THE UNIVERSITY
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Simplified Access to Low Oxidation-State Earth-Abundant Metals for Catalytic Application

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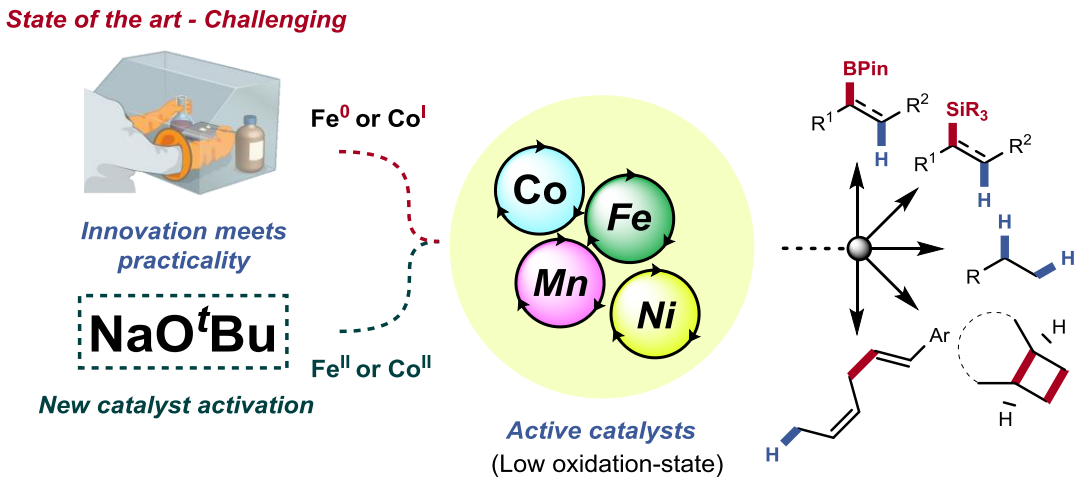
Abstract

A sustainable future lies in the use of first row, low cost, low toxicity, Earth-abundant metals. Despite this, the metals that are most abundant have yet to be widely adopted by the global community. The overarching aim at the outset of the project was to ask the question: Why is this?

Why do expensive metals such as; platinum, palladium and rhodium dominate?

Why does the synthetic chemist not instinctively use iron, manganese or cobalt?

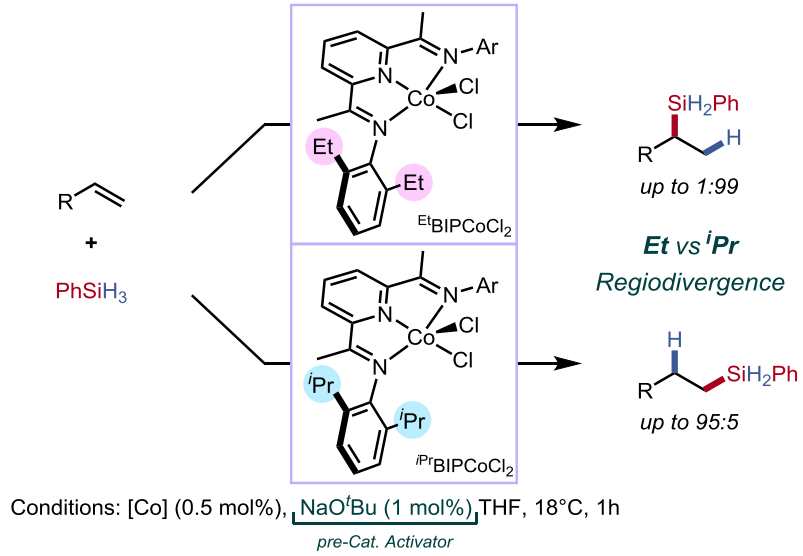
The simple answer: The non-expert chemist is simply not equipped to try.



Many modern synthetic methods for the reductive functionalisation of alkenes and alkynes rely on the use of air- and moisture-sensitive pre-catalysts or reagents, which are challenging to handle, store and transport. In the ideal scenario, all reagents and pre-catalysts would be air- and moisture-stable solids that are easily handled, and applicable in large-scale processes with minimal associated hazards.

This project entailed the development of a simple pre-catalyst activation protocol using a safe and easily handled reagent (NaO^{t}Bu) with wide commercial availability. This has allowed generic access to sustainable first-row transition metal (Fe, Co, Mn, Ni) low oxidation-state catalysis across a wide range of reductive alkene and alkyne functionlisation reactions (hydroboration, hydrosilylation, hydrogenation, hydrovinylation and [2π+2π] cyclisation reactions). Using this straightforward catalyst activation strategy a new

regiodivergent cobalt-catalyst alkene hydrosilylation manifold was discovered and mechanistically explored.



Taken together, all results are suggestive of a new and unique catalyst activation mechanism that is primed for future reaction, catalyst and mechanistic development.

Lay Summary

The majority of processes for the production and manufacture of modern bulk and fine chemicals as well as many materials require the use of a catalyst. A catalyst is a component of a chemical reaction that enables the transformation of starting substances into products that would otherwise not occur under the same conditions and without consumption of the catalyst material.

The use of catalysis is commonly applied to, but is not limited to, the production of: pharmaceuticals, agrochemicals, cosmetics, polymers, fillers, food additives and fuels. It is estimated that a catalyst is required in greater than 90% of all manufacturing processes for these commodities and everyday consumables. Given this requisite in modern industrial applications, a great deal of effort has been, and continues to be, focussed on the discovery and development of new and improved catalysts for both existing and novel chemical processes. Specifically, metals such as: rhodium, palladium and platinum have been widely adopted by the synthetic chemistry community. The high reactivity, ease-of-use and reliability have rendered this choice of metals quintessential.

Modern sustainability requirements and economic drivers have created the opportunity to develop and discover earth-abundant alternative catalysts. Logically, precious metals are intrinsically scarce, economically costly to obtain from ores and therefore expensive. Moreover, they are widely used in modern technology, jewellery and as general stores-of-value. As a result, their use in synthetic applications leads to inflated costs of chemical and materials production. In this context, earth-abundant metals such as iron, cobalt and manganese, offer a low-cost alternative solution that is yet to be widely exploited.

Several research groups in recent years have reported the use of Earth-abundant metals in catalytic applications. A majority of these reactions necessitate the use of a co-ingredient to facilitate catalyst activity - a so-called *activator*. Typical activators pose significant user hazards, such as flammability, and can be difficult to store, transport and handle. Particularly on a large-scale and in industrial settings this risk is unacceptable and renders these methods unusable. To overcome this limitation, this project aimed to replace the hazardous activator with a new class of easy-to-handle and safe alternatives. With this aim the discovery and development of a generic activator was achieved that exists as a safe and non-hazardous solid material. This has enabled the easy use of Earth-abundant metals for catalytic applications.

Declaration

I certify:

a) that the thesis has been composed by myself, and

b) either that the work is my own, or, where I have been a member of a research group, that I have made a substantial contribution to the work, such contribution being clearly indicated, and

c) that the work has not been submitted for any other degree or professional qualification except as specified.

Jamie Docherty

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Abbreviations

Ac	Acetyl
acac	Acetylacetonate
Ar	Aryl
BIP	Bis(imino)pyridine
Bn	Benzyl
Bpin	4,4,5,5-Tetramethyl-1,3,2-dioxaborolane
Bu	Butyl
COD	1,5-Cyclooctadiene
COT	1,3,5,7-Cyclooctatetraene
COE	Cyclooctene
COSY	Correlation spectroscopy
Cp	Cyclopentadienyl
Cy	Cyclohexyl
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
dppe	1,2-Bis(diphenylphosphino)ethane
dr	Diastereomeric ratio
dvtms	1,3-Divinyltetramethyldisiloxane
E	Element
ee	Enantiomeric excess
equiv.	Equivalents
ESI	Electrospray ionisation
Et	Ethyl
EWG	Electron-withdrawing group
GCMS	Gas chromatography mass spectrometry
HMBC	Heteronuclear multiple bond correlation
HMDS	Bis(trimethylsilyl)amide
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
HSQC	Heteronuclear single quantum coherence
IR	Infrared

J	Coupling constant in Hz
L	Ligand
m.p.	Melting point
M	Metal
MD'M	1,1,1,3,5,5,5-Heptamethyltrisiloxane
Me	Methyl
Mes	Mesityl
NBS	*N*-Bromosuccinimide
NMP	*N*-methylpyrrolidine
NMR	Nuclear magnetic resonance
nOe	Nuclear Overhauser effect
Ph	Phenyl
Pr	Propyl
py	Pyridine
Rf	Retention factor
r.t.	Room temperature
TBAF	Tetrabutylammonium fluoride
Terpy	Terpyridine
Tf	Trifluoromethanesulfonyl
THF	Tetrahydrofuran
TMEDA	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TON	Turnover number
Ts	*para*-Toluenesulfonyl
UV	Ultraviolet

1. Introduction

Modern synthetic chemistry relies on a myriad of catalytic methods for the construction of complex molecular frameworks. Catalysis is used to increase reaction efficiency, reduce waste and generate synthetic products that are otherwise inaccessible by other methods.[1] Transition metal catalysis remains at the forefront of chemical synthesis, with the most widely-used and well-known transformations being catalysed by metals such as platinum or palladium.[2-4] These late transition metals, generally from groups 8-10 of the periodic table, have seen widespread adoption by the synthetic community. This is a consequence of the robust and well-understood reactivity of these metals as well as their easy practical application, particularly on a large-scale. For example, palladium-catalysed Suzuki-Miyaura coupling reactions between aryl-boronic acids and aryl-halides are perhaps one of the most well-established applications of homogenous palladium catalysis. This reaction has found wide application in the preparation of many chemical sub-classes, including pharmaceuticals, agrochemicals and bulk chemicals.[5-9]

While the sustainability of any chemical process is aided by the use of a catalyst, the use of precious metals for this role remains an area that has the potential for improvement. Improved sustainability requires either reduced catalyst loadings and effective recycling or a move towards the use of low-cost and low-toxicity Earth-abundant metals, such as iron, manganese or cobalt.[10] The latter has led to a number of uses on the use of these elements in homogeneous catalysis. Many applications using Earth-abundant metals, however, rely on the use of low oxidation-state precursors or active species to facilitate productive catalysis.[11-15] Accessing and handling low oxidation-state first-row complexes is not trivial, and therefore restricts use to the specialist practitioner. Specifically, many low oxidation-state iron- and cobalt species are highly air- and moisture sensitive, rendering handling, transport and storage difficult.

To overcome this practical limitation, a number of *in situ* reductive activation strategies have been developed which has allowed for the use of higher oxidation-state pre-catalysts.[16-18] Tailored and designed pre-catalysts and alternatively an externally added organometallic reagent is necessary to effect this reductive activation. While these strategies have improved the practicality of using low oxidation-state Earth-abundant metal catalysis, these methods are still nevertheless more complex than their comparative late transition metal alternatives.

Alkene and alkyne hydrofunctionalisation reactions are an area where low oxidation-state first-row metal complexes have shown tremendous promise as a replacement for precious

metal catalysts.[16,19-20] These synthetic reactions allow for the addition of hydrofunctionalisation reagents (H-ER_x) across an alkene or alkyne, forming a new carbon-carbon or carbon-heteroatom bond. Classically these reactions have been carried out using rhodium, palladium, platinum or iridium.[20] At present, reactions such as hydrogenation, hydroboration, hydrosilylation and hydrovinylation can all be achieved using low oxidation-state first-row metal catalysis[11-20]. The majority of homogeneous catalysts for these transformations rely on the use of either reducing metals or organometallic reagents as a means to access their low oxidation-state active catalyst.

1.1 Overview of activation strategies for low oxidation-state catalysis

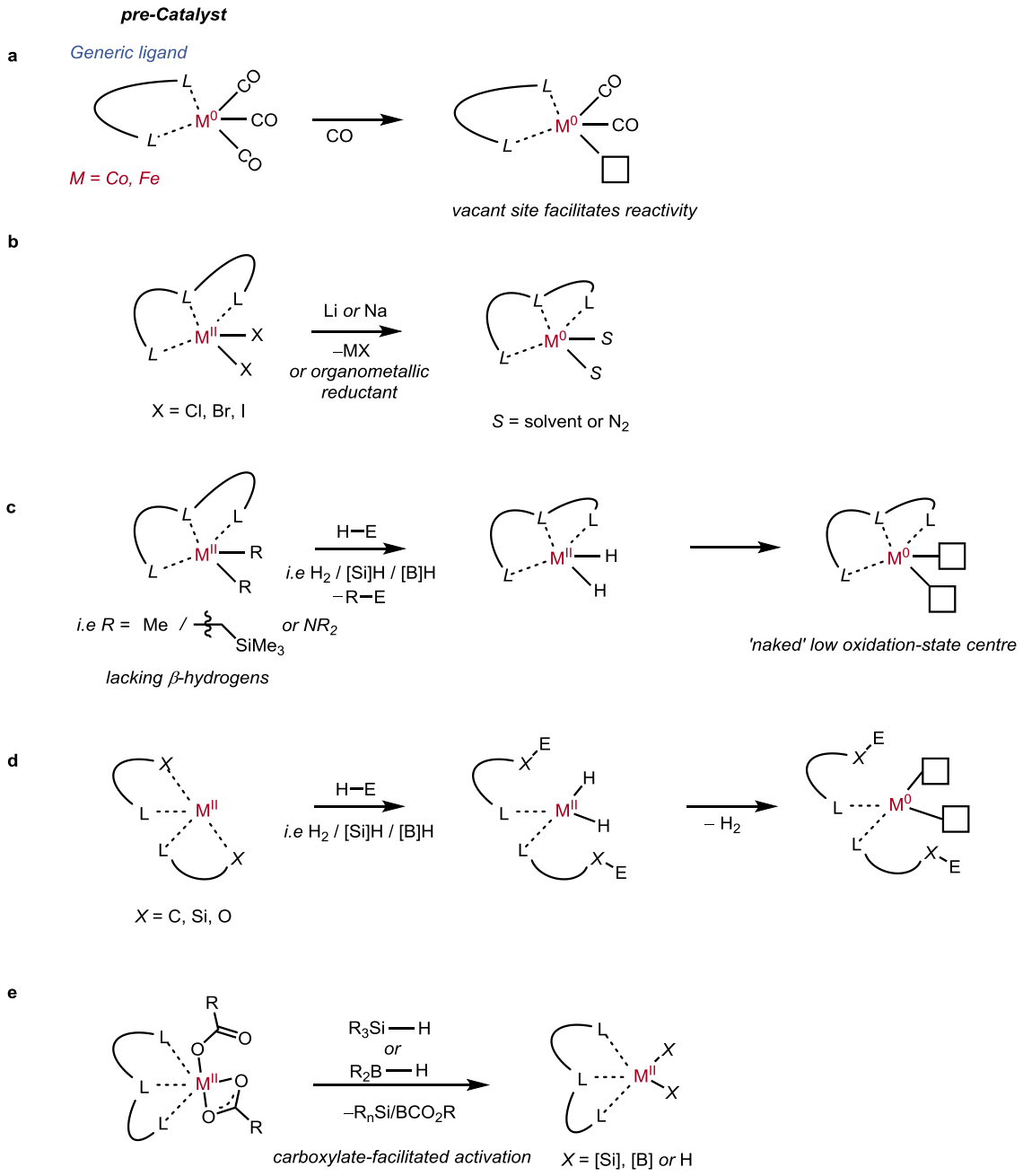
The discovery and development of synthetic methods using first-row transition metals for reductive hydrofunctionalisation reactions has relied on the use of low oxidation-state metal catalysts. Several methods have been reported as a means to access these low oxidation-state species and enable successful chemical transformations. The earliest examples utilised metal-carbonyl complexes as precursors which were activated *in situ* by thermal methods (Scheme 1.1, **a**).[21-25] These metal-carbonyl complexes were already in a low oxidation-state, typically iron(0) or cobalt(0), supported by carbon monoxide ligands.[26] In a number of examples, complexes bearing multi-dentate ligands could also be used for catalysis and were similarly activated thermally or photochemically to initiate catalysis.[21,26]

Metal-halide precursors have been reduced using strongly reducing metals, such as lithium or sodium, in the presence of solvent or dinitrogen to give their corresponding low oxidation-state complex (Scheme 1.1, **b**).[16,17,27,28] Using this activation method, iron(II)- and cobalt(II)-dihalide precursors usually bearing tridentate ligands were reduced and isolated as their solvent or dinitrogen adducts. The advantage of this method is the ability to characterise the reduction product by crystallographic methods, which has aided mechanistic studies.

Metal-alkyl complexes, whereby the metal centre is ligated by a carbon-group have been used as precursors that form an active catalyst upon reaction with a hydrofunctionalisation reagent (H-ER_x, Scheme 1.1, **c**).[18,29-33] These metal-alkyl precursors are typically prepared using alkyl-lithium or alkyl-Grignard reagents in combination with a metal-dihalide precursor. It is important to note that the alkyl-groups do not contain any available β-hydrogens, as available β-hydrogens have a propensity for β-hydride elimination and therefore complicate isolation.

Tethered complexes have been designed and used as high oxidation-state precursors for hydrofunctionalisation reactions (Scheme 1.1, **d**).[18,34-36] These complexes are designed bearing a carbon-metal or oxygen-metal bond in the pre-catalyst that has been proposed to react with a hydrofunctionalisation reagent (H-ER_x) to give a metal-hydride species. The metal-hydride species could then either partake in catalysis or serve as a precursor to a low oxidation-state metal centre following reductive elimination of dihydrogen.

Metal-carboxylate complexes have been used as stable precursors that undergo reaction with hydrofunctionalisation reagents (H-ER_3) to give reactive metal catalysts (Scheme 1.1, **e**).[37,38] This class of pre-catalyst has typically been ligated by tridentate ligands for hydroboration and hydrosilylation reactions. The reactivity of the overall system and activation ability of the carboxylate-ligands has been shown to be highly dependent on the nature of the hydrofunctionalisation reagent. Furthermore, by comparison to metal-halide precursors, the related metal-carboxylate salts have less commercial availability and in some examples are air- and moisture-sensitive. The resulting complexes of carboxylate salts and tridentate ligands have shown good air- and moisture-stablity.

