 Hz, 1, Si*H*), 2.35 (m, 3, C*H*(CH_3)$_2$), 2.28 (d, *J*(P-H) = 1.0 Hz, 3, C*H*$_3$CN), 1.32-1.25 (dd, *J*(P-H) = 13.7 Hz, *J*(H-H) = 7.1 Hz, 9, CH(C*H*$_3$)$_2$), 1.28-1.21 (dd, *J*(P-H) = 14.3 Hz, *J*(H-H) = 7.1 Hz, 9, CH(C*H*$_3$)$_2$), -9.50 (ddd+sat, *J*(P-H) = 23.0 Hz, *J*(H-H) = 2.7 Hz and 2.2 Hz, *J*(Si-H) = 48.0 Hz, 1, Si*H*). ^{31}P NMR ($CDCl_3$): δ 70.2 (s). ^{1}H-^{13}C HSQC ($CDCl_3$): δ

84.8 (Cp), 27.8 ($CH(CH_3)_2$), 19.3 ($CH(CH_3)_2$), 3.7 (CH_3CN). ^1H-^{29}Si HSQC ($CDCl_3$): δ -22.0.

Preparation of [CpRu(PPr^i_3)(CH_3CN)(η^2-$H_2SiMePh$)]BAF

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (20 mg, 18.4 μmol) was dissolved in PhCl (0.16 mL) followed by addition of $H_2SiMePh$ (0.44 mL). The solution was then transferred into NMR tube, containing D_2O in a sealed capillary. Complex [CpRu(PPr^i_3)(CH_3CN)(η^2-SiH_2MePh)]BAF was obtained as a mixture of two isomers. Selected NMR data:

^1H NMR (PhCl + $H_2SiMePh$, D_2O insert): δ 5.14 and 5.10 (bs, 1, Si*H*), 4.70 (s, 5, Cp), 1.44 and 1.43 (s, 3, CH_3CN), 1.75 (m, 3, C*H*$(CH_3)_2$), 0.87-0.67 (m, 18, CH$(CH_3)_2$), 0.62 and 0.48 (bs, 3, Si*Me*), -9.94 and -10.09 (d+sat, *J*(P-H) = 23.5 Hz and 23.5 Hz, *J*(Si-H) = 48.4 Hz and 46.7 Hz, 1, Si*H*). ^{31}P NMR (PhCl + $H_2SiMePh$, D_2O insert): δ 69.5 and 69.1 (s). ^{13}C NMR (PhCl + $H_2SiMePh$, D_2O insert): δ 83.9 and 83.8 (s, Cp), 27.9 and 27.7 (d, J(P-C) = 26.4 Hz and 25.6 Hz, *C*H$(CH_3)_2$), 18.8 (CH$(CH_3)_2$). ^1H-^{29}Si HSQC (PhCl + $H_2SiMePh$, D_2O insert): δ -1.1 and -3.7.

Preparation of [CpRu(PPr^i_3)(CH_3CN)(η^2-$HSiMe_2Ph$)]BAF

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (20 mg, 18.4 μmol) was dissolved in PhCl (0.16 mL) followed by addition of $HSiMe_2Ph$ (0.44 mL). The solution was then transferred into NMR tube, containing D_2O in a sealed capillary.

Selected NMR data:

^1H NMR (PhCl + $HSiMe_2Ph$, D_2O insert): δ 4.16 (s, 5, Cp), 1.47 (s, 3, CH_3CN), -10.3 (d+sat, *J*(P-H) = 22.5 Hz, *J*(Si-H) = 50.3, 1, Si*H*). ^{31}P NMR (PhCl + $HSiMe_2Ph$, D_2O insert): δ 66.7 (s). ^1H-^{13}C HSQC (PhCl + $HSiMe_2Ph$, D_2O insert): δ 82.9 (Cp), 2.6 (CH_3CN). ^1H-^{29}Si HSQC (PhCl + $HSiMe_2Ph$, D_2O insert): δ 8.31.

Preparation of [CpRu(PPh_3)(CH_3CN)(η^2-$HSiCl_3$)]BAF

To a solution of complex [CpRu(PPh_3)(CH_3CN)$_2$]BAF (10 mg, 8.4 μmol) in $CDCl_3$ (0.6 mL) was added $HSiCl_3$ (0.2 mL, 2.0 mmol). All the volatiles were then removed in vacuum and the residue was redissolved in $CDCl_3$ (0.6 mL). Complex [CpRu(PPh_3)(CH_3CN)(η^2-$HSiCl_3$)]BAF was obtained in a mixture with [CpRu(PPh_3)(CH_3CN)$_2$]BAF (7:1).

^{1}H NMR ($CDCl_3$): δ 7.60 – 7.30 (m, 15, Ph), 5.16 (s, 5, Cp), 1.89 (s, 3, C*H*$_3$CN), -7.75 (d+sat, J(P-H) = 18.3 Hz, J(Si-H) = 58.5 Hz, 1, Si*H*). ^{31}P NMR ($CDCl_3$): δ 45.0 (s). ^{1}H-^{13}C HSQC ($CDCl_3$): δ 133.2, 132.5 and 129.4 (Ph), 91.3 (Cp), 3.1 (*C*H$_3$CN). ^{1}H-^{29}Si HSQC ($CDCl_3$): δ 27.2.

Preparation of [CpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiMeCl$_2$)]BAF

Complex [CpRu(PPh$_3$)(CH$_3$CN)$_2$]BAF (10 mg, 8.4 μmol) was dissolved in $HSiMeCl_2$ (0.5 mL, 6.1 mmol). All the volatiles were then removed in vacuum and the residue was dissolved in $CDCl_3$. Yield 100% (according to NMR spectra).

^{1}H NMR ($CDCl_3$): δ 7.60 – 7.30 (m, 15, Ph), 5.04 (s, 5, Cp), 1.87 (d, *J*(P-H) = 1.6 Hz, 3, C*H*$_3$CN), 1.15 (s, 3, Si*Me*), - 8.29 (d+sat, *J*(P-H) = 20.8 Hz, *J*(Si-H) = 48.3 Hz, 1, Si*H*). ^{31}P NMR ($CDCl_3$): δ 47.1 (s). ^{1}H-^{13}C HSQC ($CDCl_3$): δ 133.1, 132.1, 129.2 (Ph), 89.7 (Cp), 18.3 (Si*Me*), 3.0 (*C*H$_3$CN). ^{1}H-^{29}Si HSQC ($CDCl_3$): δ 54.0.

Preparation of [CpRu(PPh$_3$)(CH$_3$CN)(η^2-HSiMe$_2$Cl)]BAF

Complex [CpRu(PPh$_3$)(CH$_3$CN)$_2$]BAF (10 mg, 8.4 μmol) was dissolved in $HSiMe_2Cl$ (0.6 mL). The resulting yellow solution was then transferred into NMR tube, containing D_2O in a sealed capillary.

^{1}H NMR ($HSiMe_2Cl$, D_2O insert): δ 7.80 – 7.60 (15, m, Ph), 5.25 (s, 5, Cp), 2.19 (s, 3, C*H*$_3$CN), 1.28 and 1.13 (s, 3, Si*Me*), -8.47 (d+sat, *J*(P-H) = 22.6 Hz, *J*(Si-H) = 47.4 Hz, 1, Si*H*). ^{31}P NMR ($HSiMe_2Cl$, D_2O insert): δ 49.9 (s). ^{1}H-^{13}C HSQC ($HSiMe_2Cl$, D_2O insert): δ 87.9 (Cp), 13.3 and 12.3 (Si*Me*), 3.1 (*C*H$_3$CN). ^{1}H-^{29}Si HSQC ($HSiMe_2Cl$, D_2O insert): δ 52.3.

V.3 *Neutral silane agostic and σ-complexes of ruthenium*

V.3.1 Silane σ-complexes with secondary Si···Cl interactions

Preparation of Cp(PPr$^i_3$)RuCl

To a solution of Cp(PPr$^i_3$)Ru(CH$_3$CN)$_2$BF$_4$ (0.420 g, 0.8 mmol) in THF (50 mL) was added LiCl (0.040 g, 0.9 mmol). The mixture was stirred overnight and then dried in vacuo. Toluene (60 mL) was added to the resulting dark residue and the solution was filtered. The filtrate was dried in vacuo to afford the product as brown crystalline solid. Yield 0.14 g (46%).

^{1}H NMR (d-toluene, 25 °C): δ 4.2 (br. s, 5, Cp), 2.8 (br. s, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.2 (br. s, 18, P(CH(C*H*$_3$)$_2$)$_3$). ^{1}H NMR (d-toluene, -24 °C): δ 4.3, 4.0 (br. s, Cp), 2.8 (br. s, P(C*H*(CH$_3$)$_2$)$_3$), 1.0-1.5 (br. m, P(CH(C*H*$_3$)$_2$)$_3$). ^{1}H NMR (d-toluene, -48 °C): δ 4.5, 4.3, 4.0 (br. s, Cp), 1.0-1.8 (br. m, P(CH(C*H*$_3$)$_2$)$_3$). ^{31}P NMR (d-toluene, -24 °C): δ 51.7. ^{31}P NMR (d-toluene, -48 °C): δ 56.1, 51.3, 51.0. ^{1}H-^{13}C HSQC NMR (d-toluene, -48 °C): δ 63.1, 65.0, 68.0 (Cp).

Preparation of Cp(PPr$^i_3$)Ru(H)(Cl)SiCl$_3$.

To a brown solution of Cp(PPr$^i_3$)RuCl (0.078g, 0.22 mmol) in toluene (20 mL) was added HSiCl$_3$ (0.022 mL, 0.22 mmol) dropwise. With the last drop of HSiCl$_3$ the colour changed to yellow. The solution was dried in vacuo and the product was recrystallised from ether at -30 °C. Yield 0.089 g (90%).

^{1}H NMR (C$_6$D$_6$): δ 4.76 (s, 5, Cp), 2.10 (m, 3, P(C*H*(CH$_3$)$_2$)$_3$), 0.87 (dd, *J*(P-H) = 13.9 Hz, *J*(H-H) = 7.0 Hz, 9, P(CH(C^a*H*$_3$)$_2$)$_3$), 0.86 (dd, *J*(P-H) = 13.5 Hz, *J*(H-H) 6.9 Hz, 9, P(CH(C^b*H*$_3$)$_2$)$_3$), -9.67 (d+sat, *J*(P-H) = 27.1 Hz, *J*(Si-H) = 33.3 Hz, 1, Ru-*H*). ^{31}P NMR (C$_6$D$_6$): δ 64.0 (s). ^{13}C NMR (C$_6$D$_6$): δ 88.5 (s, Cp), 27.6 (d, *J*(P-C) = 23.1 Hz, P(*C*H(CH$_3$)$_2$)$_3$), 20.1 (s, P(CH(*C*^{a}H$_3$)$_2$)$_3$), 19.5 (d, *J*(P-C) = 2.2 Hz, P(CH(*C*^{b}H$_3$)$_2$)$_3$). ^{1}H-^{29}Si HSQC NMR (d-toluene): δ 23.4. IR (Nujol): 1995 cm^{-1}. Anal. Calcd. for C$_{14}$H$_{27}$Cl$_4$PRuSi: C, 33.81; H, 5.47. Found: C, 33.81; H, 5.47.

Preparation of Cp(PPr$^i_3$)Ru(H)(Cl)SiMeCl$_2$.

This complex was prepared analogously to previous one with Cp(PPr$^i_3$)RuCl (0.120 g, 0.33 mmol) and HSiMeCl$_2$ (0.034 mL, 0.33 mmol). Yield 0.131 g (92%).

^{1}H NMR (C$_6$D$_6$): δ 4.73 (s, 5, Cp), 2.02 (m, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.56 (s, 3, SiC*H*$_3$), 0.87 (dd, *J*(P-H) = 13.9 Hz, *J*(H-H) = 7.3 Hz, 18, P(CH(C*H*$_3$)$_2$)$_3$, -9.75 (d+sat, *J*(P-H) = 26.4 Hz, *J*(Si-H) = 41.6 Hz, 1, Ru-*H*). ^{31}P NMR (C$_6$D$_6$): δ 65.4 (s). ^{13}C NMR (C$_6$D$_6$): δ 86.7 (s, Cp), 27.6 (d, J(P-C) = 23.0 Hz, P(*C*H(CH$_3$)$_2$)$_3$), 19.9 (s, P(CH(*C*^{a}H$_3$)$_2$)$_3$), 19.4 (s, P(CH(*C*^{b}H$_3$))$_3$), 16.7 (s, SiMe). ^{29}Si INEPT+ NMR (C$_6$D$_6$): δ 48.6 (d, J(Si-H) = 45.2 Hz). IR (Nujol): 1976 cm^{-1}. Anal. Calcd. for C$_{15}$H$_{30}$Cl$_3$PRuSi: C, 37.78; H, 6.34. Found: C, 37.88; H, 6.31.

Preparation of Cp(PPr$^i_3$)Ru(H)(Cl)SiMe$_2$Cl.

This complex was prepared analogously to previous one with Cp(PPr$^i_3$)RuCl (0.065 g, 0.18 mmol) and HSiMe$_2$Cl (0.020 mL, 0.18 mmol). Yield 0.074 g (90%).

^{1}H NMR (d-toluene): δ 4.62 (s, 5, Cp), 1.95 (m, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.33 (s, 3, Si*Me*^{a}), 1.06 (s, 3, Si*Me*^{b}), 0.96 (dd, *J*(P-H) = 13.2 Hz, *J*(H-H) = 7.2 Hz, 9, P(CH(C^a*H*$_3$))$_3$), 0.94 (dd, *J*(P-H) = 13.2 Hz, *J*(H-H) = 7.2 Hz, 9, P(CH(C^b*H*$_3$))$_3$), -9.75 (d + sat, *J*(P-H) = 26.0 Hz, *J*(Si-H) = 50 Hz, 1, Ru*H*). ^{31}P NMR (d-toluene): δ 72.5 (s). ^{13}C NMR (d-toluene): δ 84.0 (s, Cp), 27.8 (d, J(P-C) = 22.7 Hz, P(*C*H(CH$_3$)$_2$)$_3$), 20.1 (s, P(CH(*C*^{a}H$_3$))$_3$), 19.4 (s, P(CH(*C*^{b}H$_3$))$_3$, 15.0 (s, Si*Me*^{a}), 10.4 (s, Si*Me*^{b}). ^{1}H-^{29}Si HSQC NMR (^{1}H(F2): 300 MHz; ^{29}Si(F1): 59.6 MHz; d-toluene): δ 40.7. IR (Nujol): 1975 cm^{-1}. Anal. Calcd. for C$_{16}$H$_{33}$Cl$_2$PRuSi: C, 42.10; H, 7.29. Found: C, 43.15; H, 7.37.

Preparation of Cp(PPr$^i_3$)Ru(H)(Cl)SiH$_2$Ph.

This complex was prepared analogously to previous one with Cp(PPr$^i_3$)RuCl (0.090 g, 0.25 mmol) and H$_3$SiPh (0.031 mL, 0.25 mmol). Yield 0.103 g (88 %).

^{1}H NMR (d-toluene, 10°C): δ 8.0 (d, *J*(H-H) = 6.6 Hz, 2, ^{2,6}Ph), 7.32 (dd, *J*(H-H) = 7.3 Hz, 2, ^{3,5}Ph), 7.24 (dd, *J*(H-H) = 7.3 Hz, 1, ^{4}Ph), 5.78 (dd + sat., *J*(H-H) = 2.9 Hz, *J*(H-H) = 7.9 Hz, *J*(Si-H) = 215 Hz, 1, Si*H*^{a}), 5.26 (br d+sat, *J*(H-H) = 8.0 Hz, *J*(Si-H) = 208 Hz, 1, Si*H*^{b}), 4.51 (s, Cp), 2.18 (m, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.03 (dd, *J*(P-H) = 13.2 Hz, *J*(H-H) = 6.6 Hz, 9, P(CH(C^a*H*$_3$))$_3$), 1.02 (dd, *J*(P-H) = 13.2 Hz, *J*(H-H) = 6.6 Hz, 9, P(CH(C^{b}H$_3$))$_3$), -10.30 (d+sat, *J*(P-H) = 27.1 Hz, *J*(Si-H) = 39 Hz, 1, Ru*H*). ^{31}P NMR (d-toluene): δ 68.5 (s). ^{13}C NMR (d-toluene): δ 143.7, 134.8 (Ph), 83.4 (Cp), 26.8 (d, *J*(P-C) = 23.1 Hz, P(*C*H(CH$_3$)$_2$)$_3$), 19.1 (s, P(CH(*C*H$_3$)$_2$)$_3$). ^{29}Si INEPT+ NMR (d-toluene): -17.8 (dt, *J*(Si-H) = 37 Hz, *J*(Si-H) = 210 Hz). IR (Nujol): 2112, 2089 cm^{-1} (Si-H), 1985 cm^{-1} (Ru-H). Anal. Calcd. for C$_{20}$H$_{34}$PRuSi: C, 51.10; H, 7.29. Found: C, 49.55; H, 6.44.

Preparation of Cp(PPr$^i_3$)Ru(H)(Cl)SiMe$_2$Ph.

This complex was prepared in NMR tube analogously to previous one with Cp(PPr$^i_3$)RuCl (0.015 g, 0.04 mmol) and HSiMe$_2$Ph (0.006 mL, 0.04 mmol).

^{1}H NMR (toluene-d$_8$, -30°C): δ 7.97 (d, *J*(H-H) = 7.3 Hz, 2, ^{2,6}Ph), 7.40 (dd, *J*(H-H) = 7.3 Hz, 2, ^{3,5}Ph), 7.28 (dd, *J*(H-H) = 7.3 Hz, 1, ^{4}Ph), 4.35 (s, Cp), 2.05 (br. m, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.34 (s, 3, SiC*H*$_3^a$), 1.04 (br. m, 9, P(CH(C^a*H*$_3$))$_3$), 1.02 (s, 3, SiC*H*$_3^b$), 0.97 (br. m, 9, P(CH(C^{b}H$_3$))$_3$), -9.85 (d+sat, *J*(P-H) = 24.9 Hz, *J*(Si-H) = 46 Hz, 1, Ru*H*). ^{31}P NMR (toluene-d$_8$, -30°C): δ 64.9 (s). ^{13}C NMR (toluene-d$_8$, -30°C): δ 148.5, 133.8 (Ph), 81.9 (Cp), 27.3 (d, J(P-C) = 21.9 Hz, P(*C*H(CH$_3$)$_2$)$_3$), 19.1 (s,

$P(CH(CH_3)_2)_3$), 6.4 (s, $SiCH_3^a$), 5.6 (s, $SiCH_3^b$). ^{29}Si INEPT+ NMR (toluene-d_8, -30°C): δ 10.0 (d, *J*(Si-H) = 46 Hz).

Catalytic hydrosilylation of benzaldehyde in the presence of $Cp(PPr^i_3)Ru(H)(Cl)SiH_2Ph$

To a solution of benzaldehyde (25 μL, 0.2 mmol) and equimolar quantity of silane H_3SiPh in C_6D_6 (≈0.6 mL) was added 5% mol of complex $Cp(PPr^i_3)Ru(H)(Cl)SiH_2Ph$. Then the solution was heated up to 50°C. The reaction was monitored by NMR spectroscopy. Full conversion of benzaldehyde into $(PhCHO)_2SiHPh$ happened after 36 h.

V.3.2 Silylamido agostic ruthenium complexes

Preparation of $CpRu(PPr^i_3)N(t\text{-}Bu)SiMe_2H$

To a brown solution of $CpRu(PPr^i_3)Cl$ (0.020 g, 0.06 mmol) in C_6D_6 (0.6 mL) was added amide $LiN(t\text{-}Bu)SiMe_2H$*THF (0.011 g, 0.06 mmol), which resulted in the formation of the agostic complex $CpRu(PPr^i_3)N(t\text{-}Bu)SiMe_2H$ as the major product of the reaction.