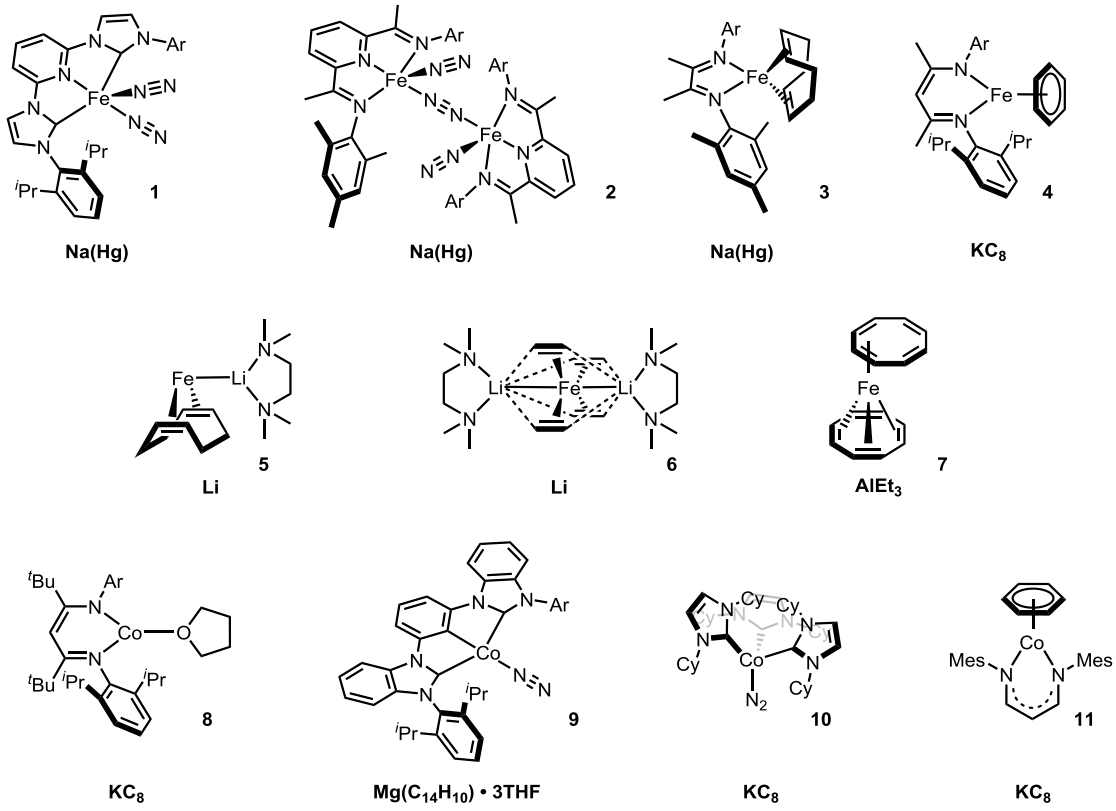


Scheme 1.1. Activation of iron and cobalt pre-catalysts for low oxidation-state catalysis. **a** Carbonyl dissociation to access active metal species. **b** Reduction of metal(II) dihalide precursors with reducing metals or reducing organometallic reagents to give low oxidation-state isolates. **c** Metal pre-catalysts bearing alkyl or amide groups that undergo reactions with reactants to form active species. **d** Metal pre-catalysts bearing ligands with tethered bonds, *i.e* carbon, silicon or oxygen, which react with substrates to give active metal species. **e** Metal-carboxylate complexes that react with substrates to give active metal species.

1.2 Low oxidation-state isolated complexes used in catalysis

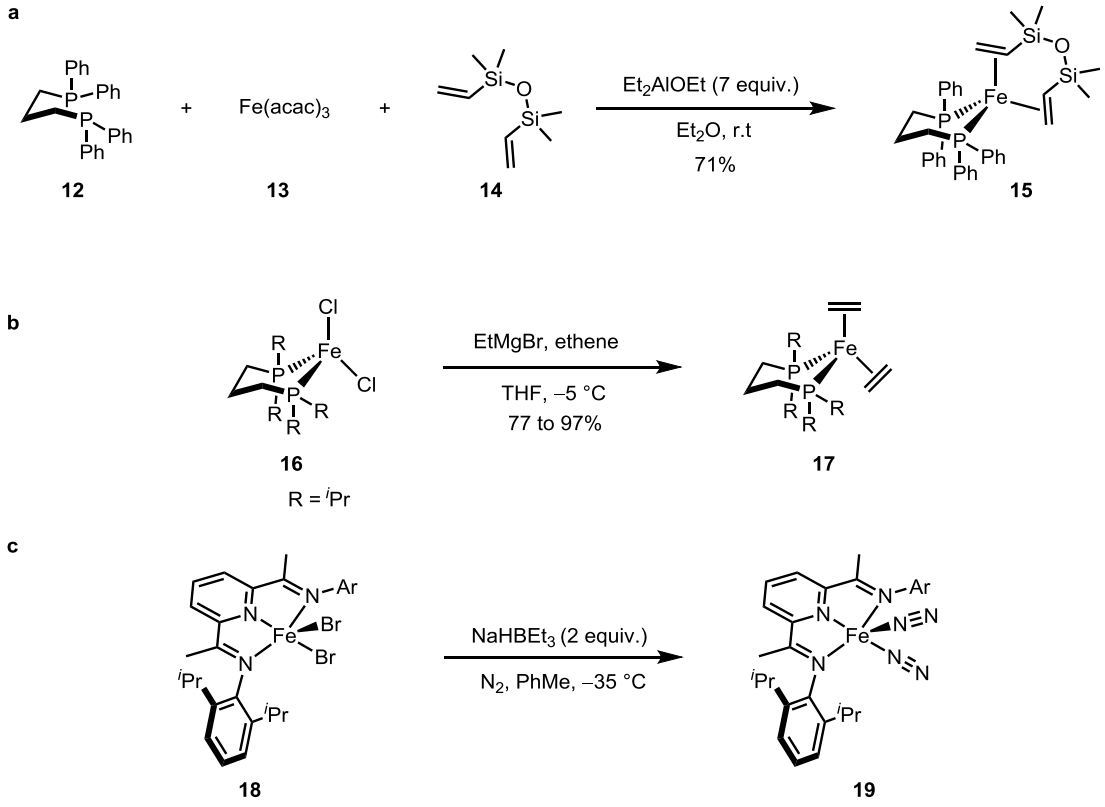
Low oxidation-state isolated complexes of alkene, solvent and dinitrogen adducts are widely used as robust catalysts for a number of hydrofunctionalisation transformations.[17,39] Crystallographic characterisation of low oxidation-state isolated complexes has provided evidence for the coordination modes and oxidation states of these complexes and aided mechanistic studies. Isolated low oxidation-state iron and cobalt-catalysts have been generally prepared by the reduction of a higher oxidation-state precursor. Typically highly reducing metals such as lithium, sodium or potassium have been used (Scheme 1.2). Chirik has demonstrated for many complexes that sodium-mercury amalgam gave access to the iron(0)-dinitrogen complexes **1** and **2** from their iron(II)-dihalide precursors.[27,40] Similarly, sodium-mercury amalgam reduction of an *N*-mesityl-subustituted bisimine iron(II) dichloride precursor in the presence of cyclooctadiene (COD) gave the resulting bisimine-iron(0)-COD adduct **3**.[41] Holland showed that potassium-graphite mediated reduction of the nacnac-iron(II)-chloride complex in benzene gave the resulting nacnac-iron(I)-benzene adduct **4**.[42] Furstner has shown that a number of low oxidation-state iron complexes in oxidation states ranging through –2, –1, 0 and +1, could be isolated following reduction of iron(II) halide salts using lithium metal in the presence of alkenes.[43] An early isolation of iron(0)biscyclooctatetraene [$Fe(COT)_2$] **7** was achieved by Allegra by reduction of iron(III)$(acac)_3$ using triethylaluminium.[44,45]

The same strategies that have been used for the reduction of higher oxidation-state iron precurors have also been applied to the reduction of cobalt(II) complexes. Holland reported the reduction of a bulky *tert*-butyl-nacnac-cobalt(II)-chloride complex using potassium graphite in THF to give the resulting *tert*-butyl-nacnac-cobalt(I)-THF adduct **8**.[46] Fout used magnesium-anthracene as a reductant in the isolation of a biscarbene-cobalt(I)dinitrogen complex **9**.[47,48] Deng showed that a tris-NHC ligated cobalt(I)-chloride complex could be reduced by potassium graphite under an atmosphere of dinitrogen to give the resulting cobalt(0)-dinitrogen complex **10**.[49] Similarly, Holland used potassium graphite for the reduction of *β*-aldiminate cobalt(II)chloride precursors in benzene to give *β*-aldiminate cobalt(I)benzene species **11**.[50] In all examples, including both iron and cobalt-complexes, higher oxidation-state precursors are transformed to a lower oxidation-state species under strongly reducing conditions.



Scheme 1.2. Low oxidation-state iron and cobalt-complexes used in catalysis. The reductant used for their preparation is noted below each respective structure.

Low oxidation-state iron and cobalt-species can also be isolated following reduction using organometallic reagents. These reagents include, but are not limited to, alkyl-lithium, alkyl-Grignard, aryl-Grignard, alkyl-aluminium and borohydride reagents. In this strategy a low oxidation-state metal is presumed to be formed by reductive elimination to give either a C-H, H-H or C-C bond. For example, Breuil used excess diethylaluminiumethoxide as a reductant in the presence of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (dvtms) **14** for the formation of a bisphosphine-iron(0)-dvtms complex **15** (Scheme 1.3, **a**).[51] An alkyl-Grignard was similarly used by Fürstner for the reduction of an bisphosphine-iron(II)dichloride complex **16** under an atmosphere of ethene which gave the corresponding bisphosphine-iron(0)-bisethene complex **17** (Scheme 1.3, **b**).[52] Chirik showed that the bis(imino)pyridine-iron(0)-dinitrogen complex **19** that was accessible by sodium-mercury amalgam reduction could also be accessed using sodium-triethylborohydride.[27]



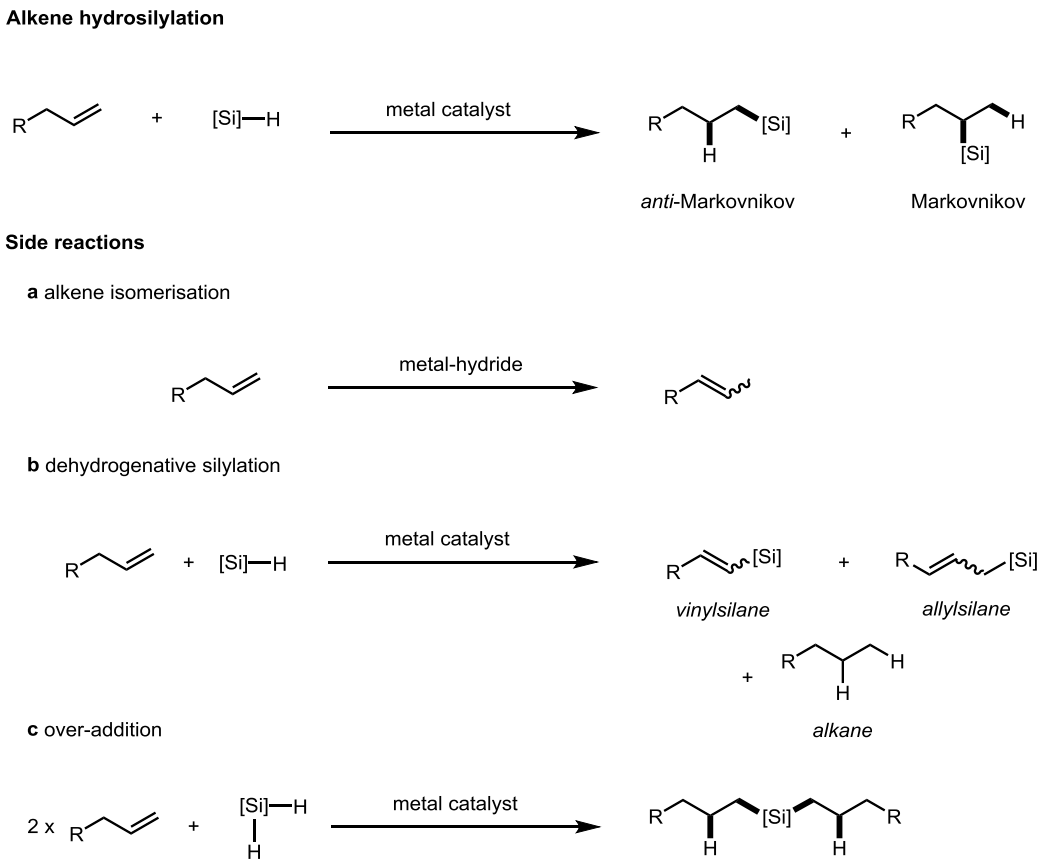
Scheme 1.3. **a** Breuil's formation of a phosphine and alkene stabilised iron(0) complex **15** using Et_2AlOEt as the reductant. **b** Furstner's formation of a phosphine and ethene stabilised iron(0) complex **17** using EtMgBr. **c** Chirik's borohydride reduction of an iron(II) precursor to give an iron(0)dinitrogen complex **19**.

1.3 Alkene hydrosilylation

Alkene hydrosilylation, the reductive functionalisation of an alkene with a silane reagent, is one of the largest applications of homogeneous catalysis.[53-57] The products of alkene hydrosilylation are used in numerous applications, including; tyres, cosmetic goods, beer additives, coatings, adhesives and surfactants. The majority of industrial alkene hydrosilylation reactions use platinum-based catalysts. However these suffer from scope limitations, such as incompatibility with amino-substituted alkenes and often give products of alkene isomerisation. A 2007 estimate suggested that the global silicones industry consumed approximately 5.6 metric tonnes of platinum annually, and that the majority of this is not recovered.[58] With the widespread utility of platinum in other areas of technology, and in emerging markets, this has encouraged the discovery of alternative metals as hydrosilylation catalysts.

1.3.1 Overview of alkene hydrosilylation and possible side reactions

Alkene hydrosilylation involves the addition of silane (Si-H) reagents reductively across a carbon-carbon double bond. This can occur with varying regioselectivity for either the Markovnikov or *anti*-Markovnikov regioisomer (Scheme 1.4). Most commonly, catalysts are selective for the linear, *anti*-Markovnikov, regioisomer, however regioselectivity is a factor of catalyst design, substrate sterics and substrate electronics.[53] While many catalysts have shown good selectivity for alkene hydrosilylation, unwanted side reactions can often be observed. This is particularly prevalent with platinum catalysts where eventual aggregation to colloidal platinum promotes side reactions, such as alkene isomerisation (Scheme 1.4, **a**).[54] Mechanistically, a metal-hydride species undergoes Markovnikov-selective alkene hydrometallation and subsequently β-hydride elimination to give an internal alkene product. Dehydrogenative silylation is another commonly observed side reaction in alkene hydrosilylation reactions (Scheme 1.4, **b**). This side reaction produces either alkenylsilane or allylicsilane products (by isomerisation and hydrosilylation) alongside an equivalent of alkane. Over-addition of primary- and secondary-silanes can also occur to give bis-alkylsilane products (Scheme 1.4, **c**).



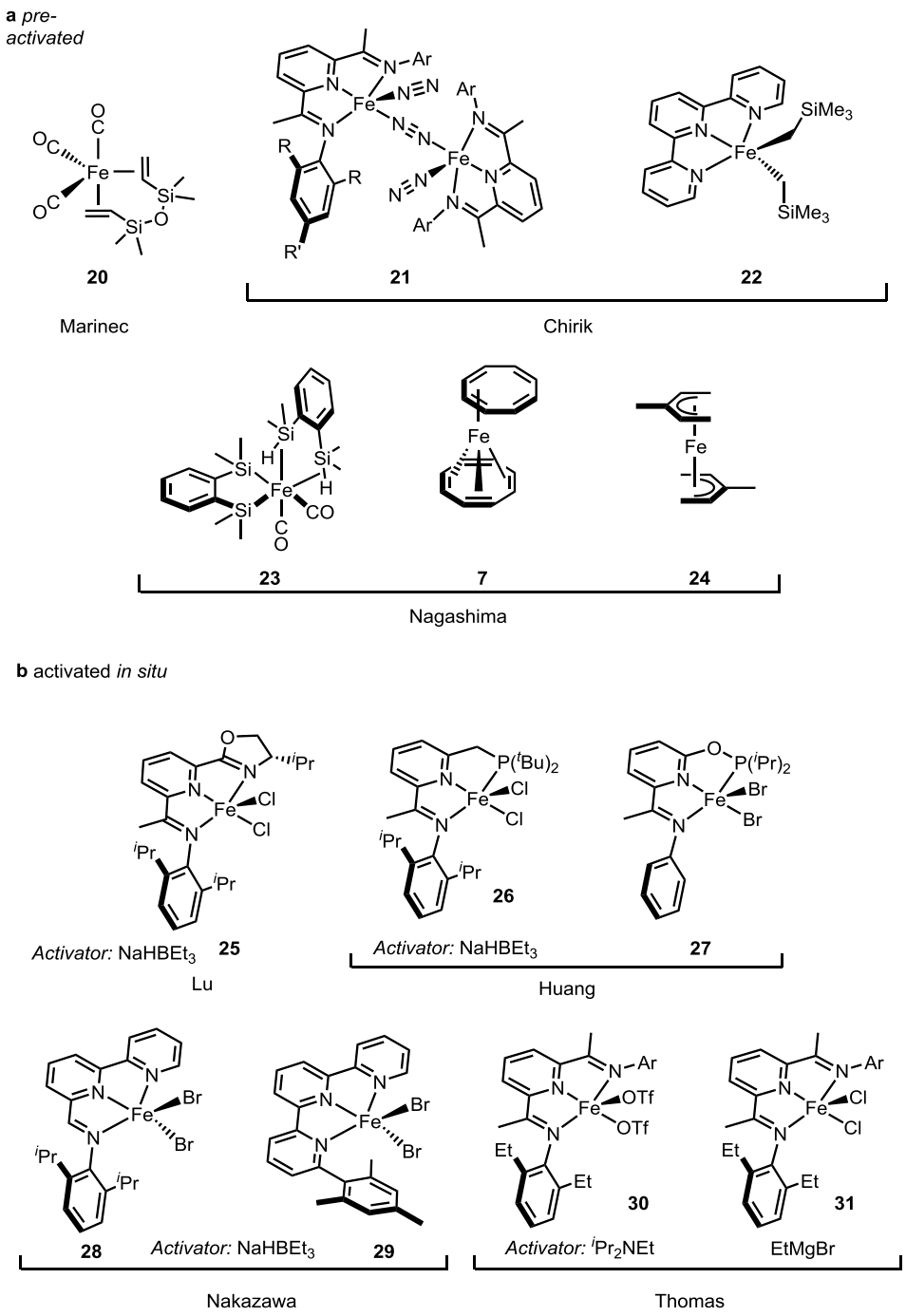
Scheme 1.4. Overview of metal-catalysed alkene hydrosilylation and potential side reactions. **a** Alkene isomerisation facilitated by metal-hydride species. **b** Dehydrogenative silylation to give alkenylsilanes, allylicsilanes and alkanes. **c** Over-addition of primary or secondary silane reagents to multiple alkenes.