^1H NMR (C_6D_6): δ 4.43 (s, 5, Cp), 1.91 (m, 3, $CH(CH_3)_2$), 1.44 (s, 9, t-Bu), 1.16-1.00 (m, 18, $CH(CH_3)_2$), 0.61 (s, 3, Si*Me*), 0.29 (s, 3, Si*Me*), -11.63 (d+sat, *J*(P-H) = 17.5 Hz, *J*(Si-H) = 64.5 Hz, 1, Si*H*). ^{31}P NMR (C_6D_6): δ 62.4. ^{13}C NMR (C_6D_6): δ 74.4 (Cp), 36.6 ($C(CH_3)_3$), 26.5 ($CH(CH_3)_2$), 20.2 and 19.8 ($CH(CH_3)_2$), 7.2 and 1.0 (Si*Me*). ^1H-^{29}Si HSQC (C_6D_6): δ -47.1.

Preparation of $CpRu(PPr^i_3)N(Ar^*)SiMe_2H$

To a brown solution of $CpRu(PPr^i_3)Cl$ (0.020 g, 0.06 mmol) in C_6D_6 (0.6 mL) was added amide $LiN(Ar^*)SiMe_2H$ (0.010 g, 0.06 mmol), which resulted in the formation of highly unstable agostic complex $CpRu(PPr^i_3)N(Ar^*)SiMe_2H$ as the major product of the reaction.

^1H NMR (C_6D_6, selected data): δ 4.26 (s, 5, Cp), 2.71 (s, 6, CCH_3), 1.89 (m, 3, $CH(CH_3)_2$), 1.12-0.83 (m, 18, $CH(CH_3)_2$), 0.61 (s, 3, Si*Me*), 0.57 (s, 3, Si*Me*), -11.02 (d+sat, *J*(P-H) = 19.5 Hz, *J*(Si-H) = 63 Hz, 1, Si*H*). ^{31}P NMR (C_6D_6): δ 60.9.

V.4 *Tris(1-pyrazolyl)borato cationic ruthenium silane complexes*

V.4.1 The syntheses of starting ruthenium complexes

Preparation of $TpRu(PPh_3)_2Cl$

The synthesis was performed analogously to previously reported procedure.[174] To a suspension of $Ru(PPh_3)_3Cl_2$ (6.00 g, 6.26 mmol) in CH_2Cl_2 (200 mL) was added TpK (1.58 g, 6.26 mmol). The resulting mixture was stirred for 1 h at room temperature. Hexane (200 mL) was then added and the mixture was filtered. The filtrate was concentrated and the precipitated complex was isolated by decantation, washed with hexane (3*20 mL) and dried under vacuum. Yield 4.5 g (83 %). The NMR data of $TpRu(PPh_3)_2Cl$ correspond to the previously reported.[174]

Preparation of $TpRu(PPh_3)(NCCH_3)Cl$

The synthesis was performed analogously to previously reported procedure.[174] Complex $TpRu(PPh_3)_2Cl$ (2.00 g, 2.36 mmol) was dissolved in THF/CH_3CN (9:1) mixture. The ratio of THF/CH_3CN is important as a different product (presumably $[TpRu(PPh_3)(NCCH_3)_2]Cl$) can be obtained with larger amount of CH_3CN in the reaction mixture. The resulting mixture was refluxed for 6 h and then all the volatiles were removed in vacuum. The resulting yellow solid was washed with ether (2*20 ml) and hexane (3*20 mL) and dried under vacuum. Yield 1.45 g (93%). The NMR data correspond to the previously reported $TpRu(PPh_3)(NCCH_3)Cl$.[174]

Preparation of $TpRu(PPr^i_2Me)_2Cl$

The synthesis was performed analogously to previously reported procedure.[174] To a solution of $TpRu(PPh_3)_2Cl$ (2.00 g, 2.36 mmol) in toluene (30 mL) was added PPr^i_2Me (0.75 mL, 5.0 mmol). The resulting mixture was refluxed for 1 h. Hexane (50 mL) was then added and the precipitated complex was separated from the solution by decantation. The yellow precipitate was washed with ether (20 mL) and hexane (3*20 mL) and then dried under vacuum. Yield 1.0 g (71 %). The NMR data correspond to the previously reported $TpRu(PPr^i_2Me)_2Cl$.[174]

Preparation of $TpRu(PPr^i_2Me)(NCCH_3)Cl$

The synthesis was performed analogously to previously reported procedure.[174] Complex TpRu(PPr$^i_2$Me)$_2$Cl (0.50g, 0.83 mmol) was dissolved in CH_3CN (30 ml) and the resulting mixture was refluxed for 2 h. The solvent was then removed in vacuum and the yellow solid was washed with hexane (3*20 mL) and dried under vacuum. Yield 0.31 g (81%). The NMR data of the product correspond to the previously reported complex TpRu(PPr$^i_2$Me)(NCCH$_3$)Cl.[174]

Preparation of [TpRu(PPh$_3$)(NCCH$_3$)$_2$]BAF

To a solution of TpRu(PPh$_3$)(CH$_3$CN)Cl (0.030 g, 0.046 mmol) in CH_2Cl_2/CH_3CN (0.9 mL/0.1 mL) was added LiBAF*Et$_2$O (0.035 g, 0.046 mmol). The resulting yellow solution was left for 3 days at ambient temperature. The mixture was then filtered and the filtrate was evaporated affording [TpRu(PPh$_3$)(NCCH$_3$)$_2$]BAF as a yellow crystalline solid. Yield 100% (according to NMR data).

^{1}H NMR (CH_2Cl_2/CH_3CN, selected data): δ 6.73 (d, J(H-H) = 1.7 Hz, 2, Tp), 6.35 (s, 1, Tp), 5.98 (t, J(H-H) = 2.3 Hz, 2, Tp), 2.26 (s, 6, CH_3CN). ^{31}P NMR (CH_2Cl_2/CH_3CN): δ 52.4. ^{1}H NMR (CD_2Cl_2, selected data): δ 6.38 (bs, 1, Tp), 6.01 (t, *J*(H-H) = 2.4 Hz, 2, Tp), 2.27 (s, 6, C*H*$_3$CN). ^{31}P NMR (CD_2Cl_2): δ 49.0.

Preparation of [TpRu(PPr$^i_2$Me)(NCCH$_3$)$_2$]BAF

To a solution of TpRu(PPr$^i_2$Me)(CH$_3$CN)Cl (0.050 g, 0.096 mmol) in CH_2Cl_2/CH_3CN (0.9 mL/0.1 mL) was added LiBAF*Et$_2$O (0.073 g, 0.096 mmol). The resulting yellow solution was left for 1 day at ambient temperature. The solution was then filtered and the filtrate was evaporated affording [TpRu(PPr$^i_2$Me)(NCCH$_3$)$_2$]BAF as a yellow crystalline solid. Yield 100% (according to NMR data).

^{1}H NMR ($CDCl_3$): δ 7.75 (d, *J*(H-H) = 2.4 Hz, 2, Tp), 7.69 (bs, 1, Tp), 7.61 (bs, 1, Tp), 7.44 (d, *J*(H-H) = 1.8 Hz, 2, Tp), 6.27 (bs, 1, Tp), 6.22 (t, *J*(H-H) = 2.2 Hz, 2, Tp), 2.39 (s, 6, C*H*$_3$CN), 2.12 (m, 2, C*H*(CH$_3$)$_2$), 1.35 (d, *J*(P-H) = 7.6 Hz, 3, PC*H*$_3$), 1.14 (dd, *J*(H-H) = 7.0 Hz, *J*(P-H) = 13.1 Hz, 6, CH(C*H*$_3$)$_2$), 0.54 (dd, *J*(H-H) = 7.1 Hz, *J*(P-H) = 15.1 Hz, 6, CH(C*H*$_3$)$_2$). ^{31}P NMR ($CDCl_3$): δ 39.2. ^{13}C NMR ($CDCl_3$, selected data): δ 144.2 (Tp), 140.3 (Tp), 136.9 (Tp), 106.6 (Tp), 25.7 (*C*H(CH$_3$)$_2$), 16.2 (CH(*C*H$_3$)$_2$), 3.8 (*C*H$_3$CN). ^{1}H NMR (CD_2Cl_2, selected data): δ 6.35 (br s, 1, Tp), 6.29 (t, J(H-H) = 2.1 Hz, 2, Tp), 2.48 (s, 6, C*H*$_3$CN). ^{31}P NMR (CD_2Cl_2): δ 39.4

Preparation of TpRu(PPh$_3$)(CD$_3$CN)Cl

To a solution of $TpRu(PPh_3)(CH_3CN)Cl$ (0.025 g, 0.038 mmol) in CH_2Cl_2 (0.8 mL) was added CD_3CN (0.2 mL) and the reaction mixture was left overnight at ambient temperature. All the volatiles were then removed under vacuum affording $TpRu(PPh_3)(CD_3CN)Cl$ as a yellow crystalline solid. Yield 100% (as evidenced by NMR spectroscopy).

Preparation of [TpRu(PPh$_3$)(CH$_3$CN)(O=CHPh)]BAF

To a solution of $TpRu(PPh_3)(CH_3CN)Cl$ (0.025 g, 0.038 mmol) in CD_2Cl_2 (0.6 mL) was added PhCHO (7.8 μL, 0.076 mmol). Full conversion of the strating ruthenium complex with a selective formation of $[TpRu(PPh_3)(CH_3CN)(O=CHPh)]BAF$ was observed within 20 min at room temperature (as evidenced by NMR spectroscopy).

^1H NMR (CD_2Cl_2, selected data): δ 8.90 (s, 1, C*H*Ph), 6.89 (d, *J*(H-H) = 2.1 Hz, 1, Tp), 6.41 (d, *J*(H-H) = 2.1 Hz, 1, Tp), 6.37 (bt, 1, Tp), 6.05 (t, *J*(H-H) = 2.5 Hz, 1, Tp), 6.01 (t, *J*(H-H) = 2.2 Hz, 1, Tp), 2.29 (s, 3, C*H*$_3$CN). ^{31}P NMR (CD_2Cl_2): δ 49.7. ^{13}C NMR (CD_2Cl_2, selected data): δ 205.1 (*C*HPh), 146.5, 143.7, 107.1, 106.9, 106.8, 106.7 (all Tp), 4.0 (*C*H$_3$CN).

Preparation of [{TpRu(PPh$_3$)(CH$_3$CN)}$_2$Cl]BAF

To a solution of $TpRu(PPh_3)(CH_3CN)Cl$ (0.150 g, 0.230 mmol) in CH_2Cl_2 (50 mL) was added LiBAF*Et_2O (0.087 g, 0.114 mmol). Complex $[\{TpRu(PPh_3)(CH_3CN)\}_2Cl]BAF$ was obtained as the main compound (>70%) in a mixture of ruthenium complexes after filtration and removal of all the volatiles under vacuum.

^1H NMR (CD_2Cl_2, selected data): δ 7.98 (d, *J*(H-H) = 2.3 Hz, 2, Tp), 7.58 (d, *J*(H-H) = 2.3 Hz, 2, Tp), 7.50 – 7.10 (m, Ph), 6.73 (d, *J*(H-H) = 2.0 Hz, 2, Tp), 6.65 (d, *J*(H-H) = 2.0 Hz, 2, Tp), 6.07 (t, *J*(H-H) = 2.2 Hz, 2, Tp), 5.68 (t, *J*(H-H) = 2.2 Hz, 2, Tp), 5.49 (bs, 2, Tp), 5.30 (bs, 2, Tp), 2.12 (s, 6, C*H*$_3$CN). ^{31}P NMR (CD_2Cl_2): δ 45.9.

V.4.2 The syntheses of cationic silane σ-complexes

Preparation of [TpRu(PPh$_3$)(η^2-HSiH$_2$Ph)(CH$_3$CN)]BAF

To a solution of $TpRu(PPh_3)(CH_3CN)Cl$ (0.020 g, 0.030 mmol) in CD_2Cl_2 (0.6 mL) was added H_3SiPh (5.0 μL, 0.040 mmol) and LiBAF*Et_2O (0.035 g, 0.045 mmol),

which resulted in precipitation of LiCl and full conversion of the starting ruthenium complex with the formation of the target complex [TpRu(PPh_3)(η^2-$HSiH_2Ph$)(CH_3CN)]BAF.

^{1}H NMR (CD_2Cl_2): δ 8.0-7.0 (m, Ph), 6.40 (bs, 1, Tp), 6.26 (bs, 1, Tp), 6.00 (t, J(H-H) = 2.1 Hz, 1, Tp), 5.91 (t, J(H-H) = 2.1 Hz, 1, Tp), 4.95 (dd, J(H-H) = 3.4 Hz and 9.3 Hz, 1, Si*H*), 4.79 (dd, J(H-H) = 3.2 Hz and 9.3 Hz, 1, Si*H*), 2.16 (s, 3, C*H*$_3$CN), -11.82 (dt+sat, J(P-H) = 19.8 Hz, J(H-H) = 3.1 Hz, J(Si-H) = 86.0 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 46.5. ^{1}H-^{13}C HSQC (CD_2Cl_2, selected data): δ 145.9, 107.3, 107.1, 106.8 (all Tp), 3.8 (*C*H$_3$CN). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -24.4.

Preparation of [TpRu(PPr^i_2Me)(η^2-$HSiH_2Ph$)(CH_3CN)]BAF

To a solution of TpRu(PPr^i_2Me)(CH_3CN)Cl (0.020 g, 0.038 mmol) in CD_2Cl_2 (0.6 mL) was added H_3SiPh (9.4 μL, 0.076 mmol) and LiBAF*Et_2O (0.043 g, 0.057 mmol), which resulted in precipitation of LiCl and full conversion of the starting ruthenium complex with the formation of the target complex [TpRu(PPr^i_2Me)(η^2-$HSiH_2Ph$)(CH_3CN)]BAF.

^{1}H NMR (CD_2Cl_2): δ 7.88 (m, 3, Tp), 7.81 (d, *J*(H-H) = 2.2 Hz, 1, Tp), 7.73 (d, *J*(H-H) = 2.1 Hz, 1, Tp), 7.50-7.35 (m, 5, Ph), 7.09 (d, *J*(H-H) = 2.0 Hz, 1, Tp), 6.41 (bt, *J*(H-H) = 2.0 Hz, 1, Tp), 6.37 (t, *J*(H-H) = 2.2 Hz, 1, Tp), 6.20 (t, *J*(H-H) = 2.2 Hz, 1, Tp), 5.12 (dd, *J*(H-H) = 2.6 Hz, *J*(H-H) = 9.3 Hz, 1, Si*H*), 4.85 (dd, *J*(H-H) = 4.5 Hz, *J*(H-H) = 9.3 Hz, 1, Si*H*), 2.49 (s, 3, C*H*$_3$CN), 2.24 (m, 1, C*H*(CH$_3$)$_2$), 2.08 (m, 1, C*H*(CH$_3$)$_2$), 1.38 (d, *J*(P-H) = 8.3 Hz, 3, P*Me*), 1.14 (dd, J(H-H) = 7.0 Hz, *J*(P-H) = 14.1 Hz, 6, CH(C*H*$_3$)$_2$), 0.50 (dd, *J*(H-H) = 7.1 Hz, *J*(P-H) = 16.1 Hz, 3, CH(C*H*$_3$)$_2$), 0.45 (dd, *J*(H-H) = 7.1 Hz, *J*(H-H) = 16.0 Hz, 3, CH(C*H*$_3$)$_2$), -12.25 (ddd+sat, *J*(H-H) = 2.6 and 4.5 Hz, *J*(P-H) = 22.6 Hz, *J*(Si-H) = 82.4 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 40.2. ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 146.4 (Tp), 143.4 (Tp), 137.7 (Tp) 137.4 (Tp), 107.5 (Tp), 107.0 (Tp), 26.7 (*C*H(CH$_3$)$_2$), 25.2 (*C*H(CH$_3$)$_2$), 16.4 (CH(*C*H$_3$)$_2$), 15.2 (CH(*C*H$_3$)$_2$), 6.3 (P*Me*), 3.7 (*C*H$_3$CN). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -24.8.

Preparation of [TpRu(PPr^i_2Me)(η^2-HSiHMePh)(CH_3CN)]BAF

To a solution of TpRu(PPr^i_2Me)(CH_3CN)Cl (0.020 g, 0.038 mmol) in CD_2Cl_2 (0.6 mL) was added $H_2SiMePh$ (10 μL, 0.076 mmol) and LiBAF*Et_2O (0.058 g, 0.076 mmol), which resulted in precipitation of LiCl and full conversion of the starting ruthenium complex with the formation of the target complex [TpRu(PPr^i_2Me)(η^2-

HSiHMePh)(CH_3CN)]BAF (>70% from NMR spectroscopy data) as a mixture of diastereomers (3:1).

Major diastereomer (selected data):

^{1}H NMR (CD_2Cl_2): δ 6.42 (bt, *J*(H-H) = 2.2 Hz, 1, Tp), 6.36 (t, *J*(H-H) = 2.2 Hz, 1, Tp), 6.34 (t, *J*(H-H) = 2.2 Hz, 1, Tp), 5.68 (dq, *J*(H-H) = 3.3 Hz and 8.3 Hz, 1, SiH), 2.53 (s, 3, CH3CN), -0.24 (dd, *J*(H-H) = 3.3 Hz and 1.5 Hz, 3, SiMe), -13.09 (ddq+sat, *J*(P-H) = 19.6 Hz, *J*(H-H) = 8.3 Hz and 1.5 Hz, *J*(Si-H) = 83 Hz, 1, SiH). ^{31}P NMR (CD_2Cl_2): δ 39.1. ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 107.1 (Tp), 106.8 (Tp), 106.7 (Tp), 4.07 (CH3CN), -4.36 (SiMe). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -6.1.

Minor diastereomer (selected data):

^{1}H NMR (CD_2Cl_2): δ 4.96 (dq, *J*(H-H) = 3.5 Hz, 1, SiH), 1.60 (bs, 3, SiMe), -13.37 (bd, *J*(P-H) = 19.7 Hz). ^{31}P NMR (CD_2Cl_2): δ 39.2. ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -11.6.

V.4.3 The syntheses of cationic agostic silane complexes

Preparation of [TpRu(PPh_3)(H_2PhSiN=$CHCH_3$)]BAF

To a solution of TpRu(PPh_3)(CH_3CN)Cl (0.020 g, 0.030 mmol) in CD_2Cl_2 (0.6 mL) was added H_3SiPh (0.006 mL, 0.048 mmol) and LiBAF*Et_2O (0.023 g, 0.030 mmol), which resulted in precipitation of LiCl and full conversion of the starting ruthenium complex with the formation of [TpRu(PPh_3)(H_2PhSiN=$CHCH_3$)]BAF (2 diastereomers 14:86) in a mixture with [TpRu(PPh_3)($NCCH_3$)$_2$]BAF after 10 min at room temperature.

Major diastereomer:

^{1}H NMR (CD_2Cl_2, selected data): δ 8.10 (q, *J*(H-H) = 5.2 Hz, 1, C*H*=N), 5.18 (1, Si*H*), 2.54 (d, *J*(H-H) = 5.2 Hz, 3, CHC*H*$_3$), -9.95 (dd+sat, *J*(P-H) = 10.5 Hz, *J*(H-H) = 6.8 Hz, *J*(Si-H) = 91.8 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 48.0. ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -33.6.

Preparation of [TpRu(PPh_3)(HMePhSiN=$CHCH_3$)]BAF

To a solution of TpRu(PPh_3)(CH_3CN)Cl (0.015 g, 0.023 mmol) and H_2SiMePh (63 μL, 0.46 mmol) in CD_2Cl_2 (0.6 mL) was added LiBAF*Et_2O (0.017 g, 0.023 mmol), which resulted in precipitation of LiCl and full conversion of the starting ruthenium complex with the formation of two diastereomers of [TpRu(PPh_3)(HMePhSiN=$CHCH_3$)]BAF (2:3 ratio) in a mixture with

[TpRu(PPh_3)($NCCH_3$)$_2$]BAF and other minor impurities after 20 min at room temperature.