1.3.2 Iron and cobalt-complexes used for alkene hydrosilylation

Early reports of iron catalysed alkene hydrosilylation reactions used iron-carbonyl compounds such as $Fe(CO)_5$ and $Fe_3(CO)_{12}$ as pre-catalysts. However these systems required forcing conditions including high temperatures or irradiation with UV light.[16,21] Additionally these catalysts were entirely unselective giving complex mixtures of products arising from side reactions such as alkene isomerisation and dehydrogenative silylation. Marinec later showed that the dvtms-iron(0)-tricarbonyl complex **20** could be used as an effective catalyst for hydrosilylation with tertriary-silanes and tertiary-hydrosiloxanes.[59] Chirik used a series of bis(imino)pyridine-iron(0)dinitrogen complexes for the highly selective hydrosilylation of alkenes.[60] These complexes have proven to be highly selective for the linear alkyl-silanes with a number of silane reagents including; triethylsilane, triethoxysilane and M'DM. Significantly this class of catalyst could operate at extremely low catalyst loadings (as low as 0.004 mol%). The terpyridine supported iron(II) bis-alkyl complex **22** could be used for selective alkene hydrosilylation with tertiary silanes.[61] This complex formed the active catalyst species on reaction of the alkyl-ligands with silane reagents. Nagashima has used a host of iron pre-catalysts for alkene hydrosilylation, including both iron(0) and iron(II) pre-catalysts.[62] The iron(II) carbonyl complex **23** bearing weakly coordinating η^2-(Si-H) bonds and a disilyl ligand could be used as a pre-catalyst for alkene hydrosilylation using several different tertriary silanes and a hydrosiloxane.[63] Nagashima also showed that both iron(0)biscyclooctatetraene **7** and the open ferrocene complex iron(II)-η^5-3-methylpentadienyl **24** could be used in combination with added monodentate isocyanide ligands for alkene hydrosilylation with tertiary silanes.[38]

Iron(II) complexes that were activated *in situ* by external reagents have also shown high activity for alkene hydrosilylation. Lu used the iminopyridineoxazoline-iron(II)dichloride complex **25** activated using $NaHBEt_3$ for the enantioselective hydrosilylation of 1,1-disubstituted alkenes using diphenylsilane.[64] The phosphine(imino)pyridine-iron(II)dichloride complex **26** could similarly be activated using $NaHBEt_3$ and was effective for *anti*-Markonikov selective alkene hydrosilylation using phenylsilane.[65] The phosphonite(imino)pyridine-iron(II)dibromide complex **27** showed chemoselectivity for the hydrosilylation of alkenes over carbonyl groups, such as a ketone but not an aldehyde.[66] This contrasts with other iron-catalysed hydrosilylation reactions which are typically incompatible with carbonyl-functionalities. It was proposed that the phosphinite group sufficiently enhanced electron-density at the reduced iron-centre to render the metal less-oxophilic.

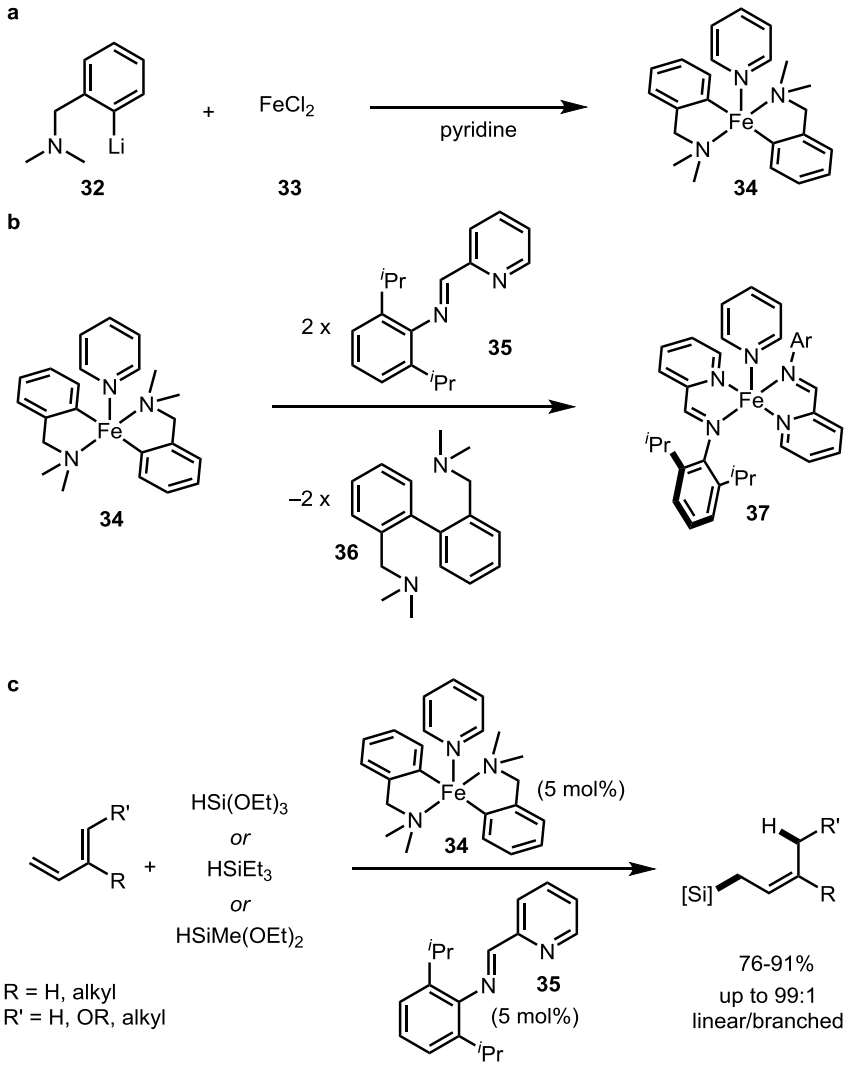
Nakazawa showed that the aldimino-bypyridyl-iron(II)dibromide complex **28** activated using $NaHBEt_3$ was effective for alkene hydrosilylation using primary, secondary and tertriary silanes.[67] The mesityl-substituted terpyridine-iron(II)dibromide pre-catalyst **29** could be activated using $NaHBEt_3$ and was used for alkene hydrosilylation with primary and secondary silanes.[68] Thomas used ethylmagnesium bromide as an activator for *N*-diethylphenyl-substituted bis(imino)pyridine-iron(II)dichloride pre-catalyst **30** which was used for alkene hydrosilylation using primary, secondary and tertiary silanes.[69] The analogous complex **31** bearing triflate counter-ions in place of chloride was activated under mild conditions using Hünigs base for alkene hydrosilylation with phenylsilane.[70]



Scheme 1.5. Examples of iron pre-catalysts used for alkene and alkyne hydrosilylation reactions. **a** Pre-activated complexes either in a low oxidation-state or bearing groups that facilitate activation upon reaction with silane reactant. **b** Iron(II) pre-catalysts used in hydrosilylation reactions that have been activated *in situ*.

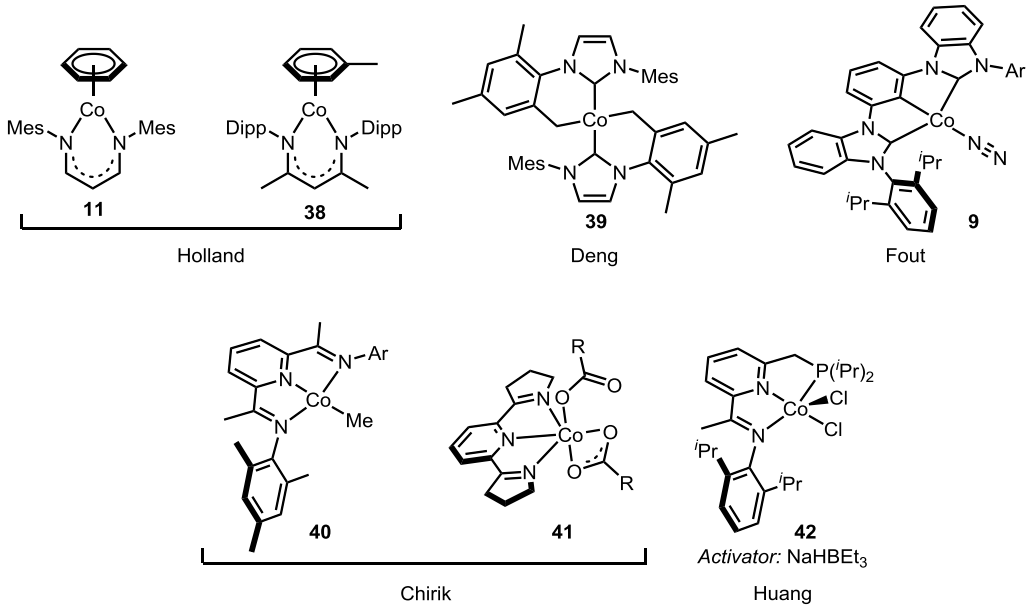
Ritter demonstrated that bidentate ligands were good promoters for the hydrosilylation of conjugated dienes.[71] For alkenes, hydrosilylation selectivity is limited to either Markonikov or *anti*-Markovnikov regioisomers, while for conjugated dienes (*i.e* 1,3-diene) the selectivity can be Markonikov or *anti*-Markovnikov and 1,2- or 1,4-hydrosilylation is possible. In this

transformation an iron(II)-bisaryl pre-catalyst **34** was formed by reaction of an aryl-lithium reagent **32** with iron(II)dichloride **33** in the presence of pyridine (Scheme 1.6, **a**). The bisaryl-iron(II) complex **34** was shown to undergo reductive elimination of the biaryl **36** upon reaction with free *N*-di*iso*propylphenyl substituted (imino)pyridine ligand **35** (Scheme 1.6, **b**). The resulting iron(0) complex **37** was isolated and characterised by both Mössbauer and single crystal X-ray analysis. The 1,4-hydrosilylation of 1,3-dienes could be achieved by *in situ* formation of the active catalyst by addition of free ligand **35** to the bisaryl-iron(II) complex **34** (Scheme 1.6, **c**). The reaction gave allylsilane products with tertiary silanes with selectivity of up to 99:1 for the linear 1,4-regioisomer.



Scheme 1.6. Ritter's iron-catalysed 1,4-hydrosilylation of 1,3-dienes using an in situ catalyst formation method. **a** Preparation of the bisaryl-iron(II) pre-catalyst. **b** Reaction of the bisaryl-iron(II) pre-catalyst with an *N*-di*iso*propylaryl substituted iminopyridine ligand to give a low oxidation-state iron complex. **c** 1,4-Hydrosilylation of 1,3-dienes using bisaryl-iron(II) pre-catalyst and iminopyridine ligand additive.

While the number of iron-catalysts for alkene hydrosilylation exceeds that of cobalt-catalysts, cobalt has shown good potential for alkene hydrosilylation reactions. Successful catalysis and selective hydrosilylation reactions rely on the formation of a low oxidation-state cobalt species, usually cobalt(I).[35] In a similar manner to that of early iron-catalysed alkene hydrosilylation reactions, cobalt(0)-carbonyl compounds were used. $Co_2(CO)_8$ was used as an efficient catalyst for *anti*-Markovnikov selective alkene hydrosilylation using tertiary silanes including dichlorophenylsilane, trimethoxysilane and triethylsilane. Unlike the analogous iron-carbonyl catalysts, the cobalt-carbonyl compounds showed no propensity for alkene dehydrogenative silylation but did promote alkene isomerisation reactions to unreactive internal alkene products.[35] In a modern example, Holland used cobalt(I)-*β*-aldiminate complex **11** and cobalt(I)-*β*-diketiminate complex **38** as catalysts for the *anti*-Markovnikov selective alkene hydrosilylation with phenylsilane or triethoxysilane.[50] Deng used bis-NHC-Co(II)-dialkyl tethered complex **39** for alkene hydrosilylation using phenylsilane.[72] In this system the tethered mesityl-groups served as activating units when reacted with phenylsilane. Fout showed that the biscarbene-cobalt(I)dinitrogen complex **9** supported by the (bis-di*iso*propylphenyl-imidazol-2-ylidene)-phenyl ligand was effective for chemoselective alkene hydrosilylation using secondary and tertiary silanes, even in the presence of highly reactive groups such as an aldehyde, ketone, hydroxyl and nitrile.[73] Chirik used the *N*-mesityl-substituted bis(imino)pyridine-cobalt (I)methyl complex **40** for the selective dehydrogenative silylation of terminal alkenes with primary, secondary and tertiary silanes.[74] Chirik separately reported the use of cyclic-*N*-alkyl-substituted bis(imino)pyridine-cobalt(II)carboxylate complexes **41** for the selective hydrosilylation of alkenes with primary, secondary and tertriary silanes.[32] It is worth noting that these cobalt(II)-carboxylate complexes **41** displayed far greater air and moisture stability to that of their cobalt(I)-alkyl analogues. Using the same ligand framework as used for the iron-catalysed alkene hydrosilylation, Huang showed that the phosphine(imino)pyridine-cobalt(II)dichloride complex **42** could be activated using $NaHBEt_3$ for the Markonivkov selective hydrosilylation of alkenes.[65] It is important to note that the selectivity in this example was regiodivergent to that observed using the analogous iron-catalyst.



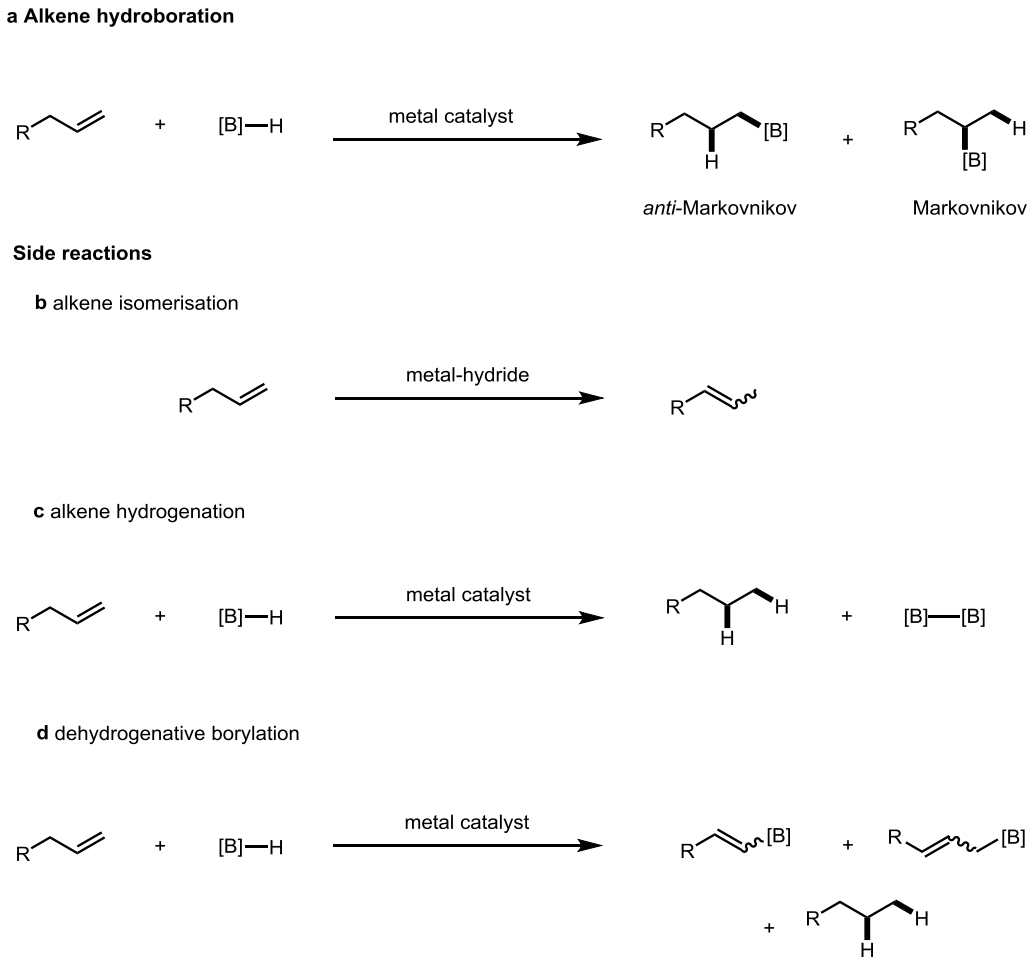
Scheme 1.7. Examples of cobalt pre-catalysts used for alkene and alkyne hydrosilylation reactions.

1.4 Alkene hydroboration

The hydroboration of alkenes has been established for decades, and the products of these reactions have a myriad of synthetic applications.[75-78] The transformation involves the reductive addition of a borane reagent (HBR_2) across a double bond to give an alkylborane product. In many examples of alkene hydroboration a catalyst is not required to complete the transformation. However this is only true for suitably reactive borane reagents, *i.e* BH_3 or H-9BBN. Borane reagents such as catecholborane can undergo hydroboration in reaction with alkynes but not alkenes in the absence of catalyst.[79] The less reactive pinacolborane **43** can neither react with alkenes or alkynes in the absence of any catalyst. Alkene hydroboration products of catecholborane, alkyl-catecholboronates, are unstable under ambient atmosphere but the corresponding alkyl-pinacolboronate esters are stable and can be easily stored for extended periods. Typically both pinacolborane **43** and catecholborane have been used with rhodium-based catalysts for alkene hydroboration.[75] However methods have rapidly emerged for alkene hydroboration in recent years based on first-row Earth-abundant elements.[16]

Alkenes react with borane reagents to give alkyl-boranes or alkyl-boronic esters. The regioselectivity of the reaction is a factor of borane reagent, substrate sterics and electronics as well as catalyst properties. Hydroboration can proceed with either Markovnikov or *anti*-Markovnikov selectivity (Scheme 1.8, **a**). Common side reactions include alkene isomerisation facilitated by metal-hydride catalysts (Scheme 1.8, **b**). Alkene hydrogenation

to give alkane products alongside concomitant formation of boron-boron compounds may also occur (Scheme 1.8, **c**). Dehydrogenative borylation to give alkenylboronates, allylicboronates and an equivalent of alkane also has potential to hinder clean reactivity (Scheme 1.8, **d**).

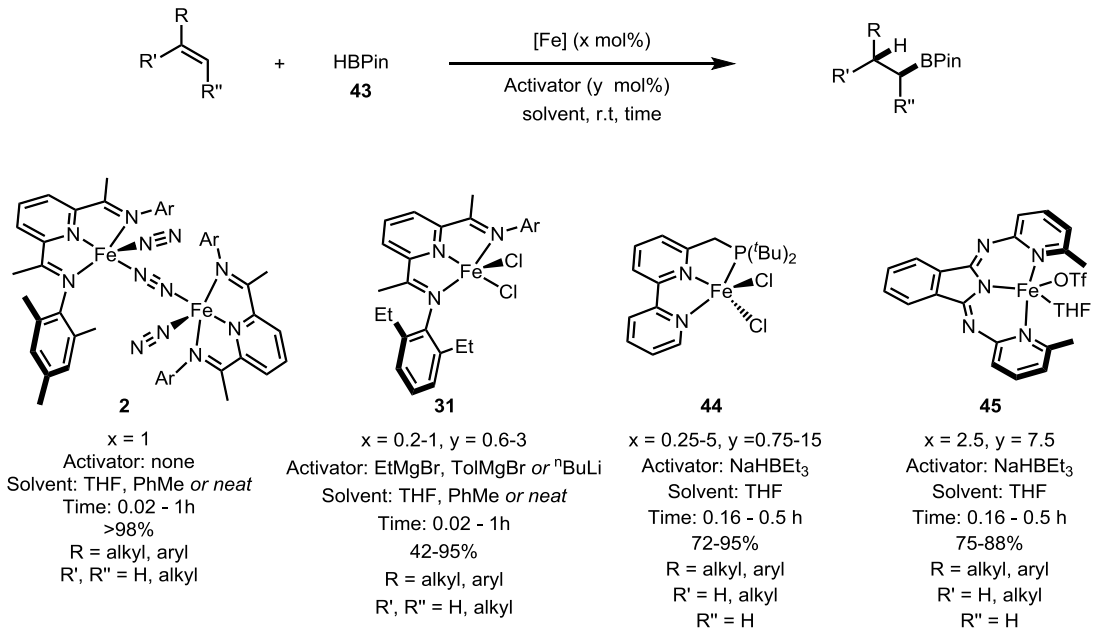


Scheme 1.8. **a** Overview of alkene hydroboration reactions and potential side reactions. **b** alkene isomerisation by metal-hydride species. **c** alkene hydrogenation and concomitant formation of boron-boron oxidation products. **d** dehydrogenative borylation to give alkenylboron, allylicboron and alkane products.