Minor diastereomer:

^{1}H NMR (CD_2Cl_2, selected data): δ 8.72 (q, *J*(H-H) = 5.0 Hz, 1, C*H*=N), 2.67 (d, *J*(H-H) = 5.0 Hz, 3, CHC*H*$_3$), -10.67 (dq+sat, *J*(P-H) = 11.4 Hz, *J*(H-H) = 1.7 Hz, *J*(Si-H) = 98.8 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 46.4. ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -27.4.

Major diastereomer:

^{1}H NMR (CD_2Cl_2, selected data): δ 8.27 (q, *J*(H-H) = 4.9 Hz, 1, C*H*=N), 2.66 ((d, *J*(H-H) = 4.9 Hz, 3, CHC*H*$_3$), -10.51 (dq+sat, *J*(P-H) = 10.7 Hz, *J*(H-H) = 1.6 Hz, *J*(Si-H) = 95.2 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 48.3. ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -18.1.

The reaction of [TpRu(PPr^i_2Me)(CH_3CN)(η^2-H-SiH_2Ph)]BAF with TpRu(PPh_3)(CH_3CN)Cl

To a solution of [TpRu(PPr^i_2Me)(CH_3CN)(η^2-H-SiH_2Ph)]BAF (generated from TpRu(PPr^i_2Me)(CH_3CN)Cl (0.020 g, 0.038 mmol)) in CD_2Cl_2 (0.6 mL) was added TpRu(PPh_3)(CH_3CN)Cl (0.025 g, 0.038 mmol). The formation of agostic complexes [TpRu(PPh_3)(H_2PhSiN=$CHCH_3$)]BAF and [TpRu(PPr^i_2Me)(H_2PhSiN=$CHCH_3$)]BAF (6:1 ratio) was observed by NMR spectroscopy.

The reaction of [TpRu(PPh_3)(CH_3CN)(η^2-H-SiH_2Ph)]BAF with TpRu(PPr^i_2Me)(CH_3CN)Cl

To a solution of [TpRu(PPh_3)(CH_3CN)(η^2-H-SiH_2Ph)]BAF, which was generated by the reaction of TpRu(PPh_3)(CH_3CN)Cl (0.015 g, 0.023 mmol), H_3SiPh (5.6 μL, 0.046 mmol), and LiBAF*Et_2O (0.026 g, 0.034 mmol) in CD_2Cl_2 (0.6 mL), was added complex TpRu(PPr^i_2Me)(CH_3CN)Cl (0.018 g, 0.034 mmol). The formation of agostic complexes [TpRu(PPh_3)(H_2PhSiN=$CHCH_3$)]BAF and [TpRu(PPr^i_2Me)(H_2PhSiN=$CHCH_3$)]BAF (8:1 ratio) was observed by NMR spectroscopy.

The reaction of [TpRu(PPh_3)(CH_3CN)(η^2-H-SiH_2Ph)]BAF with TpRu(PPh_3)(CD_3CN)Cl

To a solution of [TpRu(PPh_3)(CH_3CN)(η^2-H-SiH_2Ph)]BAF, which was generated by the reaction of TpRu(PPh_3)(CH_3CN)Cl (0.020 g, 0.030 mmol), H_3SiPh (5.7 μL, 0.046 mmol), and LiBAF*Et_2O (0.026 g, 0.034 mmol) in CD_2Cl_2 (0.6 mL), was added TpRu(PPh_3)(CD_3CN)Cl (0.022 g, 0.034 mmol). According to NMR data, about 50% of the resulting agostic complex contained deuterated silylimino group.

The reaction of [TpRu(PPr^i_2Me)(CH_3CN)(η^2-H-SiH_2Ph)]BAF with TpRu(PPh_3)(CD_3CN)Cl

To a solution of complex [TpRu(PPr^i_2Me)(CH_3CN)(η^2-H-SiH_2Ph)]BAF, which was prepared by the reaction of TpRu(PPr^i_2Me)(CH_3CN)Cl (0.020 g, 0.038 mmol), H_3SiPh (9.4 μL, 0.075 mmol), and LiBAF*Et_2O (0.032 g, 0.042 mmol) in CD_2Cl_2 (0.6 mL), was added TpRu(PPh_3)(CD_3CN)Cl (0.025 g, 0.038 mmol). The formation of agostic complexes [TpRu(PPh_3)($H_2PhSiN{=}CHCD_3$)]BAF and [TpRu(PPr^i_2Me)($H_2PhSiN{=}CHCH_3$)]BAF (4:1 ratio) was observed by NMR spectroscopy.

The reaction of [TpRu(PPh_3)($H_2PhSiN{=}CHCH_3$)]BAF with benzaldehyde

To a solution of [TpRu(PPh_3)($H_2PhSiN{=}CHCH_3$)]BAF (0.030 g, 0.021 mmol) in CD_2Cl_2 (0.6 mL) was added PhCHO (4.4 μL, 0.042 mmol). Full conversion of the starting ruthenium complex was observed within 4 h at room temperature with the formation of [TpRu(PPh_3)(HPhSi(OCH_2Ph)N=$CHCH_3$)]BAF and, presumably, [TpRu(PPh_3)($O{=}CHPh)_2$]BAF as major products of the reaction. The latter complex decomposed into a mixture of unidentified compounds after 24 h at room temperature.

[TpRu(PPh_3)(HPhSi(OCH_2Ph)N=$CHCH_3$)]BAF(selected data):

^{1}H NMR (CD_2Cl_2): δ 8.03 (q, *J*(H-H) = 4.9 Hz, 1, C*H*=N), 4.20 (d, *J*(H-H) = 11.7 Hz, 1, OCH_2), 3.84 (d, *J*(H-H) = 11.7 Hz, 1, OCH_2), 2.39 (d, *J*(H-H) = 4.9 Hz, 3, CHCH_3), -10.40 (d+sat, *J*(P-H) = 11.3 Hz, *J*(Si-H) = 112 Hz, 1, Si*H*). ^{31}P NMR (CD_2Cl_2): δ 47.3. ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 67.4 (O*C*H_2), 30.3 (CH*C*H_3). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ -33.2.

[TpRu(PPh_3)($O{=}CHPh)_2$]BAF:

^{1}H NMR (CD_2Cl_2, selected data): δ 9.15 (s, 2, O=C*H*Ph). ^{31}P NMR (CD_2Cl_2): δ 51.1.

V.5. *The catalytic reactions mediated by* $[CpRu(PPr^i_3)(CH_3CN)_2]^+$

V.5.1 Hydrosilylation of carbonyls

Reactions in solvents

Hydrosilylation of PhCHO with H_3SiPh

To a solution of H_3SiPh (20 μL, 0.16 mmol) and PhCHO (17 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (7 mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 20h at room temperature.

$(PhCH_2O)_2SiHPh$:

^1H NMR ($CDCl_3$): δ 7.80-7.70, 7.50-7.30 (m, 15, Ph), 5.13 (s, 1, SiH), 4.88 (s, 4, PhCH_2O).

Hydrosilylation of PhCHO with $HSiEt_3$

To a solution of $HSiEt_3$ (37 μL, 0.25 mmol) and PhCHO (17 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (2 mg , 3% mol). The reaction mixture was heated at 50°C for 36 h. The reaction was periodically monitored by NMR spectroscopy. About 82% conversion was achieved after 36 h at 50°C.

$PhCH_2OSiEt_3$:

^1H NMR ($CDCl_3$): δ 7.20-7.40 (m, 5, Ph), 4.75 (s, 2, PhCH_2), 0.99 (t, *J*(H-H) = 8.1 Hz, 9, $SiCH_2CH_3$), 0.65 (q, *J*(H-H) = 8.1 Hz, 6, $SiCH_2CH_3$).

Hydrosilylation of PhCHO with $H_2SiMePh$

To a solution of $H_2SiMePh$ (27 μL, 0.20 mmol) and PhCHO (20 μL, 0.20 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (5.4 mg , 5% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 20 h at room temperature.

$PhCH_2OSiHMePh$:

^1H NMR ($CDCl_3$): δ 7.70-7.65 (m, 2, Ph), 7.50-7.30 (m, 8, Ph), 5.10 (q, *J*(H-H) = 2.7 Hz, 1, Si*H*), 4.76 (s, 2, CH_2O), 0.50 (d, *J*(H-H) = 2.7 Hz, 3, Si*Me*).

Hydrosilylation of PhCHO with $HSiMe_2Ph$

To a solution of $HSiMe_2Ph$ (50 μL, 0.36 mmol) and PhCHO (25 μL, 0.25 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (4 mg , 5% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 30 min at room temperature.

$PhCH_2OSiMe_2Ph$:

^1H NMR ($CDCl_3$): δ 7.63 (m, 2, Ph), 7.45-7.20 (m, 8, Ph), 4.72 (s, 2, CH_2O), 0.43 (s, 6, Si*Me*). ^1H-^{13}C HSQC ($CDCl_3$, selected data): δ 133.5, 129.6, 128.5, 127.9, 126.5 (all Ph), 64.9 (CH_2O), -1.8 (Si*Me*). ^1H-^{29}Si HSQC ($CDCl_3$): δ 8.8.

Hydrosilylation of $PhC(O)CH_3$

To a solution of $HSiMe_2Ph$ (20 μL, 0.13 mmol) and $PhC(O)CH_3$ (15 μL, 0.13 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (3.7 mg , 5% mol). The reaction was periodically monitored by NMR spectroscopy. About 30% conversion was achieved after 24h at room temperature.

$PhCH(OSiMe_2Ph)CH_3$:

^1H NMR ($CDCl_3$): δ 7.70-7.30 (m, 10, Ph), 4.90 (q, *J*(H-H) = 6.3 Hz, 1, PhC*H*OSi), 1.46 (d, *J*(H-H) = 6.3 Hz, 3, $CHCH_3$), 0.38 (s, 3, Si*Me*), 0.33 (s, 3, Si*Me*).

Hydrosilylation of cyclohexanone

To a solution of $HSiMe_2Ph$ (33 μL, 0.24 mmol) and cyclohexanone (25 μL, 0.24 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (4 mg , 5% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 18h at room temperature.

$C_6H_{11}OSiMe_2Ph$:

^1H NMR ($CDCl_3$): δ 7.70-7.55 (m, Ph), 7.45-7.35 (m, Ph), 3.66 (m, 1, C*H*OSi), 1.79 (m, 4, CH_2CHOSi), 1.60-1.20 (m, 6, CH_2CH_2CHOSi), 0.43 (s, 6, Si*Me*).

Hydrosilylation of $CH_3C(O)Et$

To a solution of $HSiMe_2Ph$ (25 μL, 0.16 mmol) and butanone (15 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (5 mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. About 11% conversion was achieved after 20h at room temperature.

$CH_3CH(OSiMe_2Ph)Et$:

^{1}H NMR ($CDCl_3$): δ 7.70-7.60 (m, 2, Ph), 7.45-7.35 (m, 3, Ph), 3.75 (dq, *J*(H-H) = 12.3 Hz, *J*(H-H) = 6.2 Hz, 1, C*H*OSi), 1.46 (m, 2, CH_2), 1.12 (d, *J*(H-H) = 6.23 Hz, 3, CH_3CHO), 0.86 (t, *J*(H-H) = 7.4 Hz, 3, CH_2CH_3), 0.40 (s, 3, Si*Me*).

Hydrosilylation of $CH_3C(O)OEt$

To a solution of $HSiMe_2Ph$ (25 μL, 0.16 mmol) and $CH_3C(O)OEt$ (16 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (7mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion of silane was achieved after 24h at room temperature.

$CH_3CH_2OSiMe_2Ph$:

^{1}H NMR ($CDCl_3$): δ 7.60-7.55 (m, 2, Ph), 7.40 – 7.35 (m, 3, Ph), 3.68 (q, *J*(H-H) = 7.14 Hz, 2, CH_3CH_2), 1.19 (t, *J*(H-H) = 7.14 Hz, 3, CH_3CH_2), 0.39 (s, 6, Si*Me*).

Reactions under solvent free conditions

Hydrosilylation of PhCHO

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol) and PhCHO (66 μL, 0.65 mmol). Full conversion of silane with the formation of $PhCH_2OSiMe_2Ph$ was observed after 30 min at room temperature. Yield 100% (according to NMR spectra).

Hydrosilylation of $PhC(O)CH_3$

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol) and $PhC(O)CH_3$ (76 μL, 0.65 mmol). Complete conversion of silane with the formation of $PhCH(OSiMe_2Ph)CH_3$ (44 %), $PhC(OSiMe_2Ph)=CH_2$ (46 %) and $PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$ (10 %) was observed after 24 h at room temperature. The use of complex [CpRu(PPh_3)(CH_3CN)$_2$]BAF as a catalyst gave a mixture of $PhCH(OSiMe_2Ph)CH_3$ (4 %), $PhC(OSiMe_2Ph)=CH_2$ (76 %) and $PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$ (20 %).

$PhC(OSiMe_2Ph)=CH_2$:

^{1}H NMR ($CDCl_3$, selected data): δ 4.91 (d, *J*(H-H) = 1.7 Hz, 1, CH_2), 4.40 (d, *J*(H-H) = 1.7 Hz, 1, CH_2), 0.56 (s, 6, SiMe_2). ^{1}H-^{13}C HSQC ($CDCl_3$, selected data): δ 91.5 (CH_2), -1.4 (SiMe_2).

$PhC(CH_3)(OSiMe_2Ph)CH_2C(O)Ph$:

^{1}H NMR ($CDCl_3$, selected data): δ 3.63 (d, *J*(H-H) = 13.5 Hz, 1, C*H*$_2$), 3.15 (d, *J*(H-H) = 13.5 Hz, 1, C*H*$_2$), 1.84 (s, 3, C*H*$_3$).

Hydrosilylation of $CH_3C(O)CH_3$

Complex [CpRu(PPr$^i_3$)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol) and $CH_3C(O)CH_3$ (66 μL, 0.65 mmol). Full conversion of acetone with the formation of $(CH_3)_2CHOSiMe_2Ph$ (84%) and $CH_3C(OSiMe_2Ph)=CH_2$ (16%) was observed after 48 h at room temperature.

$(CH_3)_2CHOSiMe_2Ph$:

^{1}H NMR ($CDCl_3$): δ 7.60-7.55 (m, 2, Ph), 7.40-7.33 (m, 3, Ph), 3.98 (m, *J*(H-H) = 6.0 Hz, 2, i-*Pr*), 1.13 (d, *J*(H-H) = 6.0 Hz, 12, i-*Pr*), 0.37 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC ($CDCl_3$, selected data): δ 65.2 (*C*H(CH$_3$)$_2$), 25.7 (CH(*C*H$_3$)$_2$), -1.2 (Si*Me*$_2$).

$CH_3C(OSiMe_2Ph)=CH_2$:

^{1}H NMR ($CDCl_3$, selected data): δ 4.07 (br s, 1, C*H*$_2$), 4.05 (br s, 1, C*H*$_2$), 1.80 (s, 6, C*H*$_3$), 0.50 (s, 6, Si*Me*$_2$). ^{1}H-^{13}C HSQC ($CDCl_3$, selected data): δ 91.7 (*C*H$_2$), -1.3 (Si*Me*$_2$).

Hydrosilylation of PhC(O)Ph

Complex [CpRu(PPr$^i_3$)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol), PhC(O)Ph (119 mg, 0.65 mmol) and PhCl (66 μL, 0.65). Full conversion of silane with the formation of $Ph_2CHOSiMe_2Ph$ was observed after 24 h at room temperature.

$Ph_2CHOSiMe_2Ph$:

^{1}H NMR ($CDCl_3$, selected data): δ 5.77 (s, 1, C*H*), 0.31 (s, 6, Si*Me*$_2$).

Hydrosilylation of p-$NO_2(C_6H_4)C(O)CH_3$

Complex [CpRu(PPr$^i_3$)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol), p-$NO_2(C_6H_4)C(O)CH_3$ (108 mg, 0.65 mmol) and PhCl (132 μL, 1.30 mmol). Full conversion of silane with the formation of *p*-$NO_2(C_6H_4)CH(OSiMe_2Ph)CH_3$ (50 %) and *p*-$NO_2(C_6H_4)C(OSiMe_2Ph)=CH_2$ (50%) was observed after 24 h at room temperature.

p-$NO_2(C_6H_4)CH(OSiMe_2Ph)CH_3$:

^{1}H NMR ($CDCl_3$, selected data): δ 4.95 (q, *J*(H-H) = 6.4 Hz, 1, C*H*), 1.45 (d, *J*(H-H) = 6.4 Hz, 3, C*H*$_3$), 0.59 (s, 3, Si*Me*), 0.43 (s, 3, Si*Me*).

p-$NO_2(C_6H_4)C(OSiMe_2Ph)=CH_2$:

^{1}H NMR ($CDCl_3$, selected data): δ 5.07 (d, *J*(H-H) = 2.4 Hz, 1, C*H*$_2$), 4.58 (d, *J*(H-H) = 2.4 Hz, 1, C*H*$_2$), 0.37 (s, 6, Si*Me*$_2$).

Hydrosilylation of $Pr^iC(O)Pr^i$

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol) and $Pr^iC(O)Pr^i$ (92 μL, 0.65 mmol). Full conversion of silane with the formation of $(Pr^i)_2CHOSiMe_2Ph$ was observed after 24 h at room temperature.

$(Pr^i)_2CHOSiMe_2Ph$:

^{1}H NMR ($CDCl_3$, selected data): δ 3.18 (t, *J*(H-H) = 5.4 Hz, 1, C*H*O$SiMe_2Ph$), 1.78 (m, 2, C*H*(CH_3)$_2$), 0.89 (d, 6, CH(C*H*$_3$)$_2$), 0.85 (d, 6, CH(C*H*$_3$)$_2$), 0.42 (s, 6, Si*Me*$_2$).

Hydrosilylation of PhCH=CHCHO

Complex [CpRu(PPr^i_3)(CH_3CN)$_2$]BAF (5 mg, 0.7% mol) was dissolved in a mixture of $HSiMe_2Ph$ (100 μL, 0.65 mmol) and PhCH=CHCHO (82 μL, 0.65 mmol). Complex mixture of products was obtained after 24 h at room temperature (60% of silane was consumed).

V.5.2 Dehydrogenative coupling reactions

The reaction with CH_3CH_2OH

To a solution of $HSiEt_3$ (25 μL, 0.16 mmol) and CH_3CH_2OH (9.1 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr^i_3)(CH_3CN)$_2$]PF_6 (4 mg , 5% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 50h at room temperature.

$CH_3CH_2OSiEt_3$:

^{1}H NMR ($CDCl_3$): δ 3.65 (q, *J*(H-H) = 7.2 Hz, 2, C*H*$_2$), 1.15 (t, *J*(H-H) = 7.2 Hz, 3, C*H*$_3$), 0.93 (t, *J*(H-H) = 8.5 Hz, 9, Si*Et*), 0.57 (q, *J*(H-H) = 8.5 Hz, 6, Si*Et*).

The reaction with *i*-PrOH

To a solution of $HSiMe_2Ph$ (25 μL, 0.16 mmol) and *i*-PrOH (12 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr^i_3)(CH_3CN)$_2$]PF_6 (5 mg , 4% mol). The

reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 30 min at room temperature with the formation of *i*-PrOSiMe$_2$Ph.

The reaction with *t*-BuOH

To a solution of HSiMe$_2$Ph (25 μL, 0.16 mmol) and *t*-BuOH (15 mg, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (5 mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 1h at room temperature.

t-BuOSiMe$_2$Ph:

^{1}H NMR ($CDCl_3$): δ 7.62-7.57 (m, 2, Ph), 7.37-7.32 (m, 3, Ph), 1.25 (s, 9, t-*Bu*), 0.38 (s, 6, Si*Me*).

The reaction with PhOH

To a solution of HSiMe$_2$Ph (25 μL, 0.16 mmol) and PhNH$_2$ (15 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (5 mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 30 min at room temperature.