1.4.1 Iron and cobalt catalysts for alkene hydroboration with pinacolborane

A number of iron-catalysts have been reported for alkene hydroboration reactions.[16] The majority of these rely on the use of a reduced metal active catalyst. Chirik used the low oxidation-state *N*-mesityl-substituted bis(imino)pyridine iron(0)dinitrogen complex **2** for the hydroboration of alkenes with pinacolborane (Scheme 1.9).[80] This complex was reactive without the addition of any additives or activators and gave the *anti*-Markonikov

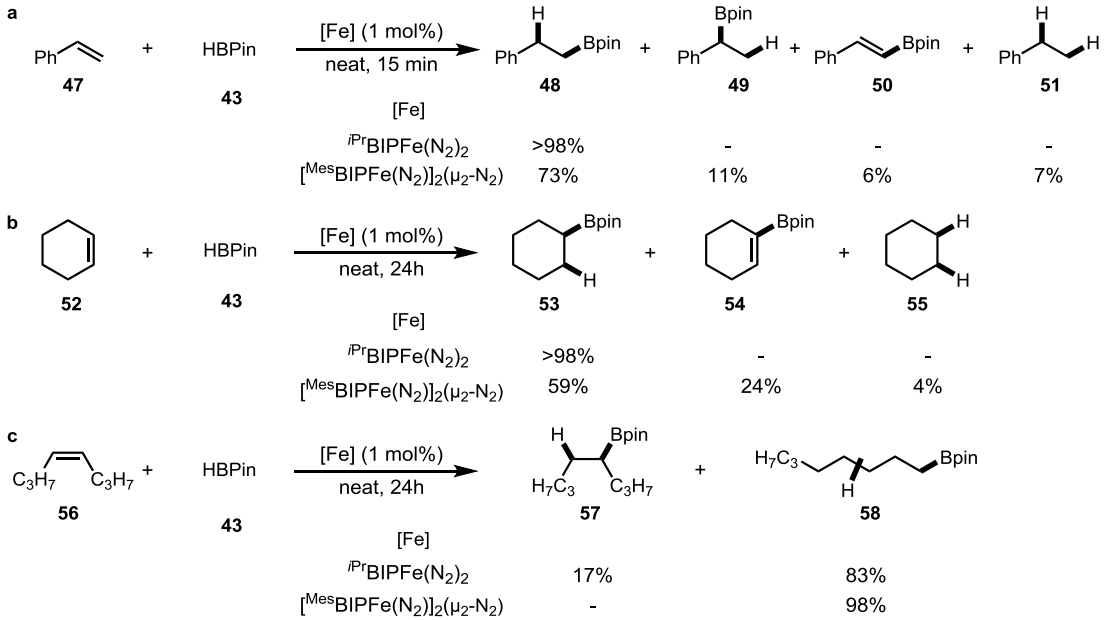
alkylboronic esters in high yields and in low reaction times. Thomas used the analogous *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dihalide complex **31** for alkene hydroboration (Scheme 1.9).[81] The high oxidation-state of the pre-catalyst necessitated the use of an added organometallic reagent to achieve *in situ* catalyst activation. It was found that both Grignard reagents and *n*-butyllithium could be used as an external *in situ* pre-catalyst activator. The catalyst displayed comparable reactivity to that of the analogous iron(0) isolated species. Huang developed the phosphine-bypyridine iron(II)dichloride pre-catalyst **44** for alkene hydroboration.[83] The pre-catalyst **44** required the addition of $NaHBEt_3$ for activation and a range of alkenes underwent hydroboration to give the *anti*-Markovnikov alkyl-boronates in high yields. Szymczak developed an iron(II) catalyst **45** supported by a tridentate pincer ligand (1,3-bis(6′-methyl-2′-pyridylimino)*iso*indolate).[86] The iron(II) complex contained a triflate counter-ion and was isolated as a THF adduct. Alkene hydroboration was achieved using $NaHBEt_3$ as an *in situ* activator, which enabled the formation of *anti*-Markovnikov alkyl-boronic esters.



Scheme 1.9. Examples of iron pre-catalysts for alkene hydroboration.

The examples of alkene hydroboration using Chirik's iron(0) dinitrogen complexes displayed unique reactivity depending on factors of substrate properties and those of catalyst. For example styrene **47** underwent hydroboration with *N*-di*iso*propylphenyl substituted bis(imino)pyridine iron(0)dinitrogen **46** to exclusively give the linear *anti*-Markovnikov regioisomer (Scheme 1.10, **a**). While this pre-catalyst was highly selective, the analogous *N*-mesityl-substituted iron(0)dinitrogen complex **2** gave a mixture of both Markovnikov and

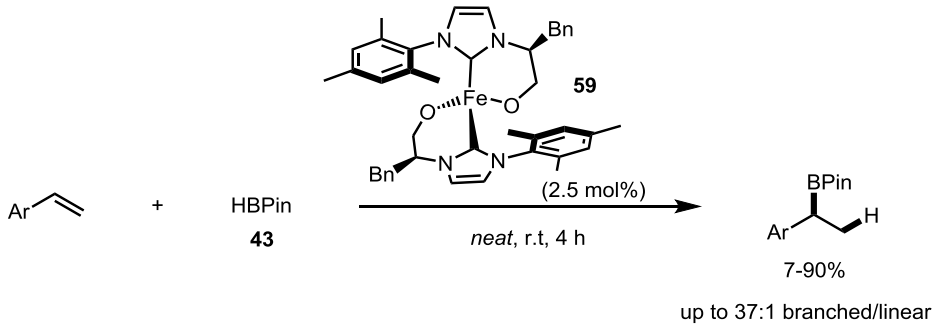
anti-Markovnikov regioisomers, as well as products owing to dehydrogenative borlyation (Scheme 1.10, **a**). Similarly in the reaction of cyclohexene **52**, the *N*-di*iso*propylphenyl substituted bis(imino)pyridine iron(0)dinitrogen complex **46** gave a single hydroboration product, whereas the analogous *N*-mesityl-substituted iron(0)dinitrogen complex **2** gave a mixture of hydroboration and dehydrogenative borylation products (Scheme 1.10, **b**). This difference in reactivity could be productively exploited in the hydroboration of (*Z*)-4-octene **56**, where the *N*-mesityl-substituted iron(0)dinitrogen complex **2** gave the terminal alkylboronic ester **58** (by alkene isomerisation and hydroboration), while the *N*-di*iso*propylphenyl substituted bis(imino)pyridine iron(0)dinitrogen complex **46** showed reduced selectivity for this product (Scheme 1.10, **c**).



Scheme 1.10 Examples of alkene hydroboration using well defined low oxidation-state iron(0) pre-catalysts. **a** Hydroboration of styrene to give alkylboronic ester, alkenylboronic ester and alkane products. **b** Hydroboration of cyclohexene to give alkylboronic ester, alkenylboronic ester and alkane products. **c** Hydroboration of (*Z*)-4-octene to give both internal alkylboronic ester and terminal alkylboronic ester products.

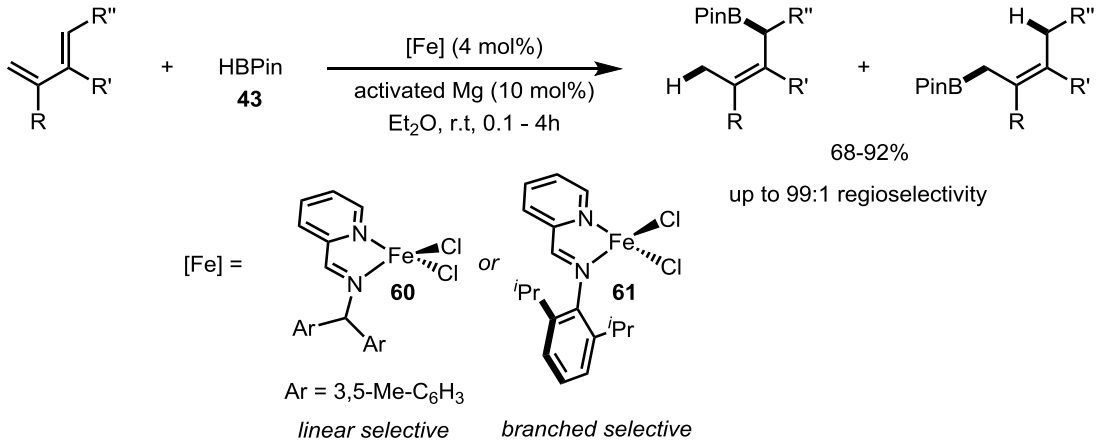
Thomas exploited an *O*-tethered-complex activation strategy for alkene hydroboration using a bis-carbene and bis-alkoxide supported iron(II) complex **59**.[34] The complex derived from an *N*-mesityl-NHC bearing an enantiopure alkoxide tether showed good reactivity for the

hydroboration of vinylarenes (Scheme 1.11). However unlike other iron catalysts used in alkene hydroboration reactions, this pre-catalyst showed a high level of regiodivergence and was selective for the Markovnikov regioisomer.



Scheme 1.11 Thomas' NHC-iron(II) complex catalysed Markovnikov-selective hydroboration of vinylarenes.

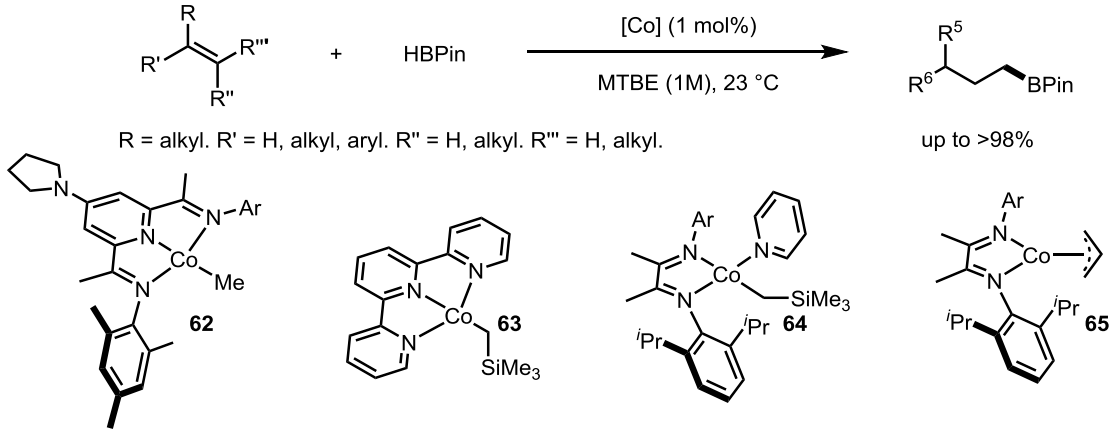
Ritter reported the 1,4-hydroboration of 1,3-dienes using iron(II) complexes supported by *N*-substituted iminopyridine ligands (Scheme 1.12).[85] The iminopyridine ligands were either substituted with an *N*-di*iso*propylphenyl group or by *N*-benzyl. The isolated *N*-substituted iminopyridine iron(II)dichloride complexes **60** and **61** were activated *in situ* using activated magnesium and gave either 1,4- or 4,1-hydroboration products in high yields. The ligands were found to be regiodivergent from each other, and the selectivity could be selected for either 1,4- or 4,1-hydroboration product.



Scheme 1.12 Ritter's iron-catalysed 1,4-hydroboration of 1,3-dienes.

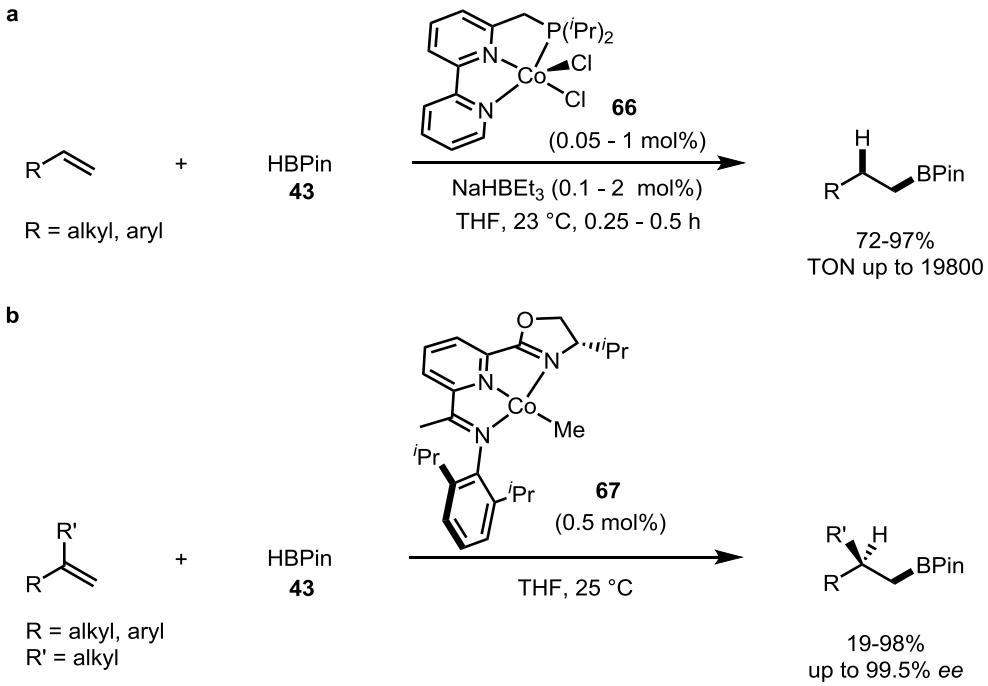
Chirik reported a variety of cobalt(I)-alkyl complexes **62-65** for alkene isomerisation-hydroboration.[86,87] In these reactions, an internal alkene is reacted with pinacolborane **43** and catalyst to give the products of terminal hydroboration, *i.e* primary alkyl-boronic esters. These complexes possess either cobalt(I)-alkyl or cobalt(I)-allyl groups that underwent reaction with added pinacolborane to form an active catalyst. The electronically modified *N*-

mesityl-substituted bis(imino)pyridine cobalt(II)-methyl complex **62** showed high selectivity and high activity for alkene hydroboration. It is significant to note that this catalyst had been rationally designed based on observations that electron-donating groups such as amino-groups on the ligand pyridyl group increased the rate of reaction. Terpyridine supported cobalt(I)-CH_2SiMe_3 **63**, *N*-di*iso*propylphenyl substituted bisimine cobalt(I)-CH_2SiMe_3 **64** and the related cobalt(I)-allyl analogue **65** all showed unique levels of reactivity depending on the substrate used.



Scheme 1.13. Chirik's cobalt-alkyl and cobalt-allyl pre-catalysts for the isomerisation-hydroboration of internal alkenes to give terminal alkyl boronic esters.

Huang developed a robust phosphine-bypyridine supported cobalt(II)dichloride pre-catalyst **66** that was activated *in situ* by $NaHBEt_3$ for the hydroboration of terminal alkenes. Although the catalyst was limited to the hydroboration of terminal alkenes, the catalyst displayed extremely high reactivity, exhibiting a turn-over number of 19800 (Scheme 1.14, **a**).[88] Separately Huang showed that the enantiopure iminopyridine-oxazoline cobalt(I)-methyl complex **67** could be effectively used for the enantioselective hydroboration of 1,1-disubstituted alkenes (Scheme 1.14, **b**).[89] The best performance was obtained with 1,1-disubstituted aryl-alkenes which gave enantiomeric excess of up to 99.5%. Significantly the same catalysis could be accessed using the higher oxidation-state iminopyridine-oxazoline cobalt(II)dichloride pre-catalyst and using $NaHBEt_3$ as an *in situ* reductant.



Scheme 1.14. Huang's cobalt-catalysed hydroboration of alkenes. **a** Phosphine-bipyridine cobalt(II) dichloride pre-catalyst **66** activated using $NaHBEt_3$ for alkene hydroboration. **b** Enantioselective hydroboration of 1,1-disubstituted alkenes using a cobalt(I)-methyl pre-catalyst **67**.

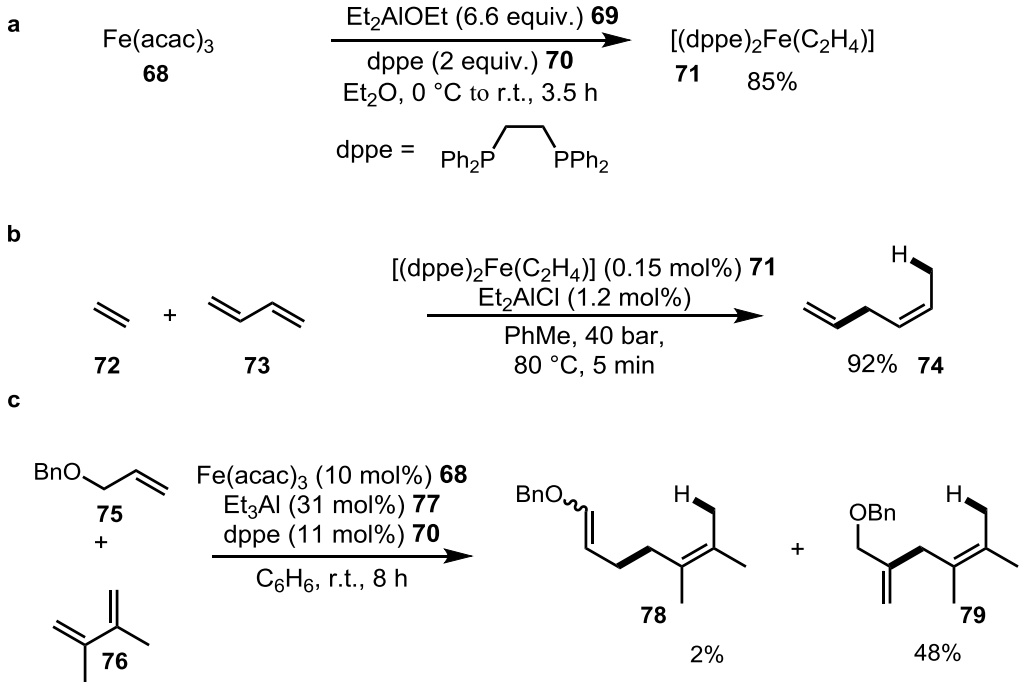
1.5 Alkene hydrovinylation

Transition metal catalysed alkene hydrovinylation between alkenes and conjugated dienes is a synthetically useful process for the formation of carbon-carbon bonds. The process involves the addition of an alkene C-H bond across a 1,3-diene to give an diene-containing product. The products obtained from 1,4-hydrovinylation of 1,3-dienes do not possess dienes that are in conjugation with each other. One difficulty encountered in hydrovinylation reactions is the fact that the products of the reaction may undergo further reaction, *i.e* undergo further hydrovinylation, which leads to polymerisation. Most hydrovinylation reactions have been achieved using nickel and palladium catalysts.[90,91] Comparatively few examples using iron-based catalysts have been reported.