PhOSiMe$_2$Ph:

^{1}H NMR ($CDCl_3$): δ 7.65-7.60 (m, 2, Ph), 7.44-7.36 (m, 3, Ph), 7.22-7.15 (m, 2, Ph), 6.97-6.90 (m, 1, Ph), 6.84-6.79 (m, 2, Ph), 0.52 (s, 6, Si*Me*).

The reaction with PhNH$_2$

To a solution of HSiMe$_2$Ph (25 μL, 0.16 mmol) and PhNH$_2$ (15 μL, 0.16 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (5 mg , 4% mol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 10 min at room temperature.

PhNHSiMe$_2$Ph:

^{1}H NMR ($CDCl_3$): δ 7.70 -7.60 (m, 2, Ph), 7.45-7.35 (m, 3, Ph), 7.15-7.05 (m, 2, Ph), 6.75-6.60 (m, 3, Ph), 3.67 (s, 1, N*H*), 0.52 (s, 6, Si*Me*).

The reaction with PhCOOH

To a solution of HSiMe$_2$Ph (12 μL, 0.08 mmol) and PhCOOH (10 μL, 0.08 mmol) in $CDCl_3$ (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (2 mg , 5% mol). The

reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after about 20 min at room temperature.

$PhCOOSiMe_2Ph$:

^{1}H NMR (CD_2Cl_2): δ 8.10-8.05 (m, 2, Ph), 7.75-7.70 (m, 2, Ph), 7.45-7.35 (m, 6, Ph), 0.69 (s, 6, Si*Me*).

V.5.3 Hydrosilylation of nitriles

Hydrosilylation of acetonitrile

Method 1. Catalyst $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.0057 g, 4% mol) was added to a solution of $HSiMe_2Ph$ (21 μL, 0.14 mmol) and acetonitrile (7 μL, 0.13 mmol) in acetone-d_6. After 20 min at ambient temperature, 100% conversion of acetonitrile was achieved (the content of $CH_3CH{=}NSiMe_2Ph$ in the reaction mixture - 90%). After 17 h, the coupling product $H_3CC(H){=}NC(H)(CH_3)N(SiMe_2Ph)_2$ became the dominant product (60%).

Method 2. Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.0045 g, 4% mol) was added to a solution of $HSiMe_2Ph$ (32 μL, 0.20 mmol) and acetonitrile (10 μL, 0.19 mmol) in acetone-d_6. After 10 min at ambient temperature 100% of the silane was consumed and 90% conversion of acetonitrile was achieved (the content of $CH_3CH{=}NSiMe_2Ph$ in the reaction mixture: 87%). After 8 h, the coupling product $H_3CC(H){=}NC(H)(CH_3)N(SiMe_2Ph)_2$ became the dominant product (80% in the reaction mixture).

Method 3. Catalyst $CpRu(PPr^i_3)(CH_3CN)_2BF_4$ (0.0026 g, 4% mol) was added to a solution of $HSiMe_2Ph$ (21 μL, 0.14 mmol) and acetonitrile (7 μL, 0.13 mmol) in acetone-d_6. After 1 h at ambient temperature, 100% of acetonitrile was consumed (the content of $CH_3CH{=}NSiMe_2Ph$ in the reaction mixture: 87%).

Method 4. (*reaction without solvent*). Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.003 g, 0.4% mol) was added to a mixture of $HSiMe_2Ph$ (200 μL, 1.3 mmol) and acetonitrile (70 μL, 1.3 mmol). After 23 h at ambient temperature, 95% of acetonitrile was converted into the coupling product $H_3CC(H){=}NC(H)(CH_3)N(SiMe_2Ph)_2$ (60%), $H_3C(H)C{=}NSiMe_2Ph$ (10%) and other products.

$CH_3(H)C{=}NSiMe_2Ph$:

^{1}H NMR (acetone-d_6): δ 8.51 (q, *J*(H-H) = 3.8 Hz, 1, C*H*=N), 7.60-7.55 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 2.02 (d, *J*(H-H) =3.8 Hz, 3, CH_3), 0.38 (s, 6, Si*Me*).

CH_3(H)C=NCH(CH_3)N($SiMe_2Ph)_2$:

^{1}H NMR (acetone-d_6): δ 7.65-7.55 and 7.40-7.30 (m, Ph), 7.26 (q, *J*(H-H) = 4.4 Hz, 1, CH_3C*H*=N), 4.45 (q, *J*(H-H) = 6.0 Hz, 1, C*H*(CH_3)NSi), 1.77 (d, *J*(H-H) = 4.4 Hz, 3, CH_3CH=N), 1.28 (d, *J*(H-H) = 6.0 Hz, 3, NCH(CH_3)NSi), 0.40-0.30 (s, Si*Me*).

Hydrosilylation of benzonitrile

Method 1. The reaction was performed in $CDCl_3$ with benzonitrile (16.6 μL, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g , 4% mol). After 4 h at ambient temperature, 100% conversion of the starting nitrile was observed.

Method 2. Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.0086 g, 5% mol) was added to a solution of $HSiMe_2Ph$ (47 μL, 0.30 mmol) and benzonitrile (30 μL, 0.29 mmol) in acetone-d_6. After 1 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

Method 3 (reaction without solvent). Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.0058 g, 1% mol) was added to a mixture of $HSiMe_2Ph$ (150 μL, 0.98 mmol) and benzonitrile (100 μL, 0.98 mmol). After 24 h at ambient temperature 100% of benzonitrile was cleanly converted into the silylimine. The product was extracted with hexane followed by removal of all volatiles under vacuum. Yield 95%.

PhCH=N($SiMe_2Ph$):

^{1}H NMR ($CDCl_3$): δ 8.95 (s, 1, C*H*=N), 7.85-7.80 (m, 2, Ph), 7.50-7.40 (m, 6, Ph), 0.57 (s, 6, Si*Me*).

Hydrosilylation of 3-pentenenitrile

The reaction was performed in $CDCl_3$ with 3-pentenenitrile (15.7 μL, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g , 4% mol). After 2.5 h at ambient temperature 100% conversion of the starting nitrile was observed. Long exposure of the reaction mixture to the ruthenium catalyst should be avoided due to slow decomposition/isomerization of the silylimine.

$CH_3CH=CH-CH_2CH=N(SiMe_2Ph)$:

^{1}H NMR ($CDCl_3$): δ 8.27 (t, *J*(H-H) = 4.4 Hz, 1, C*H*=N), 7.55-7.50 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 5.55-5.50 (m, 2, C*H*=C*H*), 3.01 (m, 2, CH_2), 1.69 (d, 3, CH_3), 0.45 (s, 6, Si*Me*).

Hydrosilylation of trimethylacetonitrile

The reaction was performed in $CDCl_3$ with trimethylacetonitrile (18.0 μL, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g , 4% mol). After 2 days at ambient temperature, 7% conversion of the starting nitrile was observed. The reaction mixture was then heated up to 50°C. After 24 h at 50°C, 14% conversion of the starting nitrile was achieved.

$(CH_3)_3CCH=N(SiMe_2Ph)$:

^{1}H NMR ($CDCl_3$): δ 8.28 (s, 1, C*H*=N), 7.55-7.50 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 1.03 (s, 9, CH_3), 0.40 (s, 6, Si*Me*).

Hydrosilylation of isobutyronitrile

Method 1. The reaction was performed in $CDCl_3$ with isobutyronitrile (14.6 μL, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g , 4% mol). After 2 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

Method 2. Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.054 g, 1.5% mol) was loaded in air into a 100 mL round-bottom flask. The flask was purged with nitrogen and was charged with 30 mL of CH_2Cl_2. The isobutyronitrile (0.6 mL, 6.7 mmol) was added followed by $HSiMe_2Ph$ (1.1 mL, 7.1 mmol). It is important to add reagents in this order as the complex decomposes by excess silane. The reaction mixture was stirred for 3 h at ambient temperature. Then hexane (30 mL) was added, and the yellow solution became cloudy. The volume was reduced to 30 mL under reduced pressure, which led to precipitation of the catalyst as a brown oil. The yellow solution was decanted from the precipitate and distilled under reduced pressure. Yield of imine: 1.2 g (86%).

Method 3 (*reaction without solvent*). Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.018 g, 1% mol) was added to a mixture of $HSiMe_2Ph$ (0.5 mL, 3.2 mmol) and isobutyronitrile (0.3 mL, 3.2 mmol). After 24 h at ambient temperature, 100% conversion of the starting nitrile was achieved. Catalyst precipitates at the end of reaction in the form of brown oil.

$(CH_3)_2CHCH=N(SiMe_2Ph)$:

^{1}H NMR ($CDCl_3$): δ 8.24 (d, *J*(H-H) = 4.4 Hz, 1, C*H*=N), 7.55-7.50 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 2.37 (m, 1, C*H*), 1.07 (d, ^{3}*J*(H-H) = 6.6 Hz, 6, CH_3), 0.44 (s, 6, Si*Me*).

Hydrosilylation of 5-hexynenitrile

The reaction was performed in $CDCl_3$ with 5-hexynenitrile (17.0 μL, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g , 4% mol). After 7 days at ambient temperature, 40% conversion of the starting nitrile was achieved .

$PhMe_2SiCH=CH(CH_2)_3CN$:

^{1}H NMR ($CDCl_3$, selected NMR data): δ 5.73 (m, 1, =C*H*CH_2), 5.52 (d, *J*(H-H) = 2.19 Hz, 1, $PhMe_2SiCH$=), 2.21 (t, *J*(H-H) = 7.13 Hz, 2, CH_2CN), 1.67 (m, 2, CH_2CH_2CN), 0.40 (s, 6, Si*Me*).

Hydrosilylation of 4-acetylbenzonitrile

The reaction was performed in $CDCl_3$ with 4-acetylbenzonitrile (0.023 g, 0.16 mmol), $HSiMe_2Ph$ (37 μL, 0.24 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (7 mg, 4% mol). After 8 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

p-$CH_3C(O)(C_6H_4)CH=N(SiMe_2Ph)$:

^{1}H NMR ($CDCl_3$): δ 8.98 (s, 1, C*H*=N), 8.03 (d, *J*(H-H) = 8.24 Hz, 2, Ph), 7.92 (d, *J*(H-H) = 8.24 Hz, 2, Ph), 7.55-7.50 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 2.65 (s, 3, CH_3), 0.58 (s, 6, Si*Me*).

Hydrosilylation of 4-formylbenzonitrile

The reaction was performed in $CDCl_3$ with 4-formylbenzonitrile (21.4 mg, 0.16 mmol), $HSiMe_2Ph$ (30 μL, 0.18 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 4% mol). After 14 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

p-$OHC(C_6H_4)CH=N(SiMe_2Ph)$:

^{1}H NMR ($CDCl_3$): δ 10.08 (s, 1, C*H*O), 8.98 (s, 1, C*H*=N), 7.96 (d, *J*(H-H) = 2.2 Hz, 4, C_6H_4), 7.65-7.60 (m, 2, Ph), 7.45-7.40 (m, 3, Ph), 0.58 (s, 6, Si*Me*).

Hydrosilylation of 3-nitrobenzonitrile

Method 1. The reaction was performed in $CDCl_3$ with 3-nitrobenzonitrile (24.0 mg, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 4% mol). After 20 h at ambient temperature, 83% conversion of the starting nitrile was achieved .

Method 2. The reaction was performed in acetone-d_6 with 3-nitrobenzonitrile (50.0 mg, 0.34 mmol), $HSiMe_2Ph$ (55 μL, 0.36 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.010 mg, 5% mol). After 4 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

m-$O_2N(C_6H_4)CH=N(SiMe_2Ph)$:

^1H NMR ($CDCl_3$): δ 8.94 (s, 1, C*H*=N), 8.64 (m, 1, C_6H_4), 8.29 (m, 1, C_6H_4), 8.14 (m, 1, C_6H_4), 7.65-7.60 (m, 2, Ph), 7.45-7.40 (m, 3, Ph), 0.57 (s, 6, Si*Me*).

IR (neat, cm^{-1}): 1658 (C=N), 1529 and 1349 (NO_2).

Hydrosilylation of 3-pyridinecarbonitrile

The reaction was performed in $CDCl_3$ with 3-pyridinecarbonitrile (0.017 g, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 4% mol). After 14 h at ambient temperature, 68% conversion of the starting nitrile was achieved.

3-($PhMe_2SiN=CH$-)pyridine:

^1H NMR ($CDCl_3$): δ 8.94 (s, 1, C*H*=N), 8.92 (d, 1, *J*(H-H) = 1.65 Hz, Py), 8.69 (dd, *J*(H-H) = 4.94 Hz, *J*(H-H) = 2.19 Hz, 1, Py), 8.19 (dt, *J*(H-H) = 8.23 Hz, *J*(H-H) = 1.65 Hz, 1, Py), 7.70-7.60 (m, 2, Ph), 7.50-7.40 (m, 3, Ph), 0.55 (s, 6, Si*Me*).

Hydrosilylation of acrylonitrile

The reaction was performed in $CDCl_3$ with acrylonitrile (6.4 μL, 0.10 mmol), $HSiMe_2Ph$ (16 μL, 0.11 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.004 g , 4% mol). After 24 h at ambient temperature, 30% conversion of the starting nitrile was achieved.

$CH_2=CHCH=NSiMe_2Ph$:

^1H NMR ($CDCl_3$): δ 8.50 (d, *J*(H-H) = 8.2 Hz, 1, C*H*=NSi), 7.70-7.60 and 7.50-7.30 (m, 5, Ph), 6.48 (m,1, C*H*CH=NSi), 6.02 (d, *J*(H-H) = 9.9 Hz, 1, CH_2=CH), 5.83 (d, *J*(H-H) = 17.0 Hz, 1, CH_2=CH), 0.52 (s, 6, Si*Me*).

Hydrosilylation of 4-methoxybenzonitrile

The reaction was performed in acetone-d_6 with 4-methoxybenzonitrile (0.0217 mg, 0.16 mmol), $HSiMe_2Ph$ (26 μL, 0.17 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.004 g, 4% mol). After 1 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

p-MeO(C_6H_4)CH=N($SiMe_2Ph$):

^{1}H NMR (acetone-d_6): δ 8.97 (s, 1, C*H*=N), 7.32 (d, *J*(H-H) = 8.78 Hz, 2, C_6H_4), 7.70-7.65 (m, 2, Ph), 7.40-7.35 (m, 3, Ph), 7.03 (d, *J*(H-H) = 8.78 Hz, 2, C_6H_4), 3.86 (s, 3, O*Me*), 0.49 (s, 6, Si*Me*).

Hydrosilylation of ethyl 4-cyanobenzoate

The reaction was performed in CH_2Cl_2 (0.6 mL) with ethyl 4-cyanobenzoate (0.0228 g, 0.13 mmol), $HSiMe_2Ph$ (21 μL, 0.14 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.0034 g, 5% mol). After 48 h at ambient temperature, 100% conversion of the starting nitrile was achieved.

p-EtOOC(C_6H_4)CH=N($SiMe_2Ph$):

^{1}H NMR (CH_2Cl_2, D_2O): δ 8.82 (s, 1, C*H*=N), 7.93 (d, *J*(H-H) = 8.1 Hz, 2, C_6H_4), 7.70 (d, *J*(H-H) = 8.1 Hz, 2, C_6H_4), 7.45 (m, 2, Ph), 7.24 (m, 3, Ph), 4.20 (q, *J*(H-H) = 7.2 Hz, 2, OCH_2CH_3), 1.22 (t, *J*(H-H) = 7.2 Hz, 3, OCH_2CH_3), 0.37 (s, 6, $SiCH_3$).

Hydrosilylation of methyl cyanoacetate

The reaction was performed in $CDCl_3$ (0.6 mL) with methyl cyanoacetate (14.4 μL, 0.16 mmol), $HSiMe_2Ph$ (25 μL, 0.16 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (7 mg, 4% mol). After 48 h at ambient temperature there was 50% conversion of starting nitrile with the formation of a complex mixture of products (no imine protons were observed in ^{1}H NMR).

Hydrosilylation of glutaronitrile

Method 1. To a solution of $HSiMe_2Ph$ (20 μL, 0.13 mmol) and glutaronitrile (6.2 μL, 0.06 mmol) in acetone-d_6 (0.6 mL) was added $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (3 mg, 4% mol). Maximum conversion of glutaronitrile (~70 %) into a mixture of silylated imines (triplets in ^{1}H NMR at 8.57 ppm and 8.54 ppm) was observed after 30 min at ambient temperature. After 10 h at ambient temperature there was > 90% conversion of the starting nitrile with the formation of a mixture of products (no imine protons in ^{1}H NMR at > 8 ppm).

Method 2 (reaction without solvent). To a mixture of glutaronitrile (62 μL, 0.60 mmol) and $HSiMe_2Ph$ (0.2 mL, 1.30 mmol) was added $(PPr^i_3)(CH_3CN)_2PF_6$ (0.003 g, 0.4% mol). There was 60% conversion of silane after 3 h at ambient temperature with the formation of a complex mixture of products, which also contained olefins (doublet at 6.19 ppm and doublet of triplets at 4.77 ppm in ^1H NMR) due to isomerisation of the silylated imines.

Hydrosilylation of 2-methylglutaronitrile

Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.006 g, 1% mol) was added to the mixture of $HSiMe_2Ph$ (200 μL, 1.3 mmol) with 2-methylglutaronitrile (74 μL, 0.6 mmol). After 24 h at ambient temperature 100% of starting nitrile was converted into a complex mixture of unidentified products.

Bishydrosilylation of benzonitrile:

The reaction was performed in $CDCl_3$ with benzonitrile (8.0 μL, 0.08 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.003 g, 5% mol). There was 100% conversion of benzonitrile after 66 h at ambient temperature.

$PhCH_2N(SiMe_2Ph)_2$:

^1H NMR ($CDCl_3$): δ 7.60-7.50 (m, 4, Ph), 7.45-7.35 (m, 6, Ph), 4.28 (s, 2, C*H*$_2$), 0.36 (s, 12, Si*Me*).

Bishydrosilylation of isobutyronitrile

The reaction was performed in CD_2Cl_2 with isobutyronitrile (11.7 μL, 0.13 mmol) $HSiMe_2Ph$ (50 μL, 0.33 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 5% mol). After 24 h at ambient temperature all the isobutyronitrile was converted into a mixture of $(CH_3)_2CHCH_2N(SiMe_2Ph)_2$ (43%) and $(CH_3)_2C{=}CHN(SiMe_2Ph)_2$ (57%).

$(CH_3)_2CHCH_2N(SiMe_2Ph)_2$:

^1H NMR (CD_2Cl_2): δ 7.60-7.50 and 7.44-7.35 (m, Ph), 2.82 (d, *J*(H-H) = 7.1 Hz, 2, C*H*$_2$), 1.66 (m, 1, C*H*), 0.82 (d, J(H-H) = 7.1 Hz, 6, C*H*$_3$), 0.39 (s, 12, Si*Me*).

$(CH_3)_2C{=}CHN(SiMe_2Ph)_2$:

^1H NMR (CD_2Cl_2): δ 7.60-7.50 and 7.44-7.35 (m, Ph), 5.69 (m, 1, C*H*), 1.64 (s, 3, C*H*$_3$), 1.54 (s, 3, C*H*$_3$), 0.33 (s, 12, Si*Me*).

Bishydrosilylation of 4-methoxybenzonitrile

The reaction was performed in CD_2Cl_2 with 4-methoxybenzonitrile (0.017 g, 0.13 mmol), $HSiMe_2Ph$ (50 μL, 0.33 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 5% mol). There was 100% conversion of 4-methoxybenzonitrile after 48 h at ambient temperature with the formation of $4\text{-}MeO(C_6H_4)CH_2N(SiMe_2Ph)_2$.

$MeO(C_6H_4)CH_2N(SiMe_2Ph)_2$:

^1H NMR (CD_2Cl_2): δ 7.60-7.53 (m, 2, Ph), 7.47-7.33 (m, 3, Ph), 7.18 (d, *J*(H-H) = 8.5 Hz, 2, C_6H_4), 6.86 (d, *J*(H-H) = 8.5 Hz, 2, C_6H_4), 3.83 (s, 3, CH_3), 0.34 (s, 12, Si*Me*).

Bishydrosilylation of 4-acetylbenzonitrile

The reaction was performed in CD_2Cl_2 with 4-acetylbenzonitrile (0.019 g, 0.13 mmol), $HSiMe_2Ph$ (50 μL, 0.33 mmol) and $CpRu(PPr^i_3)(CH_3CN)_2BAF$ (0.007 g, 5% mol). There was 100% conversion of 4-acetylbenzonitrile after 48 h at ambient temperature with the formation of a mixture of compounds, containing $CH_2=C(OSiMe_2Ph)(C_6H_4)CH_2N(SiMe_2Ph)_2$ (~40%) as one of the major products.

$CH_2=C(OSiMe_2Ph)(C_6H_4)CH_2N(SiMe_2Ph)_2$:

^1H NMR (CD_2Cl_2, selected data): δ 4.94 (d, *J*(H-H) = 1.5 Hz, 1, CH_2=C), 4.41 (d, *J*(H-H) = 1.5 Hz, 1, CH_2=C), 4.26 (s, 2, CH_2), 0.61 (s, 6, Si*Me*), 0.35 (s, 12, Si*Me*).

Recovery of the catalyst

Catalyst $CpRu(PPr^i_3)(CH_3CN)_2PF_6$ (0.0086 mg, 5% mol) was added to a solution of $HSiMe_2Ph$ (47 μL, 0.30 mmol) and benzonitrile (30 μL, 0.29 mmol) in acetone-d_6. The progress of the reaction was monitored by NMR at ambient temperature. After complete conversion of the benzonitrile, all volatiles were removed in vacuum and the product was extracted with hexane or ether. The residue was dissolved in acetone and used for the next hydrosilylation reaction with the same quantities of the reagents.

General procedure for screening of silanes and ruthenium catalysts

The catalyst $[CpRu(PR_3)(CH_3CN)_2]PF_6$ (4% mol) was added to a solution of silane and acetonitrile in a deuterated solvent. The progress of the reaction was monitored by NMR at ambient temperature.

Table 21. Screening of silanes and phosphines in the hydrosilylation of acetonitrile by $[CpRu(L)(CH_3CN)_2]PF_6$.

Silane	L					
	PPr^i_3	PPr^i_2Me	PMe_3	$PPhPr^i_2$	PPh_3	CH_3CN
$HSiEt_3$	NR			NR		

$HSiMe_2Ph$	2h	2h (mixture of products)	4h (traces of products)	NR	NR	
$H_2SiMePh$	NR			NR		
H_3SiPh	NR					
$HSiMe_2Cl$	NR				NR	NR
$HSiMeCl_2$	NR					NR
$HSiCl_3$	NR					NR
$HSi(OEt)_3$	NR					NR
PMHS	NR		NR			NR

V.5.4 Hydrosilylation of pyridines

Hydrosilylation of pyridine

Method 1. To a solution of pyridine (1.00 mL, 12.3 mmol) and $HSiMe_2Ph$ (2.00 mL, 13.0 mmol) in CH_2Cl_2 (20 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.20 g, 3% mol). The resulting solution was stirred for 6 h at ambient temperature. Then all the volatiles were removed under vacuum and the resulting oil was distilled under reduced pressure. The product was obtained in the form of a yellow oil. Yield 1.97 g (74%).

Method 2. To a solution of pyridine (10.5 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.007 g, 5% mol). There was 86% conversion of pyridine with the formation of *N*-silylated 1,4-dihydropyridine after 30 min at ambient temperature.

Method 3 (reaction without solvent). To a mixture of pyridine (1.00 mL, 12.3 mmol) and $HSiMe_2Ph$ (1.9 mL, 12.3 mmol) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.034 g, 0.5% mol). Only 10% conversion of starting pyridine was observed after 1 h at ambient temperature due to the fast decomposition of the catalyst.

Method 4 (reaction without solvent). To a mixture of pyridine (1.00 mL, 12.3 mmol) and $HSiMe_2Ph$ (1.9 mL, 12.3 mmol) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.03 g, 0.2% mol). The color of the resulting mixture turned slowly from red to yellow. There was 96% conversion of pyridine after 30 min at ambient temperature with a selective formation of N-silylated 1,4-dihydropyridine. The product was extracted with hexane followed by removal of all volatiles under vacuum. 92% Yield.

N-($SiMe_2Ph$)-1,4-dihydro-pyridine:

^1H NMR ($CDCl_3$): δ 7.55 (m, 2, Ph), 7.39 (m, 3, Ph), 5.89 (d, *J*(H-H) = 8.3 Hz, 2, NC*H*=CH), 4.45 (dt, *J*(H-H) = 8.3 Hz and 3.2 Hz, 2, NCH=C*H*CH_2), 2.95 (m, 2, CH_2),

0.42 (s, 6, Si*Me*). ^{13}C NMR ($CDCl_3$): 136.5, 133.8, 129.8, 128.7, 128.1, 100.1, 22.5, -2.4. ^{1}H-^{29}Si HSQC ($CDCl_3$): δ 1.1.

Hydrosilylation of 3-chloropyridine:

The reaction was performed in CH_2Cl_2 (0.6 mL) with 3-chloropyridine (12.4 μL, 0.13 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). Full conversion of the starting chloropyridine was observed after 15 min at ambient temperature with the formation of *N*-silylated 1,4-dihydro-3-chloropyridine.

N-($SiMe_2Ph$)-1,4-dihydro-3-chloropyridine:

^{1}H NMR (CH_2Cl_2, D_2O insert): δ 7.50-7.45 (m, 2, Ph), 7.37-7.28 (m, 3, Ph), 6.05 (s, 1, N-C*H*), 5.83 (d, *J*(H-H) = 7.9 Hz, 1, N-C*H*), 4.47 (m, 1, NCH=C*H*), 3.12 (s, 2, CH_2), 0.40 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC (CH_2Cl_2, D_2O insert, selected data): δ 127.4 (N*C*H=CH), 125.7 (N*C*H=CCl), 99.1 (NCH=*C*H), 30.2 (*C*H_2), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (CH_2Cl_2, D_2O insert): δ 3.5

Hydrosilylation of 3,5–lutidine:

The reaction was performed in CH_2Cl_2 (0.6 mL) with 3,5–lutidine (15.0 μL, 0.13 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). There was 82% conversion of the starting pyridine after 3 h at ambient temperature.

N-($SiMe_2Ph$)-1,4-dihydro-3,5-lutidine:

^{1}H NMR (CH_2Cl_2, D_2O insert): δ 7.50-7.45 (m, 2, Ph), 7.37-7.28 (m, 3, Ph), 5.72 (s, 2, NC*H*=C(CH_3)), 2.65 (s, 2, CH_2), 1.46 (s, 6, NCH=C(CH_3)), 0.38 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC (CH_2Cl_2, D_2O insert, selected data): δ 122.7 (N*C*H=C(CH_3), 33.7 (CH_2), 19.9 (NCH=C(*C*H_3)), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (CH_2Cl_2, D_2O insert): δ 2.5

Hydrosilylation of 4-Ac-pyridine:

The reaction was performed in CH_2Cl_2 (0.6 mL) with 4-AcPy (14.4 μL, 0.13 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.004 g, 5% mol). There was 50% conversion of the starting pyridine with the formation of silylated product of coupling of two acylpyridines after 15 h at ambient temperature.

(4-(C_5H_4N)CMe($OSiMe_2Ph$)-)$_2$:

^{1}H NMR (CH_2Cl_2, D_2O insert): δ 8.43 (d, *J*(H-H) = 5.8 Hz, 2, NC*H*CH), 8.20 (d, *J*(H-H) = 5.8 Hz, 2, NC*H*CH), 7.55-7.45 (m, Ph), 7.40-7.30 (m, Ph), 6.77 (d, *J*(H-H) = 5.8

Hz, 2, NCHC*H*), 1.64 (s, 6, CH_3^b), 1.36 (s, 6, CH_3), 0.25 (s, 3, Si*Me*), 0.20 (s, 3, Si*Me*), 0.07 (s, 3, Si*Me*), 0.03 (s, 3, Si*Me*). ^{1}H-^{13}C HSQC (CH_2Cl_2, D_2O insert, selected data): δ 148.5 (N*C*HCH), 147.9 ((N*C*HCH), 122.8 (NCH*C*H), 23.5 (*C*H_3), 22.9 (*C*H_3), 0.3-0.1 (Si*Me*). ^{1}H-^{29}Si HSQC (CH_2Cl_2, D_2O insert): δ 1.7.

Hydrosilylation of 2-bromopyridine

To a solution of 2-bromopyridine (12.4 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). After 3 h at ambient temperature there was 47% conversion of 2-bromopyridine into the mixture of pyridine and *N*-silylated 1,4-dihydropyridine (1:4).

Hydrosilylation of 3-pyridinecarboxaldehyde

To a solution of 3-pyridinecarboxaldehyde (12.2 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.004 g, 5% mol). After 15 min at ambient temperature 50% of 3-pyridinecarboxaldehyde and 100% of silane was converted into a complex mixture of partially reduced pyridines, which do not contain aldo-groups. Addition of a second equivalent of silane resulted in full conversion of the pyridine substrate.

Hydrosilylation of 3-acetylpyridine

To a solution of 3-acetylpyridine(14.3 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). After 15 min at ambient temperature 50% of 3-acetylpyridine and 100% of silane was converted into a complex mixture of partially reduced pyridines. Addition of second equivalent of silane resulted in full conversion of the pyridine substrate.

Hydrosilylation of 2-ethylpyridine

To a solution of 2-ethylpyridine (15 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). There was no hydrosilylation of 2-ethylpyridine after 3 h at ambient temperature, only hydrosilyation of acetonitrile ligands and slow chlorination of silane by CH_2Cl_2 was observed.

Hydrosilylation of 4-picoline

To a solution of 4-picoline (12.7 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.006 g, 5% mol). There was no reaction after 24 h at ambient temperature except hydrosilyation of acetonitrile ligands and slow chlorination of silane by CH_2Cl_2.

Hydrosilylation of 4-(dimethylamino)pyridine

To a solution of 4-(dimethylamino)pyridine (0.016 g, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.004 g, 5% mol). After 1 h at ambient temperature 53% of $HSiMe_2Ph$ was converted into $ClSiMe_2Ph$, but no hydrosilylation of 4-(dimethylamino)pyridine was observed.

Hydrosilylation of quinoline

Method 1 (reaction without solvent). To a mixture of quinoline (0.20 mL, 1.7 mmol) and $HSiMe_2Ph$ (0.26 mL, 1.7 mmol) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.009 g, 0.5% mol). There was 70% conversion of quinoline after 2 h at ambient temperature with the formation of a mixture of *N*-($SiMe_2Ph$)-1,2-quinoline and *N*-($SiMe_2Ph$)-1,4-quinoline (1:4.4). The products decomposed slowly (>20 h) with the formation of a complex mixture.

Method 2. Complex $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.007 g, 5% mol) was added to a solution of quinoline (15.4 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL). After 30 min at ambient temperature 50 % of the quinoline was converted into a mixture of *N*-($SiMe_2Ph$)-1,2-quinoline and *N*-($SiMe_2Ph$)-1,4-quinoline (1:3.6). The mixture of hydrosilylated quinolines slowly decomposed (after 24 h) with the formation of a complex mixture of products.

N-($SiMe_2Ph$)-1,4-quinoline:

^1H NMR ($CDCl_3$, selected data): δ 6.29 (d, *J*(H-H) = 7.8 Hz, 1, NC*H*CHCH$_2$), 4.77 (dt, *J*(H-H) = 7.8 Hz and 3.4 Hz, 1, NCHC*H*CH$_2$), 3.51 (d, *J*(H-H) = 3.4 Hz, 2, NCHCHC*H*$_2$), 0.60 (s, 6, Si*Me*).

^1H NMR (CH_2Cl_2, D_2O insert, selected data): δ 7.50-7.38 and 7.28-7.18 (m, Ph), 6.84-6.51 (m, 3, NC*HCHCH*), 6.18 (dt, *J*(H-H) = 7.8 Hz and 1.3 Hz, 1, NC*H*CHCH$_2$), 4.64 (dt, *J*(H-H) = 7.8 Hz and 3.4 Hz, 1, NCHC*H*CH$_2$), 3.35 (d, *J*(H-H) = 3.4 Hz, 2, NCHCHC*H*$_2$), 0.46 (s, 6, Si*Me*). ^1H-^{13}C HSQC NMR (CH_2Cl_2, D_2O insert, selected data): δ 130.3 (N*C*HCHCH$_2$), 99.5 (NCH*C*HCH$_2$), 26.3 (NCHCH*C*H$_2$), -1.13 (Si*Me*). ^1H-^{29}Si HSQC NMR (CH_2Cl_2, D_2O insert): δ 2.5.

Hydrosilylation of triazine

To a solution of triazine (0.011 g, 0.13 mmol) and $HSiMe_2Ph$ (20 μL, 0.13 mmol) in PhCl (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]BAF$ (0.007 g, 5% mol). A mixture of triazine, mono- and bishydrosilylated triazines was obtained after 30 min at ambient temperature. Addition of a second equivalent of silane resulted in 98% conversion of triazine with the formation of a bishydrosilylated product after 3 h at ambient temperature.

N,N-(SiMe$_2$Ph)-1,2,3,4-tetrahydrotriazine:

^{1}H NMR (C_6D_6): δ 7.54-7.50 (m, 2, Ph), 7.47 (s, 1, N=C*H*), 7.35-7.28 (m, 2, Ph), 7.26-7.18 (m, 6, Ph), 4.44 (s, 4, CH_2), 0.24 (s, 6, Si*Me*), 0.09 (s, 6, Si*Me*). ^{13}C NMR (C_6D_6, selected data): δ 147.9 (*C*=N), 59.5 (*C*H$_2$), -2.0 (Si*Me*), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (C_6D_6): δ 1.5 and -1.0.

Hydrosilylation of pyridine in the presence of acetone

Method 1. To a solution of pyridine (0.7 mL, 8.6 mmol) and $HSiMe_2Ph$ (1.5 mL, 9.8 mmol) in acetone (3 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.025 g, 0.5% mol). There was 93% conversion of pyridine after 5 min at ambient temperature with the formation *N*-(CMe_2OSiMe_2Ph)-1,4-dihydropyridine (less then 5% mol of $Me_2CHOSiMe_2Ph$ was also observed in the reaction mixture). Extraction of the product from the reaction mixture with hexane or benzene resulted in dehydroamination of the product with the formation of 1,4-(C_5H_6NH) and CH_2=C($OSiMe_2Ph$)CH_3.

Method 2. To the solution of pyridine (10.0 μL, 0.12 mmol), $HSiMe_2Ph$ (20 μL, 0.13 mmol) and acetone (8.8 μL, 0.12 mmol) in CD_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.003 g, 5% mol). After 4 h at ambient temperature 84% of the pyridine was converted into a mixture of silylated 1,4-dihydropyridine and the product of coupling with acetone (1.6:1). After 2 days at ambient temperature the ratio of products changed to 2.3:1 with the formation of free pyridine and $ClSiMe_2Ph$.

N-(CMe_2OSiMe_2Ph)-1,4-dihydropyridine:

^{1}H NMR (C_6D_6): δ 7.65-7.57 (m, 2, Ph), 7.27-7.17 (m, 3, Ph), 6.08 (d, *J*(H-H) = 8.0 Hz, 2, NC*H*=CHCH$_2$), 4.45 (dt, *J*(H-H) = 8.0 Hz and 3.3 Hz, 2, NCH=C*H*CH$_2$), 3.00 (m, 2, NCH=CHCH_2), 1.23 (s, 6, OC(CH_3)$_2$), 0.42 (s, 6, Si*Me*). ^{1}H NMR (acetone-d_6): δ 7.70-7.60 (m, 2, Ph), 7.40-7.30 (m, 3, Ph), 6.16 (dt, *J*(H-H) = 8.8 Hz and 1.3 Hz, 2,

NC*H*=CHCH$_2$), 4.36 (dt, *J*(H-H) = 8.8 Hz and 3.3 Hz, 2, NCH=C*H*CH$_2$), 2.87 (m, 2, NCH=CHC*H*$_2$), 0.43 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC (C_6D_6, selected data): δ 126.9 (N*C*H=CHCH$_2$), 98.6 (NCH=*C*HCH$_2$), 29.5 (OC(*C*H$_3$)$_2$), 0.7 (Si*Me*). ^{1}H-^{29}Si HSQC (acetone-d_6): δ -1.3.

Hydrosilylation of pyridine in the presence of benzaldehyde

To a solution of pyridine (20 μL, 0.25 mmol), HSiMe$_2$Ph (45 μL, 0.29 mmol) and PhCHO (25 μL, 0.25 mmol) in CD_2Cl_2 (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (0.004 g, 3% mol). There was 95 % conversion of benzaldehyde with the formation of *N*-(CHPhOSiMe$_2$Ph)-1,4-dihydripyridine.

N-(CHPhOSiMe$_2$Ph)-1,4-dihydripyridine:

^{1}H NMR (CD_2Cl_2): δ 7.72 (m, 2, Ph), 7.53-7.32 (m, 8, Ph), 5.78 (d, *J*(H-H) = 8.1 Hz, 2, NC*H*CH), 5.60 (s, 1, OC*H*), 4.44 (dt, *J*(H-H) = 8.1 Hz and 3.2 Hz, 2, NCHC*H*), 2.97 (m, 2, C*H*$_2$), 0.59 (s, 3, Si*Me*), 0.54 (s, 3, Si*Me*). ^{13}C NMR (CD_2Cl_2): δ 140.9 (Ph), 137.2 (Ph), 133.7 (Ph), 129.8 (N*C*HCH), 128.8 (Ph), 128.1 (Ph), 127.9 (Ph), 127.8 (Ph), 126.4 (Ph), 99.0 (NCH*C*H), 86.0 (O*C*H), 23.0 (*C*H$_2$), -1.3 (Si*Me*), -1.6 (Si*Me*). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ 7.2.

Hydrosilylation of pyridine in the presence of cinnamaldehyde

To a solution of pyridine (20 μL, 0.25 mmol), HSiMe$_2$Ph (45 μL, 0.29 mmol) and PhCH=CHCHO (31 μL, 0.25 mmol) in CD_2Cl_2 (0.6 mL) was added [CpRu(PPr$^i_3$)(CH$_3$CN)$_2$]PF$_6$ (0.004 g, 3% mol). Full conversion of cinnamaldehyde was observed after 30 min at ambient temperature with the formation of *N*-(CH(CH=CHPh)OSiMe$_2$Ph)-1,4-dihydropyridine.

N-(CH(CH=CHPh)OSiMe$_2$Ph)-1,4-dihydropyridine:

^{1}H NMR (CD_2Cl_2): δ 7.73 (m, 2, Ph), 7.52-7.28 (m, 8, Ph), 6.77 (dd, *J*(H-H) = 15.9 and 1.5 Hz, 1, =C*H*Ph), 6.25 (dd, *J*(H-H) = 15.9 and 4.3 Hz, 1, =C*H*CH), 5.92 (d, *J*(H-H) = 8.3 Hz, 2, NC*H*=CHCH$_2$), 5.14 (dd, *J*(H-H) = 1.5 and 4.3 Hz, 1, =CHC*H*), 4.50 (dt, *J*(H-H) = 8.3 and 3.1 Hz, 2, NCH=C*H*CH$_2$), 3.00 (m, 2, NCH=CHC*H*$_2$), 0.59 (s, 3, Si*Me*), 0.55 (s, 3, Si*Me*). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 128.8 (=*C*HPh), 128.6 (N*C*H=CHCH$_2$), 128.5 (=*C*HCH), 98.8 (NCH=*C*HCH$_2$), 84.6 (=CH*C*H), 22.6 (NCH=CH*C*H$_2$), -1.3 (Si*Me*), -1.6 (Si*Me*). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ 7.0.