1.5.1 Alkene hydrovinylation using iron catalysts

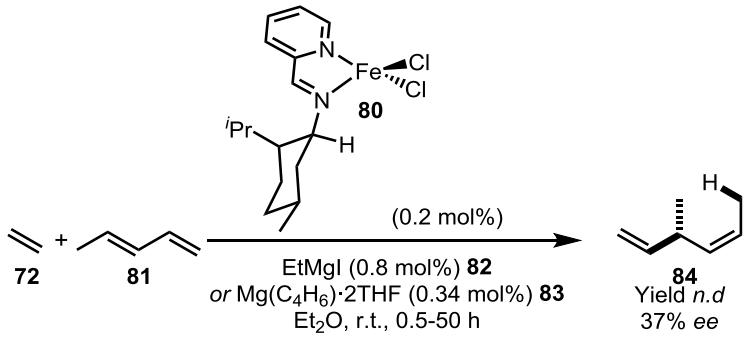
Hata demonstrated that iron(III)$(acac)_3$ **68** could be reduced using excess diethylaluminiumethoxide **69** in the presence of diphenylphosphinoethane **70** to give the bis(dppe)-iron(0)-ethene complex **71** (Scheme 1.15, **a**).[92,93] This isolated complex catalysed the 1,4-hydrovinylation reaction between ethene **72** and butadiene **73** in excellent yield (Scheme 1.15, **b**). In a similar manner, Takacs showed that iron(III)$(acac)_3$ **68** could be

reduced *in situ* using triethylaluminium **77** in the presence of diphosphinoethane **70** and this combination was effective for the hydrovinylation of 2,3-dimethylbutadiene **76** using allyl-benzylether **75** (Scheme 1.15, **c**).[94]



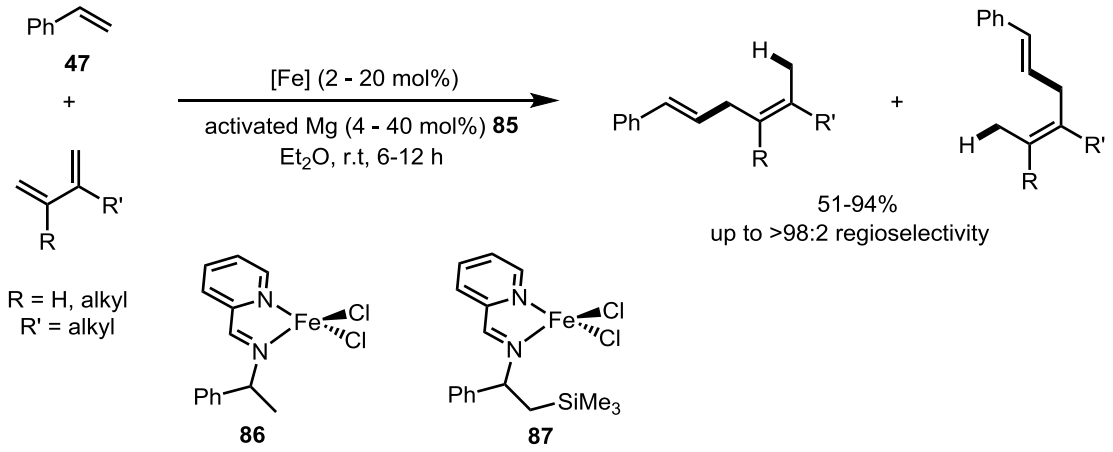
Scheme 1.15. Preparation and use of a low oxidation-state iron complex for the hydrovinylation of 1,3-dienes. **a** Preparation of a bisphosphine iron complex **71** using Et_2AlOEt **69** as the reductant. **b** 1,4-Hydrovinylation of butadiene **73** with ethene **72**. **c** 1,4-Hydrovinylation of 2,3-dimethyl-butadiene **76** with allylbenzylether **75** using an *in situ* reduced iron pre-catalyst.

tom Dieck reported the preparation of a number of enantiopure bisimine and iminopyridine ligands, which were used with iron(II)dichloride to give their corresponding complexes.[95,96] These complexes were activated *in situ* using either a Grignard reagent **82** (4 equiv.) or magnesium-butadiene **83** ($Mg(C_4H_6)$•2THF, 1.7 equiv.) to generate an active catalyst for the dimerization of 1,3-dienes. Using a menthol-derived amine, tom Dieck formed an enantiopure *N*-substituted iminopyridine iron(II)dichloride complex **80** which was activated *in situ* by either Grignard reagent **82** or magnesium-butadiene **83** and could catalyse the hydrovinylation reaction between ethene and 2,4-pentadiene **81** (Scheme 1.16). The yields for the reaction were not reported, however it was shown that the products did possess mild enantiopurity.



Scheme 1.16. Attempted enantioselective hydrovinylation of 1-methyl-butadiene with ethene using an enantiopure iminopyridine iron(II) pre-catalyst **80**.

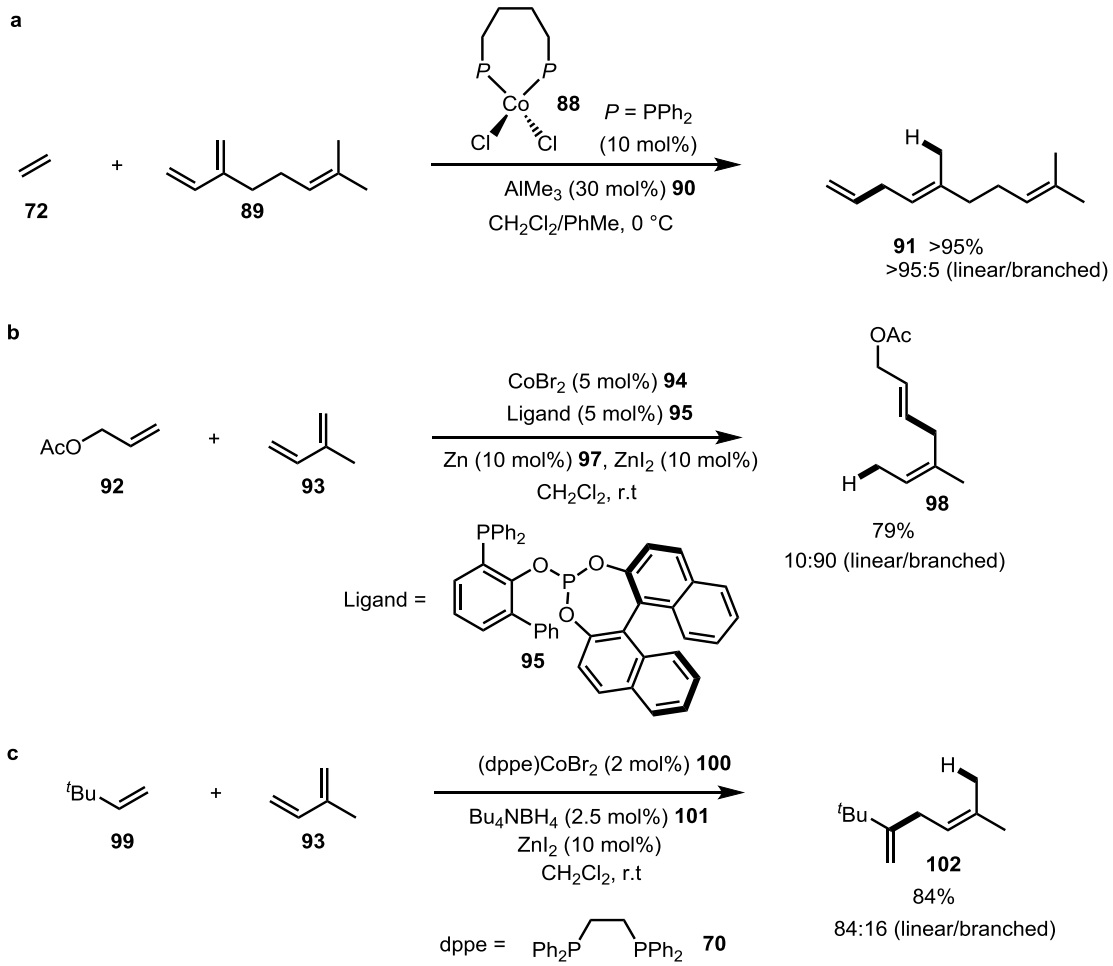
Ritter reported the 1,4-hydrovinylation of 1,3-dienes using iminopyridine iron(II)dichloride pre-catalysts **86** and **87** that were activated *in situ* using activated magnesium **85** (Scheme 1.17).[97] The reaction used vinylarenes and 1,3-dienes to give non-conjugated alkene products with perfect diastereoselectivity in every example (>99:1). Two structurally different iminopyridine iron(II)dichloride pre-catalysts **86** and **87** showed potential to effect the transformation reaction, and the pre-catalyst **87** containing an extra trimethylsilyl-group showed improved regioselectivity in a number of examples.



Scheme 1.17 Ritter's 1,4-hydrovinylations of 1,3-dienes with vinylarenes.

1.5.2 Alkene hydrovinylation using cobalt catalysts

Rajanbabu demonstrated that a bisphosphine-ligated cobalt(II)dichloride pre-catalyst **88** could be activated *in situ* using trimethylaluminium **90** and the active catalyst produced was effective for the hydrovinylation of Myrcene **89** (a 1,3-diene) with ethene **72** (Scheme 1.18, **a**).[98] The reaction gave the 1,4-hydrovinylation product in both high yield and selectivity for the linear regioisomer **91**. Hilt used zinc metal **97** as the required reductant for *in situ* activation of an *in situ* formed cobalt-phosphoramidite complex (Scheme 1.18, **b**).[99] The *in situ* formed active catalyst was efficient for the 1,4-hydrovinylation of isoprene **93** using allylacetate **92** as the coupling partner. Additionally Hilt used *tert*-butylammonium borohydride **101** as a reductant for the *in situ* activation of diphenylphosphino-cobalt(II)dibromide **100** (Scheme 1.18, **c**).[99] The active catalyst was reactive for the hydrovinylation reaction between isoprene **93** and *tert*-butylethene **99** which gave the linear hydrovinylation product **102** but with Markovnikov-selectivity for the reaction of the alkene coupling partner.

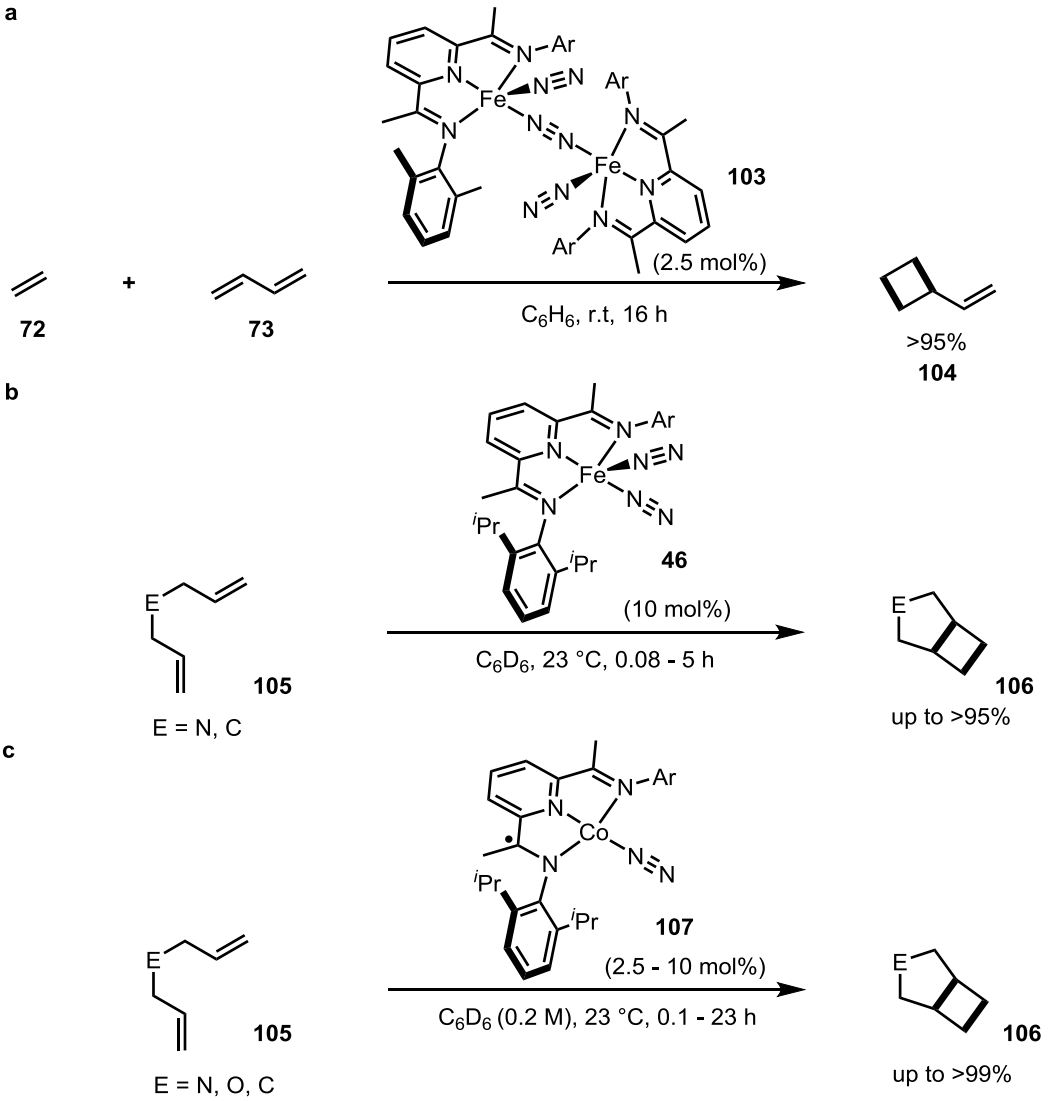


Scheme 1.18. Examples of cobalt-catalysed hydrovinylation reactions. **a** Rajanbabu's cobalt-bisphosphine pre-catalyst **88** for 1,3-diene hydrovinylation. **b** Hilt's reported cobalt-phosphoramidite combination activated by zinc metal **97** for branched-selective hydrovinylation. **c** Hilt's bisphosphine-cobalt system for 1,3-diene hydrovinylation.

1.6 Alkene [2π+2π] cycloaddition reactions catalysed by iron and cobalt complexes

Alkene [2π+2π] cycloaddition reactions have been carried out using both low oxidation-state iron and cobalt-complexes. Chirik showed that the *N*-dimethylphenyl substituted bis(imino)pyridine iron(0)dinitrogen complex **103** was effective for the intermolecular [2π+2π] cycloaddition reaction between ethene **72** and butadiene **73** to give vinylcyclobutane **104** in excellent yield and with only a single addition of ethene (Scheme 1.19, **a**).[100] Similarly, the *N*-di*iso*propylphenyl substituted bis(imino)pyridine iron(0)dinitrogen complex **46** was used for the intramolecular [2π+2π] cycloaddition of a 1,6-diene (Scheme 1.19, **b**).[101] Chirik demonstrated that the same products could be produced using the analogous cobalt

complex (Scheme 1.19, **c**). Using *N*-di*iso*propylphenyl substituted bis(imino)pyridine cobalt(I)dinitrogen complex **107** a much wider substrate scope was demonstrated, tolerating oxygen tethered 1,6-dienes.



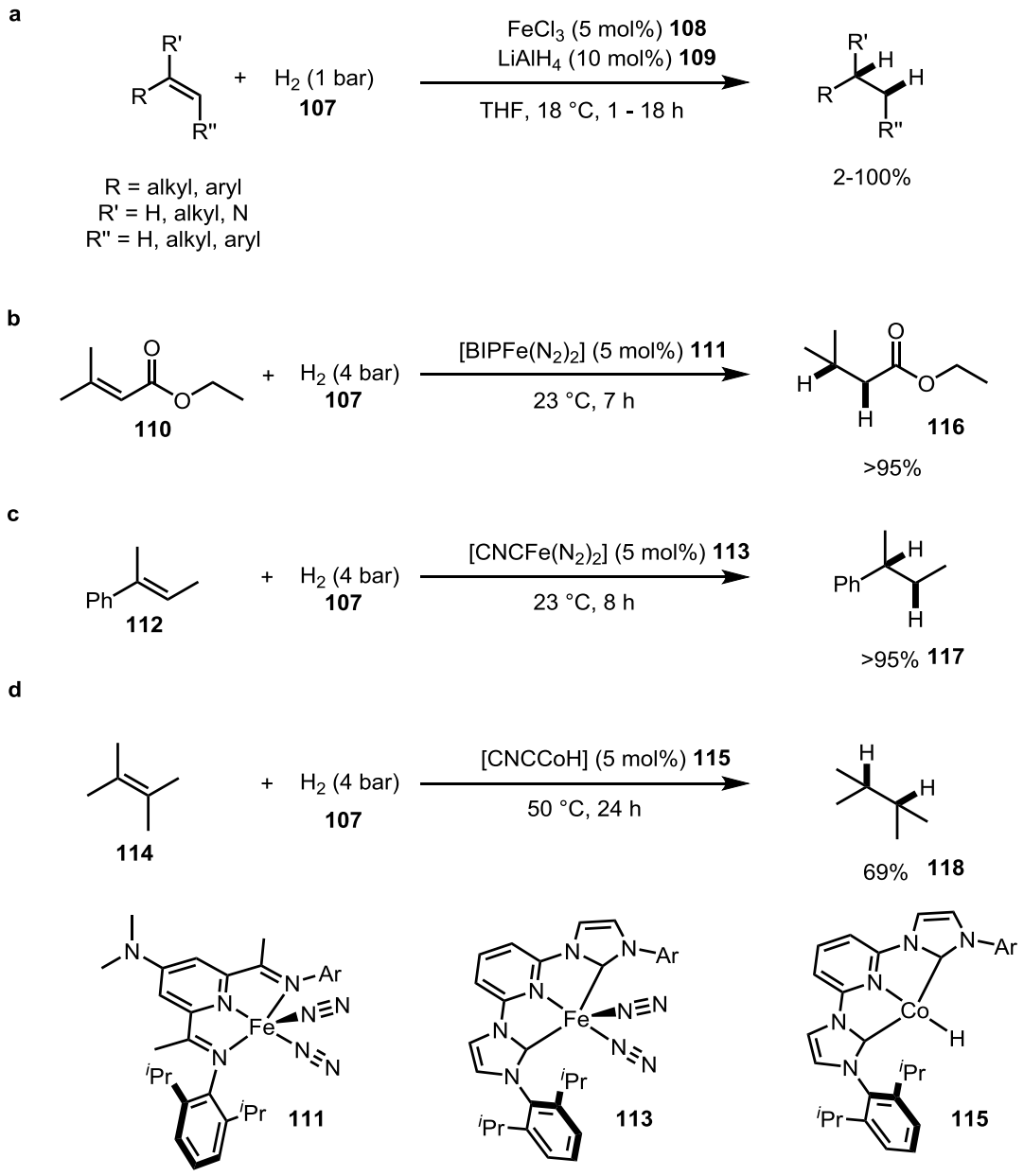
Scheme 1.19. Chirik's iron and cobalt-catalysed [2π+2π] cycloaddition reactions. **a** Iron(0)-catalysed cycloaddition between ethene **72** and butadiene **73** to give a cyclobutane product **104**. **b** Iron(0)-catalysed intramolecular [2π+2π] cycloaddition reaction. **c** Cobalt(I)-catalysed intramolecular [2π +2π] cycloaddition reaction.

1.7 Alkene hydrogenation with iron and cobalt catalysts

Alkene hydrogenation reactions have found widespread use in pharmaceutical, agrochemical and bulk chemical manufacturing processes.[103-105] The majority of these reactions have relied on both homogeneous and heterogeneous precious metal catalysts. Alternative methodologies based on iron and cobalt-catalysis have emerged as a sustainable

replacement.[105,106] Importantly the reactivity and selectivity exhibited by these metals rivals that of precious metals. Formal hydrogenation could be achieved using super-stoichiometric hydride reductants, however these reactions generate significant waste.[107,108]

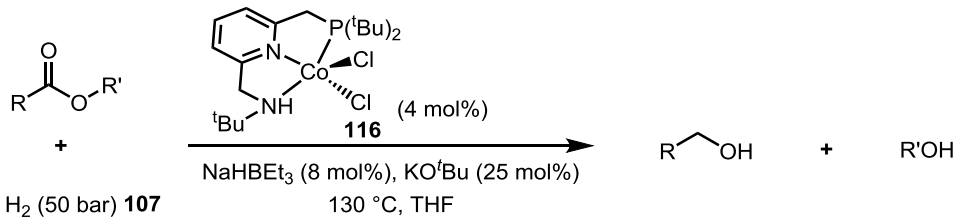
Jacobi von Wangelin reported a simple system consisting of iron(III)chloride **108** and substoichiometric lithium aluminium hydride **109** in combination with dihydrogen **107** for the reduction of a wide range of alkenes (Scheme 1.20. **a**).[109] Terminal, 1,1- and 1,2-disubstituted alkenes were hydrogenated under the reaction conditions alongside trisubstituted alkenes. Chirik showed that an electron-rich *N*-di*iso*propylphenyl substituted bis(imino)pyridine iron(0)dinitrogen complex **111** was effective for the hydrogenation of an activated trisubstituted alkene bearing an ester group **110** (Scheme 1.20, **b**).[27,111] The bis-carbene iron(0)dinitrogen complex **113** could be used for the hydrogenation of trisubstituted alkenes in good yields and with only 4 bar dihydrogen pressure (Scheme 1.20. **c**). Greater hydrogenation activity was demonstrated using the bis-carbene cobalt(I)hydride complex **115**, which was effective for the hydrogenation of 2,2,4,4-tetramethylethene **114** in good yield at elevated temperatures (Scheme 1.20, **d**).[39]



Scheme 1.20. Iron and cobalt-catalysed alkene hydrogenation. **a** Jacobi von Wangelin's simple iron-catalysed alkene hydrogenation with dihydrogen **107** and $LiAlH_4$ **109** pre-catalyst activator. **b** Chirik's low oxidation-state bis(imino)pyridine iron-complex **111** catalysed hydrogenation of an activated tri-substituted alkene **110**. **c** Chirik's bis-carbene iron-complex **113** catalysed hydrogenation of a trisubstituted alkene **112**. **d** Chirik's bis-carbene cobalt-hydride **115** catalysed hydrogenation of alkenes.

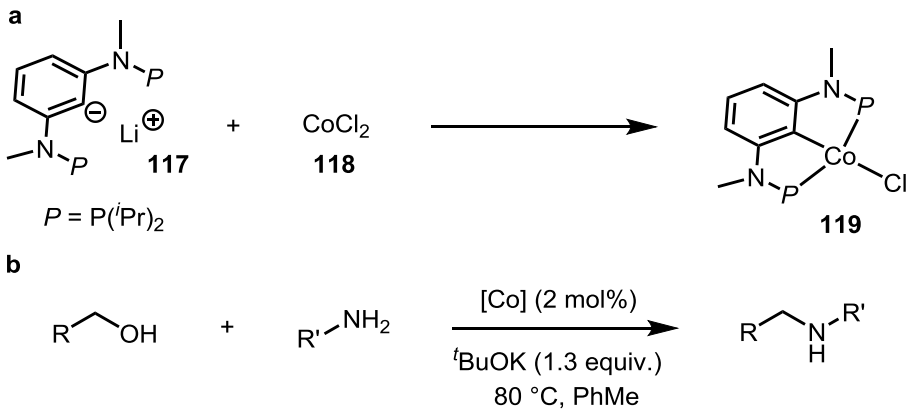
1.8 Iron and cobalt catalysis using alkoxide additives or in catalyst preparation

Many synthetic methods have been reported for synthetic transformations that utilise alkoxides as additives necessary for catalysis. However alkoxide salts have not been suggested to act as direct reductants for iron or cobalt pre-catalysts. The role of the alkoxide salt in many instances is presumed to aid active catalyst formation or catalyst turnover. For example, Milstein reported the *tert*-butylamino-pyridine-phosphine supported cobalt(II)dichloride complex **116** for the hydrogenation of esters (Scheme 1.21).[112] In this reaction $NaHBEt_3$ was required as an *in situ* pre-catalyst reductant and KO^{t}Bu was suggested to serve as a classical base aiding enolate formation. The intermediate enolates were suggested to be needed for successful ester hydrogenation.



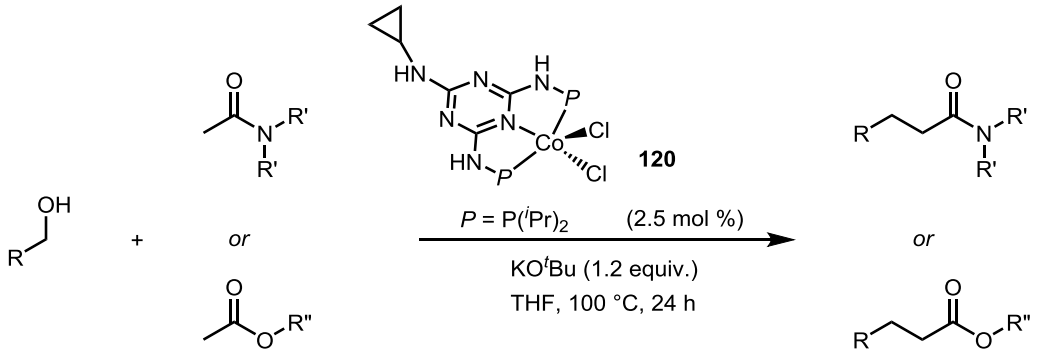
Scheme 1.21. Milstein's NNP-cobalt pre-catalyst for ester hydrogenation.

Kirchner used a cobalt(I)chloride pre-catalyst **119** bearing a tridentate aminophosphine ligand for the direct amination of alcohols (Scheme 1.22).[112,113] The pre-catalyst was formed by salt metathesis using an aryl-lithium precursor **117** and cobalt(II)dichloride **118** (Scheme 1.22, **a**). Under the reaction conditions, super-stoichiometric KO^{t}Bu was necessary for good activity.



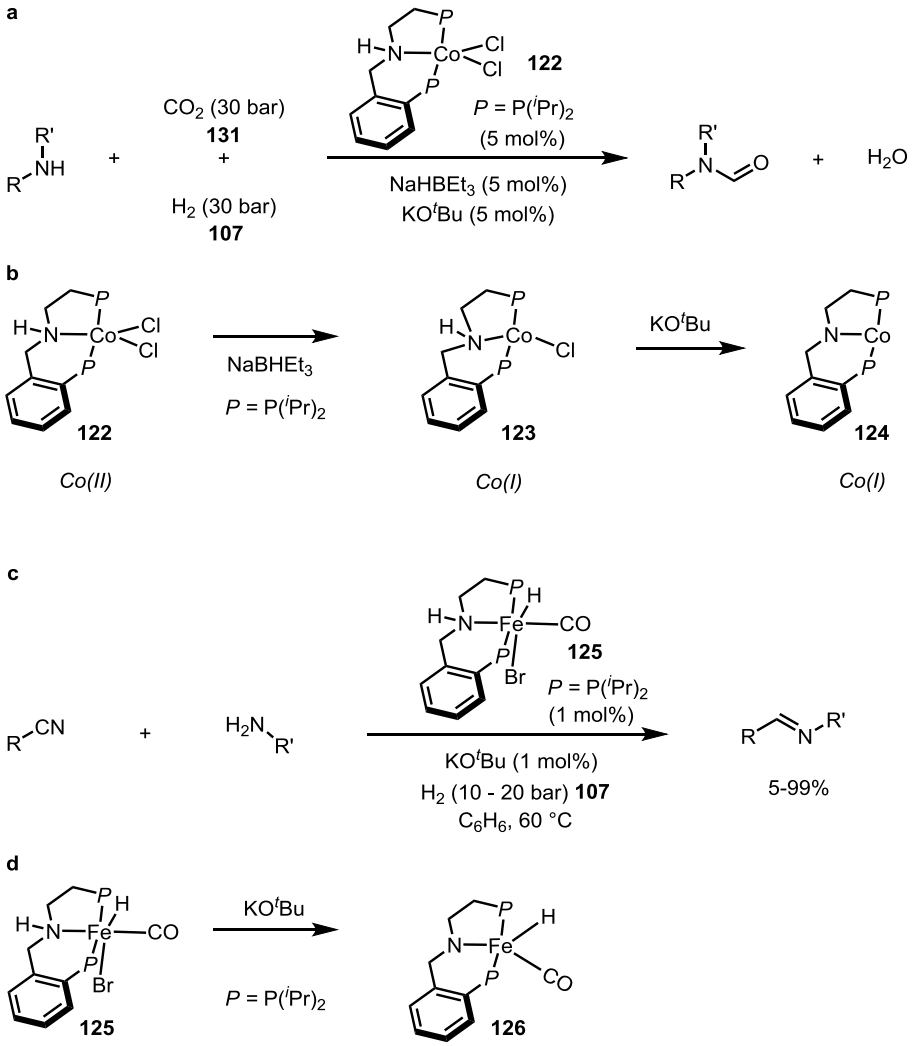
Scheme 1.22. Kirchner's cobalt catalyst for the direct alkylation of amines by alcohols. **a** Pre-catalyst formation. **b** Direct amination of alcohols.

Kempe reported the use of triazine-amino-phosphine cobalt(II)dichloride complex **120** for the direct alkylation of amides and esters with alcohols. In a similar manner to that of Kirchner, the system was reliant on super-stoichiometric quantitites of KO^{t}Bu for efficient catalysis (Scheme 1.23).



Scheme 1.23. Kempe's cobalt(II) pre-catalyst for the C-alkylation of amides and esters with alcohols.

Milstein reported the *N*-formylation of primary and secondary amines using carbon dioxide **131** and dihydrogen gas **107** (Scheme 1.24, **a**).[115] The transformation was catalysed by a phosphine-amino-phosphine cobalt(II)dichloride pre-catalyst **122** that was reduced *in situ* firstly by $NaHBEt_3$ and then reacted with KO^{t}Bu to generate the catalytically active species. The role of each additive was clarified by mechanistic investigations which revealed that $NaHBEt_3$ reduced the cobalt(II)dichloride complex **122** to the corresponding cobalt(I)chloride species **123** which subsequently underwent deprotonation and elimination of chloride on reaction with KO^{t}Bu to give cobalt(I) complex **124** (Scheme 1.24. **b**). The related iron(II)-bromo-hydride complex **125** was shown to be effective for reductive imine formation from primary amines and nitriles with dihydrogen gas **107** (Scheme 1.24, **c**).[116] Under the optimised reaction conditions KO^{t}Bu was added in substoichiometric quantities for successful catalysis. The role of the base was examined and proposed to act on the complex by deprotonation of the amine ligand which concomitantly eliminated the bromide group to form the coordinatively unsaturated active species **126** (Scheme 1.24, **d**).



Scheme 1.24. **a** Milstein's cobalt-catalysis for the *N*-formylation of amines with H_2 **107** and CO_2 **121**. **b** Mechanistic investigations on the role of each additive. **c** Milstein's iron(II)-dihydride pincer complex **125** for reductive imine formation with H_2 **107**. **d** Mechanistic role of the added alkoxide.

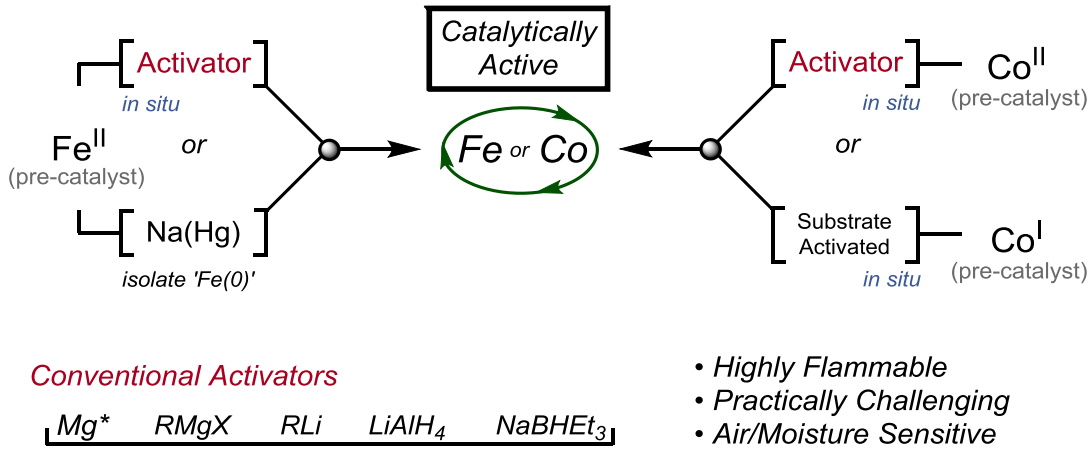
1.9 Summary

There is a growing body of work using iron- and cobalt-catalysts, most commonly accessing low oxidation-state species to perform useful synthetic transformations. Reported methods commonly use higher oxidation-state iron(II) or cobalt(II) precursors as these are often commercially available, easy to handle and readily form complexes with mono- and multidentate ligands. However iron(II) and cobalt(II) complexes are typically reduced by organometallic reductants before catalytic activity can be observed. Once accessed, the low oxidation state species, typically iron(0) or cobalt(I), have shown remarkable catalytic reactivity across several reaction classes. This includes reductive functionalisation, such as:

hydrogenation hydroboration and hydrosilylation. Additionally powerful carbon-carbon bond forming reactions have emerged, such as: hydrovinylation and cycloaddition. While all of these reactions are used for olefin functionalisation, iron- and cobalt-catalysts have also shown promise for reductive functionalisation with polar substrates, such as: ketone, ester and imine. These advances demonstrate the applicability of Earth-abundant metals to transformations previously only accessible using precious metal catalysis.

2. A novel strategy for pre-catalyst activation

2.1 State-of-the-art at the outset of the project



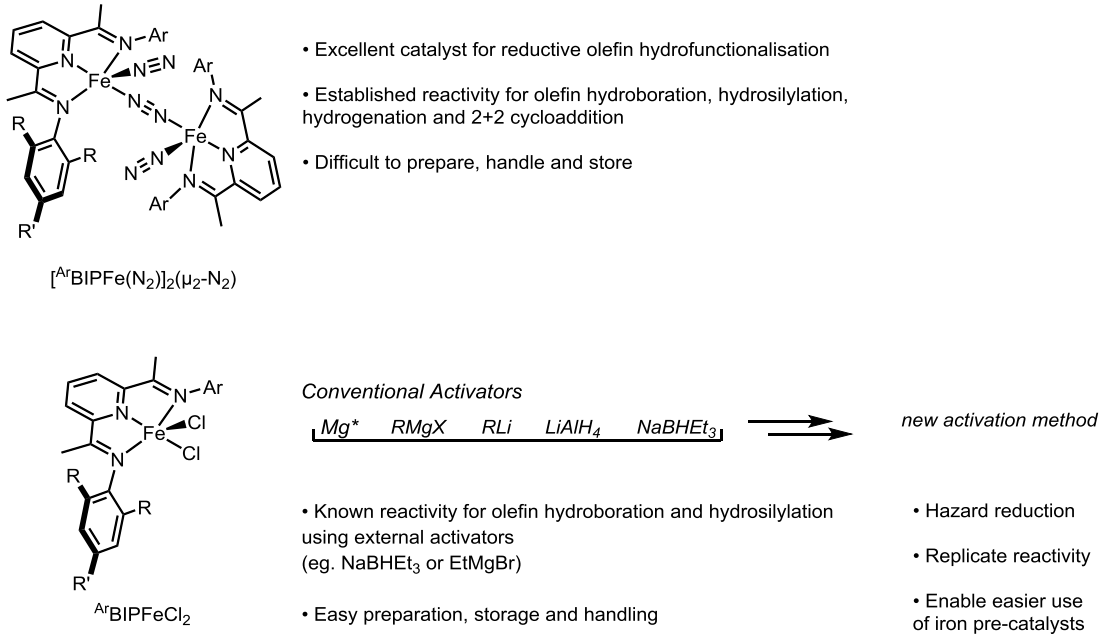
Scheme 2.1: State-of-the-art routes for the reductive use of iron and cobalt pre-catalysts.

At the project outset many examples of low-oxidation state catalytic transformations using iron and cobalt-complexes had been reported, particularly in recent years. All of the reported methodologies used either: a) a pre-formed low oxidation-state iron/cobalt complex, b) an iron/cobalt salt, exogenous ligand and external activator, or c) an iron/cobalt pre-formed complex and external activator. In every example it is clear that a prior metal reduction or *in situ* activation was necessary for reactivity. A main advantage of pre-formed low oxidation-state complexes is the fact that they are well characterised isolates, and therefore allow for easier mechanistic studies. However their high air and moisture instability hinder their practical everyday use. External activators navigate beyond these instability limitations and allow for usage by the broader chemical community, despite the active species having not been well-characterised.

Previous efforts using well-characterised low oxidation-state isolated iron and cobalt-complexes strongly suggest the requirement of a reduced metal species for catalytic reactivity. Additionally, the synthesis of low oxidation-state isolated species had been achieved using both reducing metals, *eg*. sodium, and hydride reagents.[27] Given these precedents, external activators could rationally act as *in situ* metal reductants. Mechanistically, hydridic reagents (eg. $NaBHEt_3$) may transfer, by *salt-metathesis*, hydride groups from reagent-to-metal. The resulting metal-hydride species could then undergo a classical elimination of dihydrogen, a 2-electron process. In a similar way, alkyl-organometallic reagents bearing β-hydrides may undergo classical β-hydride elimination to

give metal-hydride species that in the same way could eliminate dihydrogen. Reducing metals, such as sodium or magnesium do not possess a hydride donor group and therefore must trigger pre-catalyst activation by a different pathway, most likely by electron transfer.