The reaction of N-(SiMe$_2$Ph)-1,4-dihydropyridine with benzaldehyde

To a solution of N-($SiMe_2Ph$)-1,4-dihydropyridine (20 μL, 0.09 mmol) and PhCHO (9.5 μL, 0.09 mmol) in CH_2Cl_2 (0.6 mL) was added [$CpRu(PPr^i_3)(CH_3CN)_2$]BAF (0.005 g, 5% mol). After 24 h at ambient temperature 100% of the silylated 1,4-dihydropyridine was converted into the mixture of products, containing free pyridine and *N*-($CHPhOSiMe_2Ph$)-1,4-dihydripyridine (1:2.1).

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with $B(C_6F_5)_3$

To a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (15 μL, 0.07 mmol) in C_6D_6 (0.6 mL) was added $B(C_6F_5)_3$ (0.035 g, 0.07 mmol). Pyridinium salt $[C_5H_5N^*SiMe_2Ph]HB(C_6F_5)_3$ immediately precipitated from the solution as a colorless oil. Benzene was removed with a syringe and the pyridinium salt was dried under vacuum and then dissolved in CD_2Cl_2 (0.6 mL). Full decomposition of the pyridinium salt in CD_2Cl_2 was observed after 24 h at ambient temperature with the formation of $C_5H_5N^*B(C_6F_5)_3$ and $HSiMe_2Ph$.

$[C_5H_5N^*SiMe_2Ph]HB(C_6F_5)_3$:

^{1}H NMR (CD_2Cl_2): δ 8.54 (d, *J*(H-H) = 5.5 Hz, 2, Py), 8.48 (t, *J*(H-H) = 7.8 Hz, 1, Py), 7.98 (t, *J*(H-H) = 6.8 Hz, 2, m-Py), 7.72 (d, *J*(H-H) = 7.0 Hz, 2, Ph), 7.62 (m, 3, Ph), 3.69 (q, *J*(B-H) = 90 Hz, B*H*), 1.09 (s, 6, Si*Me*). ^{11}B NMR (CD_2Cl_2): δ -25.3 (d, *J*(B-H) = 90 Hz). ^{1}H-^{13}C HSQC (CD_2Cl_2, selected data): δ 144.8 (Py), 128.4 (Py), 126.2 (Ph), 128.7 (Ph), -5.2 (Si*Me*). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ 30.8.

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with 3,5-lutidine

Complex [$CpRu(PPr^i_3)(CH_3CN)_2$]BAF (0.005 g, 5% mol) was added to a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (20 μL, 0.09 mmol) and 3,5-lutidine (10.7 μL, 0.09 mmol) in CH_2Cl_2 (0.6 mL). After 48 h at ambient temperature a mixture of *N*-($SiMe_2Ph$)-1,4-dihydropyridine and *N*-($SiMe_2Ph$)-1,4-dihydrolutidine was obtained (3.1:1), which also contained free pyridine, 3,5-lutidine and $ClSiMe_2Ph$.

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with benzonitrile

To a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (30 μL, 0.14 mmol) and PhCN (14 μL, 0.14 mmol) in acetone-d_6 (0.6 mL) was added [$CpRu(PPr^i_3)(CH_3CN)_2$]PF_6 (0.002 g, 2% mol). There was 40% conversion of the starting dihydropyridine after 24 h at ambient temperature with the formation $PhCH{=}NSiMe_2Ph$ and pyridine. Full conversion was achieved after 18 days at ambient temperature.

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with $DSiMe_2Ph$

Complex [$CpRu(PPr^i_3)(CH_3CN)_2$]BAF (0.005 g, 5% mol) was added to a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (20 μL, 0.09 mmol) and $DSiMe_2Ph$ (14.3 μL, 0.09 mmol) in CH_2Cl_2 (0.6 mL). After 24 h at ambient temperature 25% (50% after 4 days) of hydrogen atoms in the *para*-position of *N*-($SiMe_2Ph$)-1,4-dihydropyridine were found to be the deuterium isotope. According to ^2H NMR, there were no deuterium atoms in other positions of *N*-($SiMe_2Ph$)-1,4-dihydropyridine.

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with 4-Br-(C_6H_4)C(O)Cl

To a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (30 μL, 0.14 mmol) in C_6D_6 (0.6 mL) was added 4-Br-(C_6H_4)C(O)Cl (0.030 g, 0.14 mmol). The resulting yellow solution was heated at 80°C for 1 h, which resulted in preparation of the corresponding amide and $ClSiMe_2Ph$.

4-Br-(C_6H_4)C(O)(NC_5H_6):

^1H NMR (C_6D_6, 70°C): δ 7.12 (d, *J*(H-H) = 4.2 Hz, 2, C_6H_4), 6.95 (d, *J*(H-H) = 4.2 Hz, 2, C_6H_4), 6.73 (bs, 2, NC_5H_6), 4.59 (bs, 2, NC_5H_6), 2.55 (bs, 2, NC_5H_6). ^1H-^{13}C HSQC (C_6D_6, 70°C): δ 131.5 (C_6H_4), 129.4 (C_6H_4), 106.6 (*m*-NC_5H_6), 23.1 (*p*-NC_5H_6).

The reaction of *N*-($SiMe_2Ph$)-1,4-dihydropyridine with PhCH=NPh

To a solution of *N*-($SiMe_2Ph$)-1,4-dihydropyridine (30 μL, 0.14 mmol) in ether (1 mL) was added PhCH=NPh (0.025 g, 0.14 mmol) and $ZnCl_2$ (0.019 g, 0.14 mmol). The resulting mixture was stirred for 2 days at ambient temperature. There was 50% conversion of PhCH=NPh after 2 days at ambient temperature.

$PhCH_2N(SiMe_2Ph)Ph$:

^1H NMR ($CDCl_3$, selected data): δ 4.69 (s, 2, $PhCH_2N$), 0.52 (s, 6, $SiMe$). ^1H-^{13}C HSQC ($CDCl_3$, selected data): δ 52.4 ($PhCH_2N$), -0.4 ($SiMe$). ^1H-^{29}Si HSQC ($CDCl_3$) δ 1.1.

The preparation of $CpRu(PPr^i_3)(C_5H_5N)H$

Complex [$CpRu(PPr^i_3)(CH_3CN)_2$]PF_6 (0.100 g, 0.27 mmol) was added to a solution of pyridine (0.150 mL, 2.7 mmol) in i-PrOH (30mL). After addition of t-BuOK (0.040 g, 0.54 mmol) the reaction mixture was stirred for 15 minutes. The resulting brown solution with precipitate was evaporated and the ruthenium complex was extracted

with hexane (3*20mL). Complex $CpRu(PPr^i_3)(C_5H_5N)H$ was obtained as a brown oil after evaporation of hexane. Compound $CpRu(PPr^i_3)(C_5H_5N)H$ was found to be very unstable and was used only in the presence of free pyridine.

$CpRu(PPr^i_3)(C_5H_5N)H$:

^1H NMR (C_6D_6): δ 9.10 (d, *J*(H-H) = 5.5 Hz, 2, o-Py), 6.54 (m, 1, p-Py), 5.97 (m, 2, m-Py), 4.58 (s, 5, Cp), 1.92 (m, 3, $CH(CH_3)_2$), 1.24 (dd, *J*(H-H) = 7.2 Hz, *J*(P-H) = 12.3 Hz, 9, $CH(CH_3)_2$), 1.06 (dd, *J*(H-H) = 7.1 Hz, *J*(P-H) = 12.1 Hz, 9, $CH(CH_3)_2$), -10.65 (d, *J*(P-H) = 41.08 Hz, 1, Ru*H*). ^{31}P NMR (C_6D_6): δ 84.5. ^1H-^{13}C HSQC (C_6D_6): δ 159.9 (o-Py), 130.9 (p-Py), 121.6 (m-Py), 74.2 (Cp), 27.4 ($CH(CH_3)_2$), 19.9 ($CH(CH_3)_2$), 19.7 ($CH(CH_3)_2$).

The reaction of $CpRu(PPr^i_3)(C_5H_5N)H$ with $[Et_3Si(C_5H_5N)]BAF$

Freshly prepared $CpRu(PPr^i_3)(C_5H_5N)H$ (0.05 mmol) and pyridine (0.20 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of $[C_5H_5N*SiEt_3]BAF$ in CD_2Cl_2 (0.3 mL), which resulted in the formation of N-($SiEt_3$)-1,4-dihydropyridine and $[CpRu(PPr^i_3)(C_5H_5N)_2]BAF$.

N-($SiEt_3$)-1,4-dihydropyridine:

^1H NMR (CD_2Cl_2): δ 5.90 (d, J(H-H) = 8.2 Hz, 2, NC*H*=CH), 4.43 (m, 2, NCH=C*H*), 2.96 (m, 2, CH_2), 0.99 (t, *J*(H-H) = 7.4 Hz, 9, $SiCH_2CH_3$), 0.69 (q, *J*(H-H) = 7.4 Hz, 6, $SiCH_2CH_3$). ^1H-^{13}C HSQC (CD_2Cl_2): δ 129.0 (N*C*H=CH), 98.8 (NCH=*C*H), 22.2 (CH_2), 6.3 ($SiCH_2CH_3$), 3.3 ($SiCH_2CH_3$). ^1H-^{29}Si HSQC (CD_2Cl_2): δ 13.8.

$[CpRu(PPr^i_3)(C_5H_5N)_2]BAF$:

^1H NMR (CD_2Cl_2): δ 8.59 (d, *J*(H-H) = 5.32 Hz, 4, o-Py), 7.81 (m, 1, p-Py), 7.31 (m, 2, m-Py), 4.44 (s, 5, Cp), 2.34 (m, 3, $CH(CH_3)_2$), 1.18 (dd, *J*(H-H) = 7.1 Hz, *J*(P-H) = 12.7 Hz, 18, $CH(CH_3)_2$). ^{31}P NMR (CD_2Cl_2): δ 42.3. ^1H-^{13}C HSQC (CD_2Cl_2): δ 156.7 (o-Py), 137.1 (p-Py), 74.4 (Cp), 25.5 ($CH(CH_3)_2$), 19.3 ($CH(CH_3)_2$).

V.5.5 Reduction of phenanthroline

The reduction of phenanthroline with $HSiMe_2Ph/H_2O$ or EtOH

Method 1. Complex $[CpRu(CH_3CN)_3]PF_6$ (0.006 g, 5% mol) was added to the solution of 1,10-phenanthroline (0.047 g, 0.26 mmol), $HSiMe_2Ph$ (0.4 mL, 2.6 mmol) and H_2O (50 μL, 2.6 mmol) in acetone-d_6 (0.6 mL). The reaction mixture became

brown and gas evolution was observed. After 24 h at ambient temperature 96% of 1,10-phenanthroline was converted into a mixture of 1,2- and 1,4-dihydrophenanthrolines (1:4.5). All of the silane was converted into a mixture of $HOSiMe_2Ph$ and $O(SiMe_2Ph)_2$.

Method 2. Complex $[CpRu(CH_3CN)_3]PF_6$ (0.006 g, 5% mol) was added to a solution of 1,10-phenanthroline (0.050 g, 0.28 mmol), $HSiMe_2Ph$ (0.2 mL, 1.4 mmol) and EtOH (0.08 mL, 1.4 mmol) in acetone-d_6 (0.6 mL). The reaction mixture became brown and gas evolution was observed. After 2 h at ambient temperature 99% of 1,10-phenanthroline was converted into a mixture of 1,2- and 1,4-dihydrophenanthrolines (1:4.5).

Method 3. Complex $[CpRu(CH_3CN)_3]PF_6$ (0.036 g, 5% mol) was added to a solution of 1,10-phenantroline (0.30 g, 1.66 mmol), $HSiEt_3$ (2.67 mL, 16.6 mmol) and EtOH (0.96 mL, 16.6 mmol) in acetone (20 mL). The reaction mixture became brown and gas evolution was observed. After 1 h at ambient temperature 100% of 1,10-phenanthroline was converted into a mixture of 1,2- and 1,4-dihydrophenanthrolines (1:4.5). Hexane (80 mL) was then added and the volume of the solution was reduced to 30 mL by solvent evaporation. The resulting yellow solution with brown precipitate was filtered and the product was extracted with Et_2O (3*20mL). The mixture of 1,2- and 1,4-dihydrophenanthrolines was obtained as yellow solid after evaporation of all the volatiles. Yield 0.27 g (90%).

1,4-dihydrophenanthroline:

^1H NMR (acetone-d_6): δ 8.72 (dd, *J*(H-H) = 4.1 Hz and 1.6 Hz, 1, NC*H*CHCH), 8.15 (dd, *J*(H-H) = 8.1 Hz and 1.6 Hz, 1, NCHCHC*H*), 7.40 (m, 1, NCHC*H*CH), 7.28 (d, *J*(H-H) = 8.5 Hz, 1, C*H*CH), 7.13 (d, *J*(H-H) = 8.5 Hz, 1, CHC*H*), 6.42 (m, 1, NC*H*CHCH$_2$), 4.52 (m, 1, NCHC*H*CH$_2$), 3.75 (m, 2, NCHCHC*H*$_2$). ^1H-^{13}C HSQC (acetone-d_6): δ 147.7 (N*C*HCHCH), 135.6 (NCHCH*C*H), 128.3 (CH*C*H), 127.2 (N*C*HCHCH$_2$), 120.7 (NCH*C*HCH), 117.8 (*C*HCH), 95.3 (NCH*C*HCH$_2$), 27.0 (NCHCH*C*H$_2$). IR (Nujol): 3432 cm^{-1} (N-H).

Attempted reduction of 2,2'-bipyridyl

Complex $[CpRu(CH_3CN)_3]PF_6$ (0.003 g, 5% mol) was added to a solution of 2,2'-bipyridyl (0.022 g, 0.14 mmol), $HSiMe_2Ph$ (33 μL, 0.21 mmol) and H_2O (4 μL, 0.22 mmol) in acetone-d_6 (0.6 mL). Gas evolution was observed for a period of 20 minutes.

Full conversion of $HSiMe_2Ph$ into $HOSiMe_2Ph$ was observed after 0.5 h without reduction of 2,2'-bipyridyl.

The synthesis of [CpRu(1,10-phenanthroline)(CH_3CN)]PF_6

To a solution of [CpRu(CH_3CN)$_3$]PF_6 (0.300 g, 0.69 mmol) in CH_3CN (40 mL) was added solution of 1,10-phenantroline(0.124 g, 0.69 mmol) in toluene (40mL). The reaction mixture turned red after about 5 minutes of stirring. After stirring for 3 h at ambient temperature the red solution was concentrated until red crystals formed. The crystals were separated from the solution by decantation and washed with Et_2O (3*20mL). After drying under reduced pressure complex [CpRu(1,10-phenanthroline)(CH_3CN)]PF_6 was obtained as red powder. Yield 0.300 g (81%).

[CpRu(1,10-phenanthroline)(CH_3CN)]PF_6:

^{1}H NMR (CD_2Cl_2): δ 9.74 (dd, *J*(H-H) = 4.9 Hz and 1.1 Hz, 2, o-phen), 8.52 (dd, *J*(H-H) = 8.0 Hz and 1.1 Hz, 2, p-phen), 8.06 (s, 2, phen), 7.88 (dd, *J*(H-H) = 4.9 Hz and 8.0 Hz, 2, m-phen), 4.52 (s, 5, Cp), 2.01 (s, 3, C*H*$_3$CN). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 155.0 (o-phen), 135.7 (p-phen), 126.9 (phen), 124.8 (m-phen), 70.8 (Cp), 3.6 (*C*H$_3$CN). Anal. Calcd. for $C_{19}H_{16}F_6N_3PRu$: C, 42.86; H, 3.03; N, 7.89. Found: C, 42.72; H, 3.02; N, 7.81.

The synthesis of [(CpRu(1,10-phenanthroline))$_2$H]PF_6

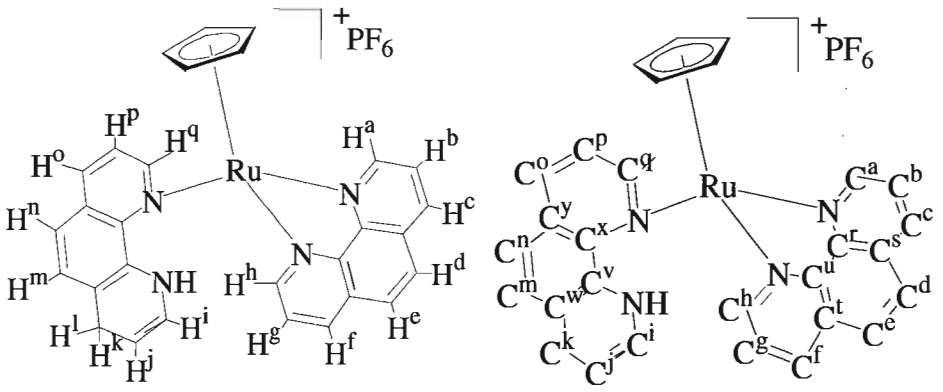
To a red solution of complex [CpRu(1,10-phenanthroline)(CH_3CN)]PF_6 (0.030 g, 0.05 mmol) in THF (10 mL) was added solution of L-selectride (28 μL of 1M solution in THF, 0.015 mmol). To the resulting brown solution was added hexane, which led to precipitation of [(CpRu(1,10-phenantroline))$_2$H]PF_6 as dark brown crystals. Pure product was obtained after crystallization from CH_2Cl_2/Et_2O solution. Yield (0.023 g, 97%).

[(CpRu(1,10-phenanthroline))$_2$H]PF_6:

^{1}H NMR (CD_2Cl_2): δ 8.68 (d, *J*(H-H) = 0.9 Hz, 4, *o*-phen), 8.66 (d, *J*(H-H) = 0.9 Hz, 4, *p*-phen), 7.63 (s, 4, phen), 7.04 (dd, *J*(H-H) = 0.9 Hz, 4, *m*-phen), 4.39 (s, 10, Cp), -15.26 (s, 1, Ru*H*). ^{13}C NMR (CD_2Cl_2): δ 153.0, 131.2, 129.0, 126.7 and 122.5 (phen), 71.3 (Cp). Anal. Calcd. for $C_{38}H_{37}F_6N_4OPRu_2$ (contained Et_2O): C, 50.00; H, 4.09; N, 6.14. Found: C, 49.82; H, 3.95; N, 6.04.

The synthesis of the ruthenium complex with partially reduced 1,10-phenanthroline

To a red solution of [CpRu(1,10-phenanthroline)(CH_3CN)]PF_6 (0.049 g, 0.09 mmol) in CD_2Cl_2 (0.6 mL) was added a mixture of 1,2- and 1,4-dihydrophenanthrolines (0.020 g, 0.11 mmol), which resulted in color change from red to brown. All volatiles were then removed under vacuum and the residue was dissolved in CH_2Cl_2 (1 mL). Complex [CpRu(phenanthroline)(dihydrophenanthroline)]PF_6 was obtained as a brown crystalline solid by crystallization from CH_2Cl_2/hexane solution at -30°C. Yield 0.05 g (81%).