2.2 Initial project aims



Scheme 2.2: Initial project targets – the facile use of iron pre-catalysts in reductive transformations.

The overall goal of the project was to discover and develop an activation strategy that improved upon previous methods. Targeting the isolation of low-oxidation state precursors was not an aim due to their instability and difficulties encountered in their practical application. Addition of external activators to already established, widely reported and enhanced stability higher oxidation-state pre-catalysts was the most attractive scenario. Most typically, previously reported activators were organometallic reagents in nature. This class of compounds are well known to be highly reactive and as a result can be difficult to use. In common examples, activators such as: ^{n}BuLi, EtMgBr and $NaBHEt_3$ had been used. These all offer intrinsically high reduction potentials and therefore have a high propensity for the reduction of *high* oxidation-state metal centres. A new method for pre-catalyst activation would therefore have to mimic the high reductive power of this class of reagent. Conceptually any reagent with equivalent reductive potential would likely have reactivity similar to that of classic organometallic reagents, *i.e* they would react with air and moisture. As a result, discovery of any new method would have to navigate this limitation. The ideal external pre-catalyst activator would be an air- and moisture-stable solid that could be easily

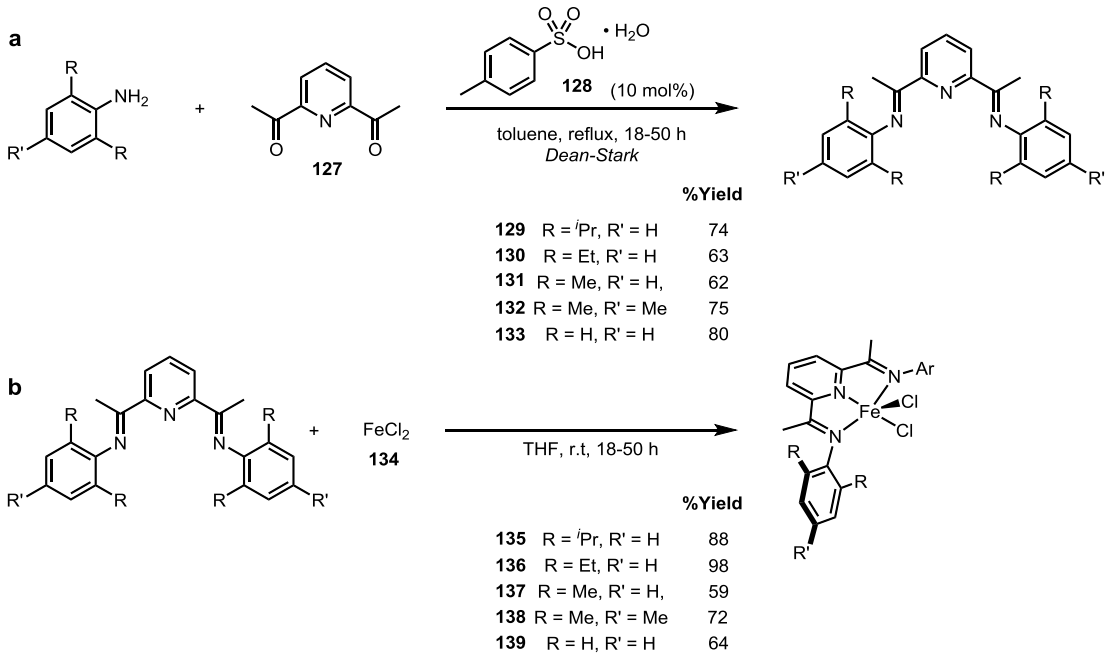
handled, stored and transported with minimal hazards. As described, this advance would enable straightforward and widespread access to low-oxidation state reactive catalysts.

2.3 Method discovery and development

2.3.1 Ligand and complex preparation

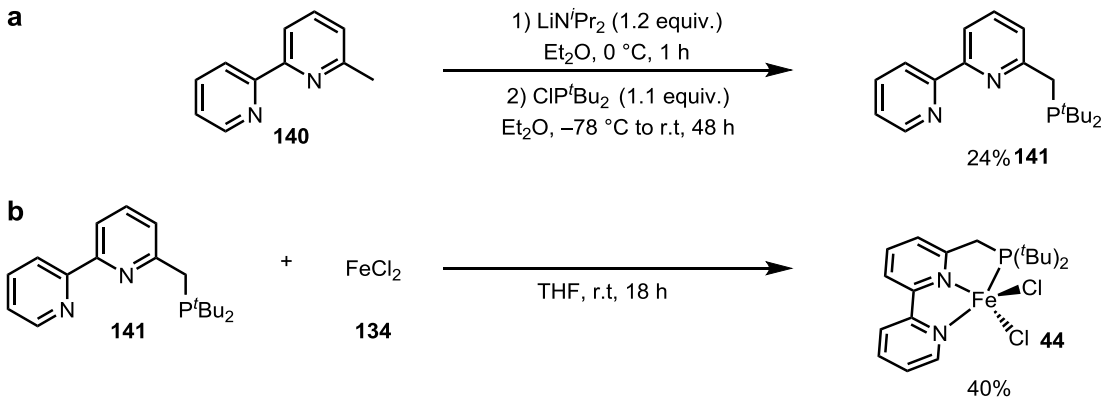
A requisite component for the discovery and development of any new activation procedure would be the preparation of established ligand and metal salt combinations. It was important to find literature reported examples of iron complexes which had well-established reactivity. Preferably this would include both low-oxidation state isolated complex based reactivity as well as the analogous *in situ* activated variant using external organometallic activators. Of all reported low-oxidation state homogeneous iron catalysis, examples of olefin hydrofunctionalisation were most prevalent and could act as platform reactions for novel activator discovery. The most well-established, and best performing, complexes for this reaction class were bis(imino)pyridine ligated iron dihalide complexes. Examples fulfilled both preferred pre-requisite conditions of established reactivity with isolated low-oxidation state iron complexes and examples with external activators, *eg*. Grignard or $NaBHEt_3$. In addition, the synthetic preparation of this class of metal complex was straightforward and well-known.

Pre-formed bis(imino)pyridine ligated iron dihalide complexes could be produced in two steps from commercially available starting materials, and a range of sterically varied examples could be produced using the same protocol. In this regard, both substituted and unsubstituted anilines were reacted with 2,6-diacetylpyridine **127** under dehydrating Dean-Stark conditions to form a sterically varied range of bis(imino)pyridine ligands **129-133** in generally high yields (Scheme 2.3, **a**). The ligands were then each complexed with iron(II) chloride **134** to give their respective products **135-139** which were easily purified by successive washing with Et_2O and CH_2Cl_2 (Scheme 2.3, **b**).



Scheme 2.3. **a** Bis(imino)pyridine ligand preparation. **b** Ligand and iron(II) dichloride complexation.

The utility of any novel activation method would rely on a general applicability to a range of structurally varied and unique pre-catalysts. Given that organometallic activators are a typical choice for the activation of numerous iron(II) pre-catalysts, it was logical to presume that any new method applicable to bis(imino)pyridine iron dihalide complexes would also be useful for structurally different complexes that had previously shown similar reactivity. To demonstrate applicability beyond a single catalyst class, another structurally differentiated pre-catalyst would also have to be successfully activated using the same method. Therefore, in anticipation of general extension of a new activation method, the PNN-iron(II) dichloride pre-catalyst **44**, which had been used by Huang for alkene hydroboration was prepared.[65] From 6-methyl-2,2'-bypyridine **140**, the PNN ligand **141** was prepared by LDA deprotonation and addition to di-*tert*-butylchlorophosphine in low but usable yield (Scheme 2.4, **a**). Complexation of **141** with iron(II) dichloride **134** gave the resulting pre-catalyst **44** in useful yields (Scheme 2.4, **b**). It is worthwhile to note that while the free ligand **141** is highly air-sensitive, the iron(II) complex **44** displays good air- and moisture-stability on the week/month timescale.



Scheme 2.4. **a** Preparation of Milstein's phosphine-bipyridine PNN ligand. **b** Complexation of the PNN ligand with iron(II) dichloride.

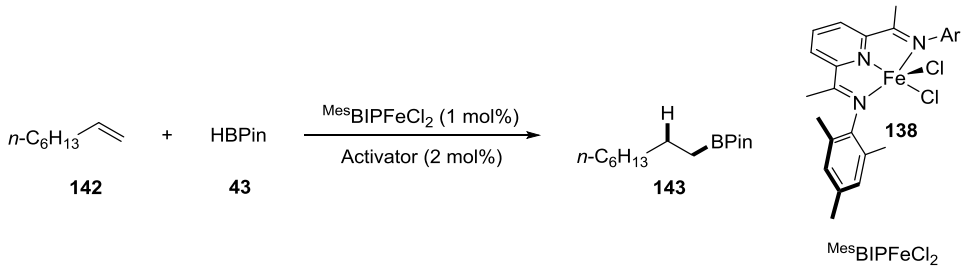
2.3.2 Activation method discovery and development

With a suitable variety of iron(II) pre-catalysts in hand, the attempted activation with novel reagents could be pursued. A typical reaction of 1-octene with HBpin was selected as a model test reaction for discovery. It had been previously established that terminal alkenes, such as 1-octene, were compatible with the prepared pre-catalysts for hydroboration using HBpin **43**.[80] In these literature reports, the iron(II) complexes had shown success when used in combination with either EtMgBr or $NaBHEt_3$ as external organometallic activators.[81] Therefore investigations began by testing and confirming this reactivity using the mesityl-substituted version of the bis(imino)pyridine iron(II) dichloride precatalyst **138**, $^{Mes}BIPFeCl_2$. Reaction of pre-catalyst, 1-octene **142** and HBpin **43** together in THF - a control reaction - with no added additives or activator confirmed the reliance of an added activator for any catalytic activity (Table 2.1, entry 1). Classically used organometallics, that had been successful previously, were confirmed as suitable activator reagents (Table 2.1, entries 2-4). Under all test reaction conditions, and according to previous literature precedent, it was assumed that two hydride equivalents would be necessary for pre-catalyst reduction and therefore a 2:1 ratio of activator/pre-catalyst was used. Under the chosen test reaction conditions, EtMgBr (2 equivalents wrt. pre-catalyst) could be used as the activator to give the product in low yields (Table 2.1, entry 3). Hydride reagents showed much greater activation potential; $NaBH_4$ gave the product in a moderate yield, and the most commonly used $NaBHEt_3$ gave the hydroborated product in significantly higher yields (Table 2.1, entries 4-5). Having confirmed the expected reactivity of the $^{Mes}BIPFeCl_2$ pre-catalyst **138** with established organometallic reagents, it was clear that this system could be used as a discovery platform for a new and simplified activation strategy.

With prior precedent suggestive of pre-catalyst reduction as a key step in enabling reductive catalysis, clearly any new external activator would be required to perform the same role as already successful reagents. The intrinsic reduction potential required to overcome the Fe(II) to Fe(I/0/-I/-II) oxidation state barrier would therefore be necessarily high, in line with that of alkali metals or organometallic reagents.[82] Unfortunately many reagents with these physical properties have issues with air- and moisture-stability.

Given the requisite set criteria for any newly discovered external activating reagent, of air- and moisture stability, this trait and tendency to use strongly reducing reagents would have to be broken. In opposition to the use of organometallic reagents, the selected standard test reaction conditions were applied in combination with common laboratory stored reagents (Table 2.1, entries 6-21). The aim of this assessment was to quickly test whether any readily available and easily handled reagents could be applicable to the activation of ^{Mes}BIPFeCl$_2$ **138**. As a surprise initial result, the nucleophilic fluoride source TBAF led to the formation of small but observable quantities of the hydroborated alkyl boronic ester product **143** (Table 2.1, entry 6). Triethylamine, triphenylphosphine, free-ligand (MesBIP), sodium carbonate, sodium hydrogen carbonate and sodium sulfate showed no propensity for pre-catalyst activation (Table 2.1, entries 7-12). Alkoxide salts, however, showed tremendous activation power and the use of NaO^{t}Bu enabled pre-catalyst activation and formation of the expected alkyl boronic ester in both high yield and selectivity (Table 2.1, entry 13). Importantly for practical and widespread adoption, the use of NaO^{t}Bu was highly robust, and the result could be repeated to generate the same product in high yield in multiple separate reactions. It was also worthwhile documenting the reactivity of generic commercially available NaO^{t}Bu (97% purity, Sigma-Aldrich) and refined NaO^{t}Bu (99.99% purity, Sigma-Aldrich) which both had equivalent reactivity (Table 2.1, entries 13 &14). Additionally, NaO^{t}Bu synthetically produced by different methods, from NaH and HO^{t}Bu or Na(s) and HO^{t}Bu, both showed equivalent reactivity (Table 2.1, entries 15-16). The analogous potassium and lithium salts, KO^{t}Bu and LiO^{t}Bu, were tested for their activation ability, however in each case lower product yield was observed (Table 2.1, entries 18-19). Presumably the significantly lower reactivity of the lithium analogue is due to its comparably poor solubility of this salt in THF. Alternative sodium alkoxide salts with varying alkyl groups were also successful activators; sodium methoxide and sodium phenyl-methanolate worked well for pre-catalyst activation which was clear from the high yield of alkyl boronic ester **143** produced in these reactions. Nevertheless, NaO^{t}Bu proved to be best over all other alternative activators for the model reaction, giving the best product yields regardless of source or purity.

Table 2.1 - Activator discovery: iron-catalysed hydroboration of alkenes



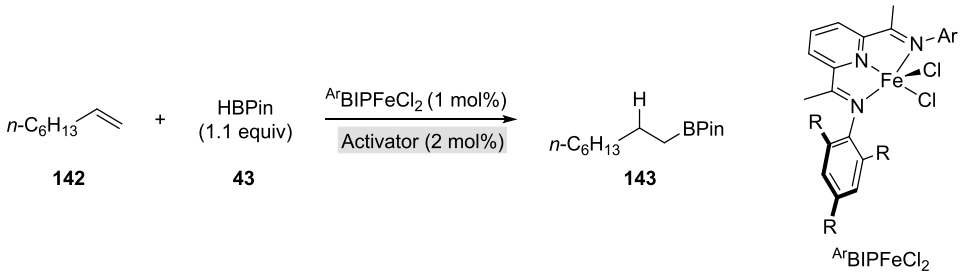
142 **43** **143**

Entry[a]	Activator	Yield (%)[c]
1	-	0
2[b]	Na(Hg)	>98
3	EtMgBr	27[d]
4	$NaBH_4$	45[e]
5	$NaBHEt_3$	80[d]
6	TBAF	3[d]
7	NEt_3	0
8	PPh_3	0
9	^{Mes}BIP	0
10	Na_2CO_3	0
11	$NaHCO_3$	0
12	Na_2SO_4	0
13	**NaO^{t}Bu**	**90[d]**
14[f]	**NaO^{t}Bu (99.99%)**	**92[d]**
15	NaO^{t}Bu (from NaH + HO^{t}Bu)	88[d]
16	NaO^{t}Bu (from Na + HO^{t}Bu)	90[d]
17	KO^{t}Bu	85[d]
18	LiO^{t}Bu	10[d]
19	NaOMe	82[d]
20	NaOBn	87[d]
21	NaOH	5[d]

[a]Reaction conditions: 1-Octene (0.4 mmol), HBPin (0.48 mmol), [Fe] (1 mol%), Activator (2 mol%), THF (0.5 mL), 25°C, 60 minutes. [b]Reaction from ref. 80, reported yield is based on conversion of 1-octene. Isolated Fe(0) complex isolated following Na(Hg) reduction. [c]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [d]Average of three runs. [e]1 mmol scale. [f]Reaction conducted using NaO^{t}Bu (99.99% purity from Sigma-Aldrich) and ^{Mes}BIPFeCl$_2$ prepared from $FeCl_2$ (99.99% purity from Sigma-Aldrich).

To assess general applicability beyond the activation of a single pre-catalyst, the newly discovered activation method was applied to the family of $BIPFeCl_2$ pre-catalysts that had been previously prepared (Table 2.2). Initial control reactions showed reliance on both pre-catalyst and activator for any productive catalytic reactivity (Table 2.2, entries 1-3). However, the combination of pre-catalyst and NaO^tBu under the standard test reaction conditions led to successful catalytic activity and the formation of the expected alkylboronic ester **143** in each case as a single regioisomer (Table 2.2, entries 4-7). While all pre-catalysts showed successful catalyst activation the ethyl-substituted variant ($^{Et}BIPFeCl_2$) gave the best yield (Table 2.2, entry 4). The sterically more hindered ($^{iPr}BIPFeCl_2$), and less hindered ($^{Mes}BIPFeCl_2$ and $^{2,6\text{-}Me}BIPFeCl_2$) gave the product **143** in comparably reduced yields (Table 2.2, entries 5-7).

Table 2.2 – BIP Catalyst scope for the 1,2-hydroboration of 1-octene



Entry[a]	(pre-)Catalyst	Ar	Activator	Yield (%)[b]
1	$^{Et}BIPFeCl_2$	2,6-Et-C_6H_3	*none*	0
2	*none*	-	NaO^tBu	0
3	^{Et}BIP	2,6-Et-C_6H_3	NaO^tBu	0
4	$^{Et}BIPFeCl_2$	2,6-Et-C_6H_3	NaO^tBu	>95
5	$^{Mes}BIPFeCl_2$	2,4,6-Me-C_6H_2	NaO^tBu	90
6	$^{2,6\text{-}Me}BIPFeCl_2$	2,6-Me-C_6H_3	NaO^tBu	82
7	$^{iPr}BIPFeCl_2$	2,6-^{i}Pr-C_6H_3	NaO^tBu	29

[a]Reaction conditions: Following general procedure C; 1-Octene (0.4 mmol), HBPin (0.44 mmol), [Fe] (1 mol%), NaO^tBu (2 mol%), THF (0.5 mL), 25°C, 60 minutes. [b]Yield determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

With an optimal pre-catalyst found, the dependence of NaO^tBu loading was investigated. In all initial discovery reactions, a low pre-catalyst loading (1 mol%) and 1:2 ratio of pre-catalyst/activator had been used. These pre-set conditions were based on prior literature precedent which anticipated the requirement of a 2-electron reduction of the pre-catalyst. To verify if a 2:1 ratio for NaO^tBu was optimal in this case, the rate profile of the optimally

found reaction conditions was monitored using both a 1:2 and 1:2 ratio of pre-catalyst/activator (Figure 2.5). The reaction with a 1:2 ratio was best and gave an overall higher yield. The reaction with higher equivalents of NaO^{t}Bu was significantly slower, suggesting an inhibitory role for excess NaO^{t}Bu following initial pre-catalyst activation. Significantly, these studies show that the overall rate of reaction is rapid, giving 88% of the expected alkylboronic ester in only 15 minutes.