[CpRu(phen)(phenH$_2$)]PF$_6$:

^{1}H NMR (CD_2Cl_2): δ 9.79 (d, *J*(H-H) = 5.5 Hz, 1, H^a), 9.33 (d, *J*(H-H) = 5.2 Hz, 1, H^h), 8.49 (d, *J*(H-H) = 4.4 Hz, 1, H^q), 8.40 (d, *J*(H-H) = 8.1 Hz, 1, H^c), 7.97 (dd, *J*(H-H) = 8.1 Hz and 5.2 Hz, 1, H^b), 7.70 (d, *J*(H-H) = 8.9 Hz, 1, H^d), 7.60 (d, *J*(H-H) = 7.7 Hz, 1, H^o), 7.53 (dd, *J*(H-H) = 6.8 Hz and 4.0 Hz, H^j), 7.38 (d, *J*(H-H) = 8.5 Hz, 1, H^f), 7.38 (d, *J*(H-H) = 8.9 Hz, 1, H^e), 7.21 (dd, *J*(H-H) = 4.4 Hz and 7.7 Hz, 1, H), 7.19 (dd, *J*(H-H) = 5.2 Hz and 8.5 Hz, H^g), 6.19 (d, *J*(H-H) = 8.3 Hz, 1, H^n), 5.33 (d, *J*(H-H) = 8.3 Hz, 1, H^m), 5.20 (m, 1, H^j), 4.72 (s, 5, Cp), 3.64 (dd, *J*(H-H) = 17.9 Hz and 3.3 Hz, H^k), 2.13 (dd, *J*(H-H) = 17.9 Hz and 1.7 Hz, H^l). ^{1}H-^{13}C HSQC and HMBC (CD_2Cl_2): δ 156.0 (C^a), 156.0 (C^h), 147.7 (C^q), 146.5 (C^r), 146.4 (C^u), 135.2 (C^c), 135.1 (C^o), 134.5 (C^x), 132.7 (C^f), 132.6 (C^v), 130.0 (C^s), 127.8 (C^t), 126.8 (C^d), 126.4 (C^e), 126.0 (C^y), 125.5 (C^m), 125.3 (C^g), 124.8 (C^b), 121.2 (C^p), 118.9 (C^n), 116.8 (C^w), 89.8 (C^i), 79.6 (Cp), 45.2 (C^j), 25.8 (C^k). IR (Nujol): 3369 cm^{-1} (N-H).

The reaction of [CpRu(CH_3CN)$_3$]PF_6 with a mixtrure of dihydro-1,10-phenanthrolines

To a solution of $[CpRu(CH_3CN)_3]PF_6$ (0.020 g, 0.046 mmol) in CD_2Cl_2 (0.6 mL) was added a mixture of dihydro-1,10-phenantrolines (0.008 g, 0.046 mmol). Fast formation of the ruthenium complex with 3,4-dihydro-1,10-phenanthroline was observed by NMR spectroscopy.

[CpRu(3,4-dihydro-1,10-phenanthroline)(CH$_3$CN)]PF$_6$:

^{1}H NMR (CD_2Cl_2): δ 9.47 (dd, J(H-H) = 4.9 Hz and 1.1 Hz, 1, N=C*H*CHCH), 8.87 (t, J(H-H) = 3.2 Hz, 1, N=C*H*CH$_2$CH$_2$), 8.30 (dd, J(H-H) = 8.6 Hz and 1.1 Hz, 1, N=CHCHC*H*), 7.85 (d, J(H-H) = 8.4 Hz, 1, C*H*=CH), 7.51 (dd, J(H-H) = 8.6 Hz and 4.9 Hz, N=CHC*H*CH), 7.46 (d, J(H-H) = 8.4 Hz, 1, CH=C*H*), 4.32 (s, 5, Cp), 3.20-3.00 (m, 4, N=CHC*H*$_2$C*H*$_2$), 2.17 (s, 3, C*H*$_3$CN). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 156.5 (N=*C*HCHCH), 148.8 (N=*C*HCH$_2$CH$_2$), 135.8 (N=CHCH*C*H), 128.4 (CH=*C*H), 128.2 (*C*H=CH), 122.9 (N=CH*C*HCH), 69.9 (Cp), ~28.0 (N=CH*C*H$_2$*C*H$_2$), 3.3 (*C*H$_3$CN).

EPR experiment

EPR spectra were collected on a Bruker Elexsys E580 spectrometer operating in cw mode. EPR samples were prepared by adding $[CpRu(PPr^i_3)(CH_3CN)_3]BAF$ (0.050 g, 20% mol) or $[CpRu(PPr^i_3)(CH_3CN)_3]PF_6$ (0.066 g, 10% mol) to a solution of pyridine (19.7 μL, 0.24 mmol) and $HSiMe_2Ph$ (37.4 μL, 0.24 mmol) in CH_2Cl_2 (0.4 mL). The resulting solution was allowed to react for several minutes, frozen in liquid nitrogen and then placed in the cooled spectrometer resonator at either 120 K or 80 K.

V.5.6 Reduction of acyl chlorides

NMR reactions

In a representative procedure, to a solution of 4-Br(C_6H_4)C(O)Cl (0.043 g, 0.20 mmol), $HSiMe_2Ph$ (0.030 mL, 0.20 mmol), and CH_3CN (0.020 mL, 0.40 mmol) in acetone-d_6 (0.6 mL) was added $[Cp(Pr^i_3P)Ru(NCMe)_2]PF_6$ (0.005 g, 5% mol). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by NMR spectroscopy.

Recycling of the catalyst on a large scale

In a representative procedure on a large scale, to a solution of 4-Br(C_6H_4)C(O)Cl (0.500 g, 2.28 mmol), $HSiMe_2Ph$ (0.400 mL, 2.61 mmol) and t-BuCN (0.025 mL, 10% mol) in CH_2Cl_2 or acetone (30 mL) was added complex [Cp(Pr^i_3P)Ru($NCMe)_2$]PF_6 (0.065 g, 5% mol). The resulting mixture was stirred at room temperature. Full conversion of acyl chloride was observed within 3h (in acetone) or 1 day (in CH_2Cl_2). To the resulting mixture was added hexane (30 mL) and the solution was concentrated to 5 mL under vacuum. The products of the reaction were extracted with hexane (3*10 mL). The remaining catalyst was used again (4 times) with the same amounts of the starting reagents. Aldehyde was each time recrystalysed from the hexane solutions at -80°C. Yield 70% (reactions in CH_2Cl_2) or 90% (reactions in acetone).

V.5.7 Reduction of primary amides

Dehydration of benzamide

To a mixture of $PhC(O)NH_2$ (0.015 g, 0.124 mmol) and $HSiMe_2Ph$ (40 μL, 0.260 mmol) in PhCl (0.6 mL) was added [CpRu(PPr^i_3)($NCMe)_2$]BAF (0.006 g, 5% mol), which resulted in a rapid evolution of hydrogen gas. Slow dissolution of the starting benzamide in PhCl was observed as the reaction proceeded. After 2 h at room temperature most of the benzamide (>90%) was fully silylated and the reaction mixture was then heated at 100°C for 16 h, which resulted in the formation of siloxane $O(SiMe_2Ph)_2$ and PhCN.

Reduction of benzamide

To a mixture of $PhC(O)NH_2$ (0.015 g, 0.124 mmol) and $HSiMe_2Ph$ (120 μL, 0.780 mmol) in PhCl (0.6 mL) was added [CpRu(PPr^i_3)($NCMe)_2$]BAF (0.006 g, 5% mol), which resulted in a rapid evolution of hydrogen gas. Full conversion of the starting amide into $PhC(O)N(SiMe_2Ph)_2$ was observed within 1.5 h at room temperature. The reaction mixture was then heated at 100°C, which resulted in about 60% conversion of the amide into $PhCH_2N(SiMe_2Ph)_2$.

Reduction of other amides

Attempted reduction of other amides, such as $CH_3C(O)NH_2$, $CH_2=C(Me)C(O)NH_2$, and $CF_3C(O)NH_2$, was performed analogously to the reduction of benzamide.

V.6 *Hydridosilyl complexes of iron*

Preparation of $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$.

The synthesis was performed analogously to previously reported procedure for the preparation of complex $CpFe(PPh_3)(CH_3CN)_2PF_6$.[175] To a solution of $CpFe(naphthalene)PF_6$[176] (3.41 g, 8.6 mmol) in CH_3CN (300 ml) was added PPr^i_2Me (1.14 g, 8.6 mmol). The resulting red solution was photolysed for 3 h at ambient temperature. Then the reaction mixture was filtered and the filtrate was concentrated to 10 ml by evaporation of CH_3CN under vacuum. To the resulting solution was added 100 ml of Et_2O. Red crystals of the final product were obtained after 2 days at -30°C. The solution was then decanted and the crystals were dried under vacuum. Yield 3.6g (88%).

^1H NMR (DMSO-d_6): δ 4.14 (s, 5, Cp), 2.03 (s, 6, CH_3CN), 1.59 (br m, 2, $P(CH(CH_3)_2)$, 0.96 (br q, J(P-H) = 12.8 Hz, J(H-H) = 6.8 Hz, 6, $PCH(CH^a_3)$), 0.92 (br m, 6, $PCH(CH^b_3)$), 0.81 (br s, 3, PCH_3). ^{31}P NMR (DMSO-d_6): δ -11.1 (br s, displacement with DMSO, PPr^i_2Me), -144.18 (sept, J(P-F) = 710.6 Hz, PF_6). ^{13}C NMR (DMSO-d_6): δ 118.6 (s, CH_3CN), 68.1 (s, Cp), 23.6 (d, J(P-C) = 8.8 Hz, $PCH(C^aH_3)$), 20.1 (d, J(P-C) = 16.5 Hz, $P(CH(CH_3)_2)$, 18.1 (s, $PCH(C^bH_3)$), 4.1 (d, J(P-C) = 18.7 Hz, PCH_3), 1.58 (s, CH_3CN). IR (Nujol): 2272 cm^{-1}.

Preparation of $CpFe(PPr^i_2Me)(BH_4)$.

To a solution of $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (1.0 g, 2.1 mmol) in THF (50ml) at 0°C was added $NaBH_4$ (1.4 g, 37 mmol). The colour of the reaction mixture immediately changed to dark green. After stirring for 30 minutes at 0°C the reaction mixture was evaporated to dryness. The resulting dark residue was extracted with hexane (3*20 ml). Hexane was then evaporated from the combined hexane fractions to afford **2** in a form of green oil. Yield 0.41 g (73%).

^1H NMR (C_6D_6): δ 7.8 (br s, 1, BH), 4.8 (br s, 1, BH), 3.9 (br s, 5, Cp), 1.34 (br m, 2, $P(CH(CH_3)_2)$, 0.84 (br m, 12, $P(CH(CH_3)_2)$, 0.60 (br s, 3, PCH_3), -20.8 (br s, 2, FeHB). ^{31}P NMR (C_6D_6): δ 65.8. ^{13}C NMR (C_6D_6): δ 70.2 (s, Cp), 25.4 (d, J(P-C) =

20.1 Hz, P(*C*H(CH$_3$)$_2$), 18.1 (s, PCH(*C*^{a}H$_3$)), 17.2 (s, PCH(*C*^{b}H$_3$)), 7.3 (d, *J*(P-C) = 21.0 Hz, P*C*H$_3$). IR (Nujol): 2371 cm^{-1}.

Preparation of CpFe(PPr$^i_2$Me)H$_2$SiCl$_3$.

To a green solution of CpFe(PPr$^i_2$Me)(BH$_4$) (0.36 g, 1.3 mmol) in ether (20 ml) was added NEt$_3$ (0.67 ml, 4.8 mmol) and HSiCl$_3$ (0.9 g, 6.7 mmol). After 2 h of stirring at ambient temperature the colour changed to yellow. After this the reaction mixture was stirred for an additional 1 h and then all the volatiles were removed under vacuum and the residue was extracted with ether (2*20 ml). After concentration of the ether fractions under vacuum to 5 ml, the solution was cooled down to -30°C and the product precipitated after 2 days in a form of yellow crystals. Yield 0.39 g (76%).

^{1}H NMR (C$_6$D$_6$): δ 4.22 (s, 5, Cp), 1.48 (m, 2, P(C*H*(CH$_3$)$_2$), 0.77 (dd, *J*(P-H) = 15.9 Hz, *J*(H-H) = 7.1 Hz, 6, PCH(C*H*$^a_3$)), 0.62 (d, *J*(P-H) = 8.8 Hz, 3, P*C*H$_3$), 0.58 (dd, *J*(P-H) = 13.5 Hz, J(H-H) = 6.4 Hz, 6, PCH(C*H*$^b_3$)), -14.6 (d, *J*(P-H) = 50.6 Hz, 2, Fe*H*). ^{31}P NMR (C$_6$D$_6$): δ 78.0 (s). ^{13}C NMR (C$_6$D$_6$): δ 80.4 (s, Cp), 26.9 (d, *J*(P-C) = 27.5 Hz, P(*C*H(CH$_3$)$_2$), 17.8 (s, PCH(*C*^{a}H$_3$)), 16.7 (s, PCH(*C*^{b}H$_3$)), 9.7 (d, *J*(P-C) = 24.2 Hz, P*C*H$_3$). ^{29}Si NMR (C$_6$D$_6$): δ 39.6 (dt, *J*(Si-P) = 14.5 Hz, *J*(Si-H) = 18.9 Hz). IR (Nujol): 1923 cm^{-1}. Anal. Calcd. for C$_{12}$H$_{24}$Cl$_3$PFeSi: C, 37.00; H, 6.21. Found: C, 37.27; H, 6.41.

Preparation of CpFe(PPr$^i_2$Me)H$_2$SiMeCl$_2$.

To a green solution of CpFe(PPr$^i_2$Me)(BH$_4$) (0.40 g, 1.5 mmol) in ether (20 ml) was added NEt$_3$ (0.7 g, 7.5 mmol) and HSiMeCl$_2$ (0.86 g, 7.5 mmol). After 2 h of stirring at ambient temperature the colour changed to yellow. After this the reaction mixture was stirred for an additional 1 h and then all the volatiles were removed under vacuum and the residue was extracted with ether (2*20 ml). After concentration of the ether fractions under vacuum to 5 mL, the solution was cooled down to -30°C and the product precipitated after 1 day in a form of yellow crystals. Yield 0.44 g (80%).

^{1}H NMR (C$_6$D$_6$): δ 4.25 (s, 5, Cp), 1.35 (m, 2, P(C*H*(CH$_3$)$_2$), 1.16 (s, 3, SiC*H*$_3$), 0.75 (dd, *J*(P-H) = 15.4 Hz, *J*(H-H) = 7.3 Hz, 6, PCH(C*H*$^a_3$)), 0.59 (dd, *J*(P-H) = 13.5 Hz, *J*(H-H) = 7.0 Hz, 6, PCH(C*H*$^b_3$)), 0.56 (d, *J*(P-H) = 8.1 Hz, 3, P*C*H$_3$), -15.06 (d+sat, *J*(P-H) = 50.6 Hz, *J*(Si-H) = 18.3 Hz, 2, Fe*H*). ^{31}P NMR (C$_6$D$_6$): δ 80.6 (s). ^{13}C NMR (C$_6$D$_6$): δ 79.5 (s, Cp), 27.2 (d, *J*(P-C) = 26.4 Hz, P*C*H(CH$_3$)$_2$), 22.5 (s, Si*C*H$_3$), 17.8 (s, PCH(*C*^{a}H$_3$)), 16.7 (s, PCH(*C*^{b}H$_3$)), 10.1 (d, *J*(P-C) = 23.1 Hz, P*C*H$_3$). ^{29}Si (sel.

decoupled from Me group) NMR (C_6D_6): δ 70.0 (dt, *J*(Si-P) = 14.1 Hz, *J*(Si-H) = 19.2 Hz). IR (Nujol): 1922 cm^{-1}. Anal. Calcd. for $C_{13}H_{27}Cl_2PFeSi$: C, 42.30; H, 7.37. Found: C, 42.16; H, 7.54.

Preparation of $CpFe(PPr^i_2Me)H_2SiMe_2Cl$.

To a green solution of $CpFe(PPr^i_2Me)(BH_4)$ (0.39 g, 1.4 mmol) in ether (20 ml) was added NEt_3 (0.7 g, 7.5 mmol) and $HSiMe_2Cl$ (0.66 g, 7 mmol). After 2 h of stirring at ambient temperature the colour changed to yellow. After this the reaction mixture was stirred for an additional 1 h and then all the volatiles were removed under vacuum and the residue was extracted with ether (2*20 ml). After concentration of the ether fractions under vacuum to 5 mL, the solution was cooled down to -30°C and the product precipitated after 1 day in a form of yellow crystals. Yield 0.39 g (80%).

^1H NMR (C_6D_6): δ 4.21 (s, 5, Cp), 1.37 (m, 2, $P(CH(CH_3)_2)$, 0.91 (s, 3, $SiCH_3$), 0.80 (dd, *J*(P-H) = 15.1 Hz, *J*(H-H) = 6.9 Hz, 6, $PCH(CH^a_3)$), 0.67 (dd, *J*(P-H) = 13.1 Hz, *J*(H-H) = 7.1 Hz, 6, $PCH(CH^b_3)$), 0.62 (d, *J*(P-H) = 9.1 Hz, 3, PCH_3), -15.70 (d, *J*(P-H) = 50.5 Hz, 2, Fe*H*). ^{31}P NMR (C_6D_6): δ 83.1 (s). ^{13}C NMR (C_6D_6): δ 78.1 (s, Cp), 27.3 (d, J(P-C) = 25.3 Hz, $PCH(CH_3)_2$), 17.9 (s, $PCH(C^aH_3)$), 17.6 (s, $SiCH_3$), 16.9 (s, $PCH(C^bH_3)$), 10.5 (d, J(P-C) = 22.0 Hz, PCH_3). ^{29}Si (sel. decoupled from Me groups) NMR (C_6D_6): δ 63.8 (dt, *J*(Si-P) = 13.1 Hz, *J*(Si-H) = 21.8 Hz). IR (Nujol): 1930 cm^{-1}.

Preparation of $CpFe(PPr^i_2Me)H_2SiH_2Ph$.

To a green solution of $CpFe(PPr^i_2Me)(BH_4)$ (0.34 g, 1.3 mmol) in ether (20 ml) was added NEt_3 (0.7 g, 7.5 mmol) and H_3SiPh (0.7 g, 6.5 mmol). After 1 day of stirring at ambient temperature the colour changed to yellow. All the volatiles were then removed under vacuum and the residue was extracted with ether (2*20 ml). All the attempts to crystallize this complex were unsuccessful. The final product was obtained in a form of yellow oil after drying the solution under vacuum. Yield 0.38 g (80%).

^1H NMR (C_6D_6): δ 8.15 (m, 2, Ph), 7.37 (m, 2, Ph), 7.27 (m, 1, Ph), 5.39 (s+sat, J(Si-H) = 183.4 Hz, 2, Si*H*), 4.09 (s, 5, Cp), 1.44 (m, 2, $P(CH(CH_3)_2)$, 0.87 (dd, *J*(P-H) = 14.7 Hz, *J*(H-H) = 6.6 Hz, 6, $PCH(CH^a_3)$), 0.75 (dd, *J*(P-H) = 12.5 Hz, *J*(H-H) = 6.6 Hz, 6, $PCH(CH^b_3)$), 0.65 (d, *J*(P-H) = 7.3 Hz, 3, PCH_3), -15.24 (d+sat, *J*(P-H) = 52.1 Hz, *J*(Si-H) = 19.8 Hz, 2, Fe*H*). ^{31}P NMR (C_6D_6): δ 85.0 (s). ^{13}C NMR (C_6D_6): δ 145.5 (s, Ph), 135.0 (s, Ph), 76.9 (s, Cp), 27.4 (d, *J*(P-C) = 24.2 Hz, $PCH(CH_3)_2$), 18.0

(s, PCH(C^aH_3)), 17.2 (s, PCH(C^bH_3)), 10.3 (d, J(P-C) = 25.3 Hz, PCH_3). ^{29}Si NMR (C_6D_6): δ -13.8 (m). IR (Nujol): 2064, 2025, 1916 cm^{-1}.

Preparation of CpFe(PPr$^i_2$Me)H_2SiHMePh.

To a green solution of CpFe(PPr$^i_2$Me)(BH_4) (0.3 g, 1.1 mmol) in ether (20 ml) was added NEt_3 (0.7 g, 7.5 mmol) and H_2SiMePh (0.67 g, 5.5 mmol). After 1 day of stirring at ambient temperature the colour changed to yellow. All the volatiles were then removed under vacuum and the residue was extracted with ether (2*20 ml). All the attempts to crystallize this complex were unsuccessful. The final product was obtained in a form of yellow oil after drying the solution under vacuum. Yield 0.34 g (82%).

^{1}H NMR (C_6D_6): δ 8.02 (m, 2, Ph), 7.37 (m, 2, Ph), 7.25 (m, 1, Ph), 5.33 (bs+sat, J(Si-H) = 181 Hz, 1, SiH), 4.06 (s, 5, Cp), 1.43 (m, 2, P(CH(CH_3)$_2$), 0.90 (bs, 3, SiCH_3), 0.89 (m, 6, PCH(CH^a_3)), 0.78 (m, 6, PCH(CH^b_3)), 0.66 (d, J(P-H) = 8.0 Hz), 3, PCH_3), -15.34 (d+sat, J(P-H) = 53.0 Hz, J(Si-H) = 21.2 Hz, 1, Fe-H^a), -15.52 (d+sat, J(P-H) = 54 Hz, J(Si-H) = 17.0 Hz, 1, Fe-H^b). ^{31}P NMR (C_6D_6): δ 85.5 (s). ^{13}C NMR (C_6D_6): δ 149.4 (s, Ph), 134. 2 (s, Ph), 76.7 (s, Cp), 27.4 (d, J(P-C) = 25.2 Hz, PCH(CH_3)$_2$), 18.1 (s, PCH(C^aH_3)), 17.2 (s, PCH(C^bH_3)), 10.5 (d, J(P-C) = 24.0 Hz, PCH_3). ^{29}Si INEPT+ NMR (C_6D_6): δ 5.1 (d, J(Si-H) = 183 Hz). IR (Nujol): 2052, 1927 cm^{-1}.

Preparation of CpFe(PPr$^i_2$Me)H_2SiMe$_2$Ph

To a green solution of CpFe(PPr$^i_2$Me)(BH_4) (0.35 g, 1.3 mmol) in ether (20 ml) was added NEt_3 (0.67 ml, 4.8 mmol) and HSiMe$_2$Ph (0.88 g, 6.5 mmol). After 1 day of stirring at ambient temperature the colour changed to yellow. All the volatiles were then removed under vacuum and the residue was extracted with ether (2*20 ml). After concentration of the ether fractions under vacuum to 5 ml, the solution was cooled down to -30°C and the product precipitated after 5 days in a form of yellow crystals. Yield 0.39 g (76%).

^{1}H NMR (C_6D_6): δ 7.97 (m, 2, Ph), 7.36 (m, 2, Ph), 7.23 (m, 1, Ph), 4.03 (s, 5, Cp), 1.34 (m, 2, P(CH(CH_3)$_2$), 0.90 (dd, J(P-H) = 14.9 Hz, J(H-H) = 7.1 Hz, 6, PCH(CH^a_3)), 0.75 (s, 6, SiMe), 0.74 (dd, J(P-H) = 12.8 Hz, J(H-H) = 7.1 Hz, 6, PCH(CH^b_3)), 0.59 (d, J(P-H) = 8.2 Hz, 3, PCH_3), -15.75 (d+sat, J(P-H) = 52.8 Hz, J(Si-H) = 21.1 Hz, 2, Fe-H). ^{31}P NMR (C_6D_6): δ 85.3 (s). ^{13}C NMR (C_6D_6): δ 159.1 (s,

Ph), 133.5 (s, Ph), 76.9 (s, Cp), 27.5 (d, J(P-C) = 24.1 Hz, P*C*H(CH$_3$)$_2$), 18.2 (s, PCH(*C*^{a}H$_3$)), 17.0 (s, PCH(*C*^{b}H$_3$)), 10.6 (d, J(P-C) = 21.4 Hz, P*C*H$_3$). ^{29}Si NMR (C_6D_6): δ 16.6 (m). IR (Nujol): 1942 cm^{-1}.

The reaction of CpFe(PPr$^i_2$Me)H$_2$SiMe$_2$Cl with [Ph$_3$C]BAF

To a solution of CpFe(PPr$^i_2$Me)H$_2$SiMe$_2$Cl (0.010 g, 0.03 mmol) in CD_2Cl_2 (0.6 mL) was added [Ph$_3$C]BAF (0.026 g, 0.03 mmol). Mixture of products was obtained, which gave many broad signals in NMR spectra.

The reaction of CpFe(PPr$^i_2$Me)H$_2$SiMe$_2$Cl with LiBAF

To a solution of CpFe(PPr$^i_2$Me)H$_2$SiMe$_2$Cl (0.040 g, 0.12 mmol) in CD_2Cl_2 (0.6 mL) was added LiBAF (0.087 g, 0.12 mmol). Only one broad signal from 10 to 0 ppm was observed in ^{1}H NMR, suggesting preparation of paramagnetic compounds.

The reaction of CpFe(PPr$^i_2$Me)H$_2$SiCl$_3$ with LiBAF

To a solution of CpFe(PPr$^i_2$Me)H$_2$SiCl$_3$ (0.017 g, 0.043 mmol) in CD_2Cl_2 (0.6 mL) was added LiBAF (0.033 g, 0.043 mmol). The reaction led to broadening of all the signals in ^{1}H NMR, mixture of complexes was obtained.

The reaction of CpFe(PPr$^i_2$Me)(CH$_3$CN)$_2$PF$_6$ with HSiCl$_3$ in the presence of LiCl

To a solution of CpFe(PPr$^i_2$Me)(CH$_3$CN)$_2$PF$_6$ (0.020 g, 0.041 mmol) and $HSiCl_3$ (4.2 μl, 0.041 mmol) in $CDCl_3$ (0.6 mL) was added LiCl (0.002 g, 0.041 mmol). Mixture of compounds was obtained with broad signals in ^{1}H NMR.

General procedure for catalytic hydrosilylation of benzaldehyde in the presence of CpFe(PPr$^i_2$Me)H$_2$SiR$_3$

To a solution of benzaldehyde (25 μl, 0.2 mmol) and equimolar quantity of silane $HSiR_3$ in C_6D_6 (≈ 0.6 ml) was added 5% mol of coplex CpFe(PPr$^i_2$Me)H$_2$SiR$_3$. Then solution was heated up to 50°C. The reaction was monitored by NMR analysis.

Hydrosilylation of carbonyls in the presence of [CpFe(PPr$^i_2$Me)(CH$_3$CN)$_2$]$^+$

Hydrosilylation acetone with H$_3$SiPh

Method 1. To a solution of H_3SiPh (20 μL, 0.16 mmol) in acetone-d6 was added $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (0.004 g, 5% mol). The color of the solution changed from red to yellow in about 10 seconds. There was 80% conversion of H_3SiPh into a mixture of $R_{4-n}Si(OCH(CD_3)_2)_n$ after 2 h at ambient temperature. Full conversion of the starting silane was observed on the next day with the formation of a mixture of $PhHSi(OCH(CD_3)_2)_2$ (83%)and $PhH_2Si(OCH(CD_3)_2)$ (17%).

Method 2. Complex $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (0.002 g, 0.5% mol) was added to pyridine (65 μL, 0.81 mmol), followed by addition of H_3SiPh (100 μL, 0.81 mmol). Part of the resulting brown mixture was then dissolved in acetone-d_6. Immediate full conversion of the starting silane into $PhHSi(OCH(CH_3)_2)_2$ was observed.

Note: No reaction was observed between PhC(O)Me and H_3SiPh in the presence of $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (5% mol) and pyridine (10% mol) under solvent-free conditions or in $CDCl_3$. Also, no reaction was observed between acetone and H_3SiPh in the presence of $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (5% mol) and pyridine (10% mol) in $CDCl_3$, THF, and CD_3CN.

Hydrosilylation of acetone with $H_2SiMePh$

Method 1. To a mixture of $H_2SiMePh$ (0.56 mL, 4.08 mmol), acetone (0.3 mL 4.08 mmol) and pyridine (33 μL, 10% mol) was added $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (0.002 g, 0.1% mol). There was 70% conversion of $H_2SiMePh$ with a formation of $HMePhSi(OCH(CH_3)_2)$ after 24h at ambient temperature.

Method 2. To a solution of pyridine (15 μL, 0.18 mmol) and $CpFe(PPr^i_2Me)(CH_3CN)_2PF_6$ (0.004, 5% mol) in acetone-d6 (0.6 mL) was added $H_2SiMePh$ (25 μL, 0.18 mmol). Full conversion of $H_2SiMePh$ into a mixture of products ($HMePhSi(OCH(CD_3)_2)$ (77%)) was observed after 30 min at ambient temperature.

General procedure for hydrosilylation of carbonyls under solvent-free conditions

To a mixture of H_3SiPh (100 μL, 0.81 mmol) and a carbonyl substrate (0.81 mmol) was added $CpFe(PPr^i_2Me)(CH_3CN)_2BAF$ (0.5% mol). The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by NMR spectroscopy.

VI. Appendix

Table 22. Crystal structure determination parameters for $CpRu(PPr^i_3)(H)(Cl)SiMeCl_2$

Empirical formula	$C_{15}H_{30}Cl_3PRuSi$
Formula weight	476.87
Colour, habit	yellow, block
Crystal size, mm^3	0.22x0.18x0.16
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	14.0955(12)
b, Å	10.1064(8)
c, Å	14.5917(13)
α, deg.	90.00
β, deg.	99.837(4)
γ deg.	90.00
Volume, $Å^3$	2048.1(3)
Z	4
Density (calculated), g/cm^3	1.547
Absorption coefficient, mm^{-1}	1.286
F(000)	976
Diffractometer	Bruker SMART
Temperature, K	123(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K_α
Scan mode	ω
Scan step (in omega), deg	0.3
Time per step, sec.	15
Theta range for data collection, deg	1.47 to 29.99

Index ranges	$-18 \leq h \leq 19, -14 \leq k \leq 14, -20 \leq l \leq 20$
Reflections collected	23649
Independent reflections	5173 [R(int) = 0.0432]
Absorption correction	multi-scan
Max. transmission	0.7651
Min. transmission	0.8207
Refinement method	Full-matrix least-squares on F^2 (SHELXTL-Plus)
Data / restraints / parameters	5844/0/298
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(I)]	$R_1 = 0.0432$, $wR_2 = 0.1215$
R indices (all data)	$R_1 = 0.0477$, $wR_2 = 0.1268$
Largest diff. peak and hole, e.Å^{-3}	
Extinction coefficient	

Table 23. Crystal structure determination parameters for $CpRu(PPr^i_3)(H)(Cl)SiMe_2Cl$

Empirical formula	$C_{16}H_{33}Cl_2PRuSi$
Formula weight	456.45
colour, habit	yellow, block
Crystal size, mm^3	0.20x0.16x0.10
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	14.1429(13)
b, Å	10.1525(9)
c, Å	14.5883(13)
α, deg.	90.00
β, deg.	99.779(2)
γ deg.	90.00

Volume, $Å^3$	2064.2(3)
Z	4
Density (calculated), g/cm^3	1.469
Absorption coefficient, mm^{-1}	1.147
F(000)	944
Diffractometer	Bruker SMART
Temperature, K	120(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K_α
Scan mode	ω
Scan step (in omega), deg	0.3
Time per step, sec.	15
Theta range for data collection, deg	2.455 to 29.872
Index ranges	$-17 \leq h \leq 5$, $-12 \leq k \leq 9$, $-16 \leq l \leq 17$
Reflections collected	8892
Independent reflections	4026 [R(int) = 0.0589]
Absorption correction	multi-scan
Max. transmission	0.8030
Min. transmission	0.8939
Refinement method	Full-matrix least-squares on F^2 (SHELXTL-Plus)
Data / restraints / parameters	4026/0/201
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	$R_1 = 0.0525$, $wR_2 = 0.1028$
R indices (all data)	$R_1 = 0.0834$, $wR_2 = 0.1105$
Largest diff. peak and hole, $e.Å^{-3}$	
Extinction coefficient	

Table 24. Crystal structure determination parameters for $CpFe(PPr^{i}_{2}Me)H_2SiMeCl_2$

Empirical formula	$C_{13}H_{27}Cl_2FePSi$
Formula weight	369.16
Colour, habit	yellow, block
Crystal size, mm^3	0.36x0.18x0.08
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	11.6589(3)
b, Å	12.7671(3)
c, Å	12.0791(4)
α, deg.	90.00
β, deg.	94.9630(10)
γ deg.	90.00
Volume, Å3	1791.24(9)
Z	4
Density (calculated), g/cm^3	1.369
Absorption coefficient, mm^{-1}	1.280
F(000)	776
Diffractometer	Bruker SMART
Temperature, K	120(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K_α
Scan mode	ω
Scan step (in omega), deg	0.3
Time per step, sec.	15
Theta range for data collection, deg	2.33 to 30.00
Index ranges	$-15 \leq h \leq 16, -17 \leq k \leq 16, -14 \leq l \leq 16$
Reflections collected	11306

Independent reflections	4761
Absorption correction	multi-scan
Max. transmission	0.7651
Min. transmission	0.8207
Refinement method	Full-matrix least-squares on F^2 (SHELXTL-Plus)
Data / restraints / parameters	4761/0/271
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	$R_1 = 0.0344$, $wR_2 = 0.0704$
R indices (all data)	$R_1 = 0.0550$, $wR_2 = 0.0754$

Table 25. Crystal structure determination parameters for $CpFe(PPr^i_2Me)H_2SiCl_3$

Empirical formula	$C_{12}H_{24}Cl_3FePSi$
Formula weight	389.57
Colour, habit	yellow, block
Crystal size, mm^3	0.40 0.20x0.10
Crystal system	orthorhombic
Space group	Pbcm
Unit cell dimensions:	
a, Å	8.6134(3)
b, Å	16.7404(6)
c, Å	12.0404(4)
α, deg.	90.00
β, deg.	90.00
γ deg.	90.00
Volume, $Å^3$	1736.13(10)
Z	4
Density (calculated), g/cm^3	1.490
Absorption coefficient, mm^{-1}	1.474

F(000)	808
Diffractometer	Bruker SMART
Temperature, K	120(2)
Radiation, (lambda, Å) ,	(0.71073) Mo K_α
Scan mode	ω
Scan step (in omega), deg	0.3
Time per step, sec.	15
Theta range for data collection, deg	2.36 to 29.00
Index ranges	$-10 \leq h \leq 11$, $-22 \leq k \leq 22$, $-15 \leq l \leq 15$
Reflections collected	10323
Independent reflections	2358
Absorption correction	multi-scan
Max. transmission	0.7651
Min. transmission	0.8207
Refinement method	Full-matrix least-squares on F^2 (SHELXTL-Plus)
Data / restraints / parameters	2358/0/124
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	$R_1 = 0.0381$, $wR_2 = 0.0892$
R indices (all data)	$R_1 = 0.0573$, $wR_2 = 0.0946$

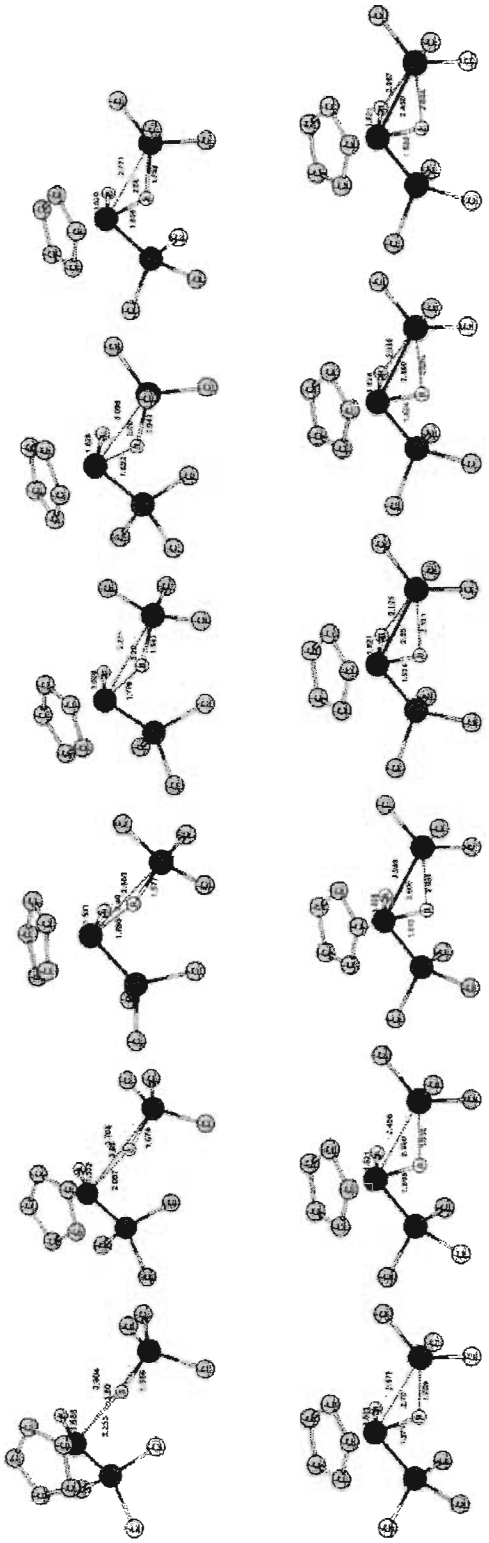


Figure 26. Snap-shots for the addition of trimethylsilane to $CpFe(PMe_3)(H)$. Non-hydridic hydrogen atoms are omitted for clarity. Selected distances are given in Å.

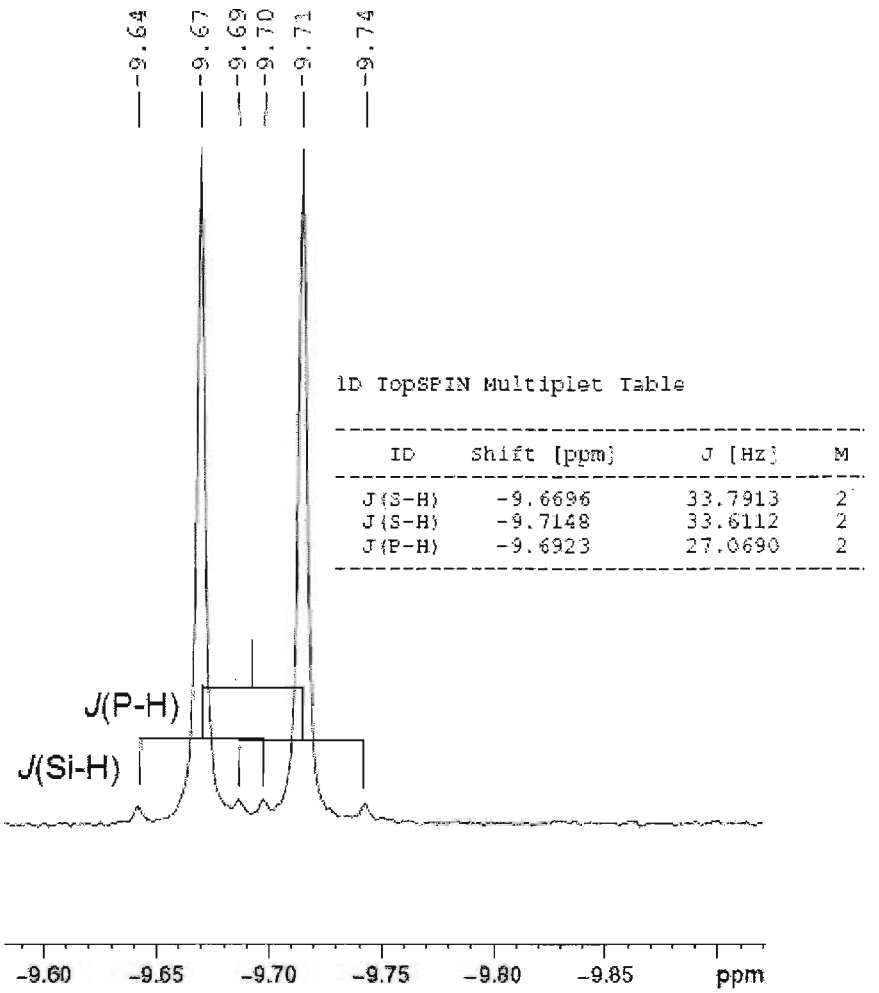


Figure 27. The hydride signal of $CpRu(PPr^i_3)Cl(\eta^2\text{-}HSiCl_3)$ in ^1H NMR with ^{31}P-^1H and ^{29}Si-^1H coupling.

VII. References

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