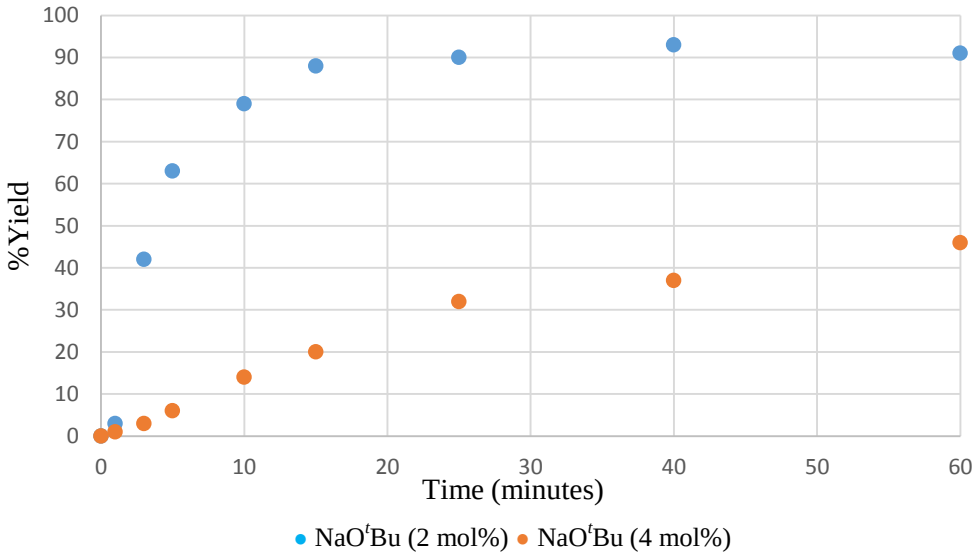


Figure 2.5 – Reaction progress monitoring for the hydroboration of 1-octene using pinacolborane, catalysed by ^{Et}BIPFeCl$_2$ + NaO^{t}Bu (1:2 ● & 1:4 ●) under standard reaction conditions.

2.3.3 Control studies for trace element *hidden* catalysis

Given the role of trace metals contained within additives and reagents in base-metal catalysed reactions, it was prudent to check whether a component of this newly discovered method was contaminated with a potential "*hidden* catalyst".[117] There are many examples of precious metal-catalysed olefin hydroborations, the most common examples use Rh, Ru or Cu as the transition metal catalyst. The ICP-MS technique was used to assess the quantity of trace metal contaminants as this has sensitivity for as low as ppb concentrations of metal contaminants. The model reaction used included: ^{Et}BIPFeCl$_2$ **136** (1 mol%), 1-octene (0.5 mmol), HBPin **43** (1.1 eq) and NaO^{t}Bu (2 mol%). A portion of the reaction mixture was analysed by ICP-MS and the concentrations of trace elements determined by comparison against a multi-element standard solution (Table 3, *n.b experiment performed and data provided by Dr Lorna Eades*). This revealed that the most abundant trace element contaminants were: Mn, Al and Ni (Table 2.3, entries 1, 3 & 6). However the concentrations of these elements in the mixture were significantly lower than the concentration of iron (*the*

catalyst); ratios of *ca.* 0.001:1, *i.e* 1000-fold less. Precious metal contaminants were detected at much lower concentrations (Table 2.3, entries 8-16). For example, the noteworthy metals of concern; Rh and Ru were observed at ratios of *ca.* 1×10^{-6}:1, *i.e* a million-fold less (Table 2.3, entries 8 & 9). This information taken together with the previously conducted control reactions, in the absence of catalyst, ligand or activator, suggest that the reactivity observed is a result of successful activation of the $BIPFeCl_2$ **136** pre-catalyst with NaO^tBu and not reliant on, or a result of, trace element contaminants.

Table 2.3 - ICP-MS analyses for trace metal contaminants

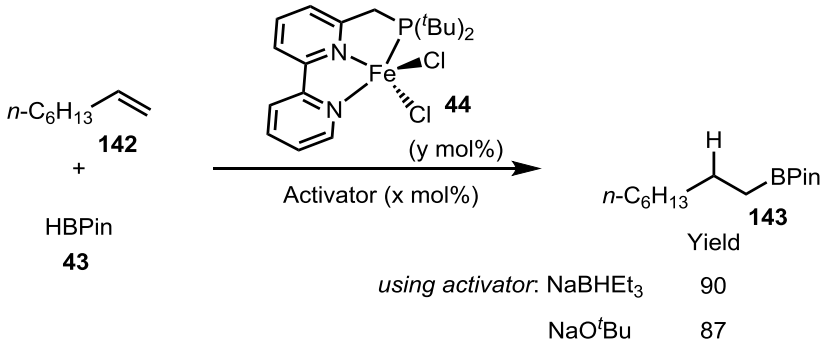
Entry	Element	Mass	Concentration (ppb)	Relative to Fe (Element/Fe)
1	Al	29	5.000	2.63×10^{-3}
2	Cr	53	0.032	1.68×10^{-5}
3	Mn	55	1.700	8.95×10^{-3}
4	Fe	57	1900.000	1.00
5	Co	59	0.260	1.37×10^{-3}
6	Ni	60	3.700	1.95×10^{-3}
7	Cu	63	0.200	1.05×10^{-3}
8	Ru	101	0.008	4.21×10^{-6}
9	Rh	103	0.002	1.05×10^{-6}
10	Pd	105	0.02	1.05×10^{-5}
11	Ag	107	0.100	5.26×10^{-5}
12	Os	189	0.011	5.79×10^{-6}
13	Ir	193	0.007	3.68×10^{-6}
14	Pt	195	0.007	3.68×10^{-6}
15	Au	197	0.009	4.74×10^{-6}
16	Hg	202	0.16	8.42×10^{-5}

[a]Analysis of the reaction mixture by ICP-MS: $^{Et}BIPFeCl_2$ (1 mol%), 1-Octene, HBPin (1.1 eq), NaO^tBu (2 mol%).

2.3.4 Method applicability to alternative pre-catalyst systems

2.3.4.1 Application to Milstein's PNN-iron(II) pincer complex for alkene hydroboration

With the successful activation of the $BIPFeCl_2$ pre-catalyst family achieved using NaO^tBu, this outlined conditions that may be applicable to a broader range of catalyst systems. The aim was to therefore extend the activation method to structurally unique pre-catalysts to assess the ability and generality of NaO^tBu as an activator. Huang had previously used $NaBHEt_3$ for the activation of Milstein's phosphine-bipyridine iron(II) dichloride pre-catalyst $^{tBu}PNNFeCl_2$ **44** for the hydroboration of alkenes using pinacolborane. Using the same standard conditions as those used for $BIPFeCl_2$ pre-catalyst activation, NaO^tBu was applied and the activation of $^{tBu}PNNFeCl_2$ **44** could be achieved to generate octyl-boronic ester **143**, in both equivalent yield and selectivity to that reported by Huang using an organometallic reagent (Scheme 2.4).[83]



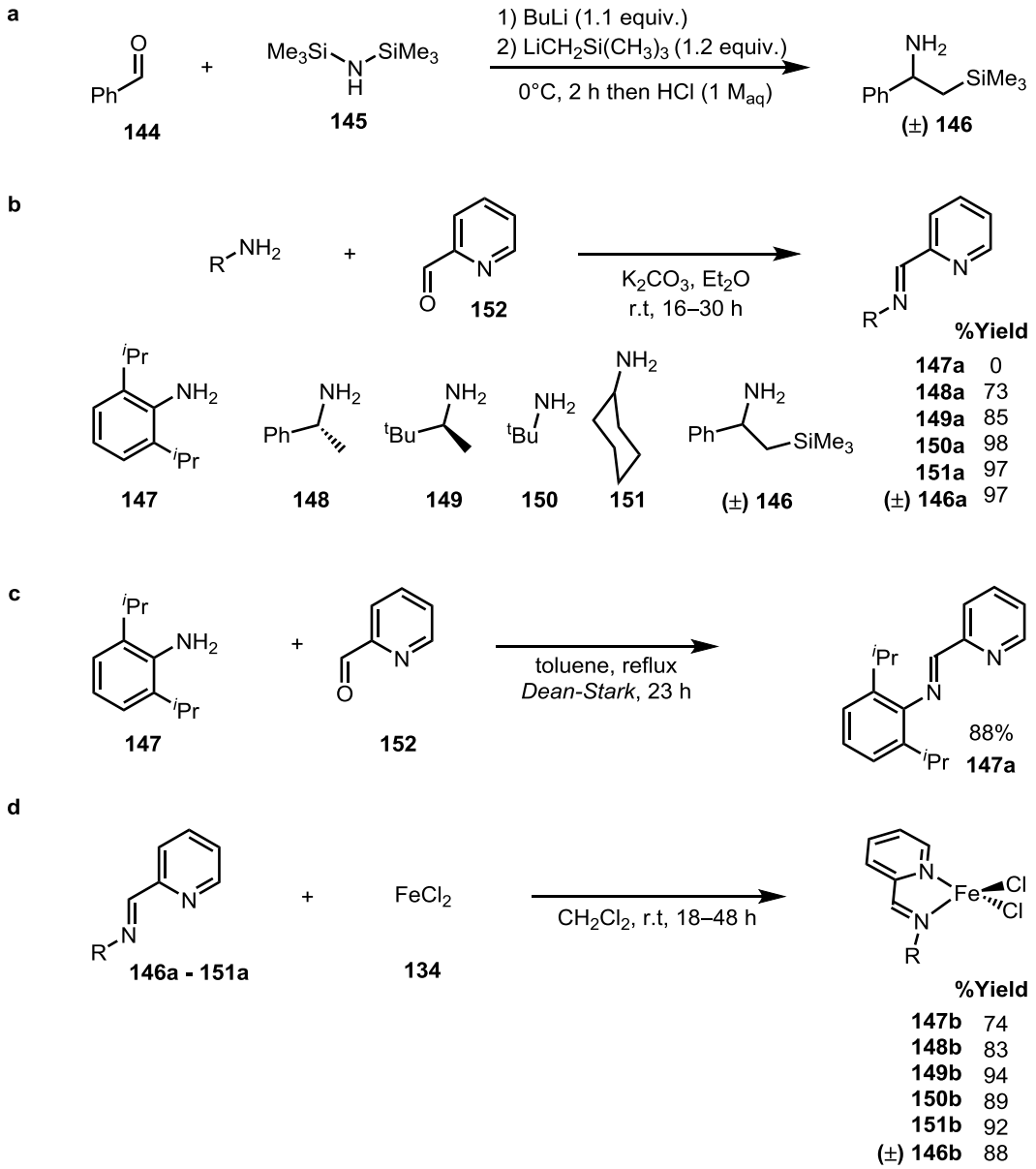
Scheme 2.4. 1-Octene hydroboration with Milstein's PNN-iron(II) complex using $NaBHEt_3$ and NaO^tBu activation. Reaction conditions: Huang: pre-catalyst (0.25 mol%), $NaBHEt_3$ (0.75 mol%), THF, 25 °C, this work: pre-catalyst (1 mol%), NaO^tBu (2 mol%), THF, 23°C.

2.3.4.2 Application to tom Dieck's bidentate iminopyridine ligand framework

Activation of two structurally distinct pre-catalysts had been achieved for both BIP and PNN ligand frameworks. These classes of catalyst featured tridentate ligands. The NaO^{t}Bu activation method was therefore further tested for applicability toward pre-catalysts that did not contain strongly chelating tridentate ligands.

Bidentate iminopyridine ligated iron(II) chloride complexes have been used for polymerisation and hydrofunctionalisation reactions.[118] Ritter has previously used a class of simple iminopyridine ligands, originally reported by tom Dieck,[96] for a range of olefin hydrofunctionalisation reactions.[71,85,97] Ritter showed that 1,3-dienes could be functionalised using pinacolborane using iminopyridine-iron complexes.[85] The resulting products were mixtures of 1,4- and 4,1-functionalised allyl-pinacolboronate ester products. Activated magnesium was used as the pre-catalyst activator, which had been freshly prepared by reduction of magnesium dibromide using lithium naphthalenide.

To investigate the applicability and generality of NaO^{t}Bu activation for olefin hydroboration reactions using bidentate iminopyridine ligand complexes, a series of iminopyridine ligands and corresponding complexes were prepared. The main focus aimed at preparation of the same structures that had previously been used for 1,4-hydrofunctionalisation by Ritter as this would provide an easy reactivity comparison (Scheme 2.5).



Scheme 2.5. **a** Preparation of Me_3Si-substituted sterically hindered amine ligand precursor. **b** Imine-condensation reactions for the formation of iminopyridine ligands. **c** Alternative imine condensation reaction method required to install aryl-imine group. **d** Ligand complexation of the iminopyridine ligands with iron(II) dichloride.

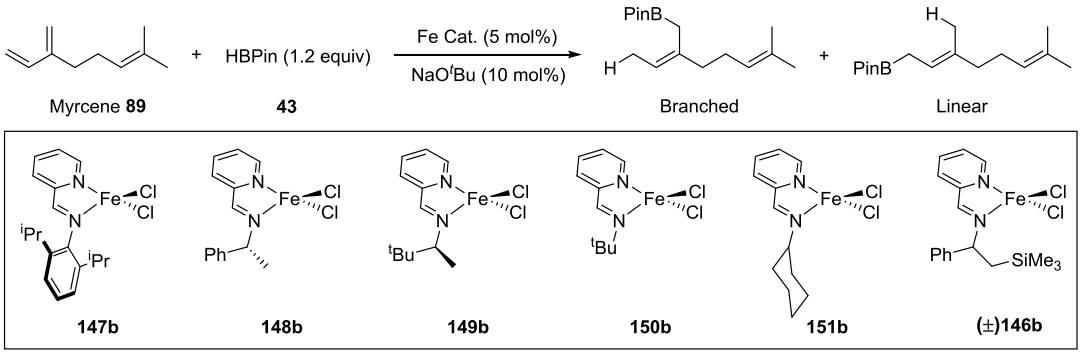
A range of sterically varied iminopyridine ligands had been trialled by Ritter for 1,3-diene functionalisation.[71,85] Many used simple commercially available amines as the requisite precursor for the subsequent imine condensation reactions. One example, however, involved a two-step synthesis of an amine with greater steric requirements **146a**. This amine was prepared from the reaction between benzaldehyde **144**, hexamethyldisilazane **145** and lithium tetramethylsilane to give **146** (Scheme 2.5, **a**). The resulting amine and multiple commercially available amines were condensed with 2-pyridinecarboxaldehyde **152** to give

iminopyrdine ligands **146a** and **148a-151a** (Scheme 2.5, **b**). However, the reaction using aryl amine **147** was entirely unsuccessful under these conditions. High temperature and Dean-Stark conditions were therefore used for the formation of aryl-iminopyridine ligand **147a** (Scheme 2.5, **c**). Iminopyridine iron(II) dichloride complexes **146b-151b** were easily prepared by ligation in CH_2Cl_2 (Scheme 2.5, **d**). In all complexation reactions an almost immediate colour change was observed. With regards to the air- and moisture stability of these complexes; while tridentate examples ($BIPFeCl_2$, $PNNFeCl_2$) were highly robust, the bidentate iminopyridine iron(II) chloride complexes were much less stable and decompose within one week if left entirely open to ambient atmosphere.

Ritter used pre-catalyst **147b** with added activated magnesium as the activator to perform the 1,4-hydroboration of myrcene **89** using pinacolborane **43**.[85] This reaction gave a 17:83 ratio of linear/branched-regioisomers in 92% yield. Using NaO^tBu as an activator for the same pre-catalyst **147b**, instead of activated magnesium, enabled reactivity in the same way to generate the product mixture in high yield and equivalent regioselectivity to that reported previously (17:83 *vs* 18:82, Table 2.4, entry 1). This result indicates that NaO^tBu can act in place of activated magnesium to the same, if not improved, efficiency, and is suggestive of the formation of the same active catalyst species. It is noteworthy that in both Ritter's work and this example, 5 mol% pre-catalyst and 10 mol% activator were used. Additionally with regards to product purification, while literature precedent suggests purification by silica column chromatography, the allyl-boronate ester products are only moderately stable under these conditions and greater yields could be obtained by direct distillation from the reaction mixture.

With the successful activation of pre-catalyst **147b** established, the applicability could be further demonstrated with application to an entire iminopyridine-iron(II) pre-catalyst family **146b** and **148b-151b** (Table 2.4, entries 2-6). In all examples where the pre-catalyst imine-group contained an α-nitrogen secondary carbon ($C_{sp}{}^3$) centre, the catalytic activity was high and the products could be generated in high yields. An exception to high reactivity was observed with the use of pre-catalyst **150b**, which contains the *tert*-butyl-imino functionality (Table 2.4, entry 4). Interestingly, the examples of pre-catalysts bearing alkyl ($C_{sp}{}^3$) imino groups displayed regiodivergence to that of the aryl ($C_{sp}{}^2$) imino pre-catalyst **147b**.

Table 2.4 – Iminopyridine pre-catalyst scope for the 1,4-hydroboration of myrcene



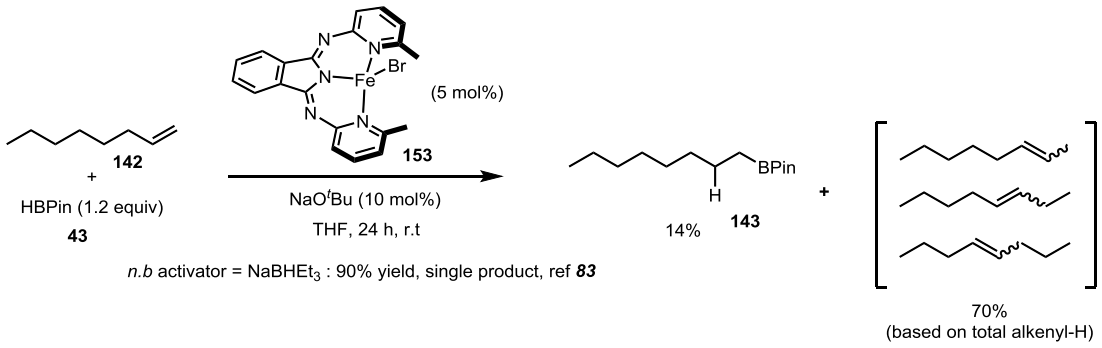
Entry[a]	(pre-)Catalyst	Overall Yield (%)[b]	Linear: Branched[c]
1	**147b**	>95	18:82
2	**148b**	79	80:20
3	**149b**	74	68:32
4	**150b**	12	58:42
5	**151b**	91	74:26
6	**(±) 146b**	94	82:18

[a]Reaction conditions: Following general procedure A; Myrcene (0.4 mmol), HBPin (0.48 mmol), [Fe] (5 mol%), NaO^{t}Bu (10 mol%), THF (0.5 mL), 25 °C, 60 minutes. [b]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Regioselectivity determined by ^{1}H NMR.

2.3.4.3 Attempted activation of Szymczak's hydroboration pre-catalyst

Having demonstrated pre-catalyst activation of both tridentate and bidentate ligand bearing pre-catalysts, an attempt was made to expand this methodology to other pre-catalysts that would perform the same hydrofunctionalisation reaction. A recent report by Szymczak showed that an amide-derived *N,N,N*-Fe(II) complex **153** could catalyse the hydroboration of alkenes, albeit at higher pre-catalyst and activator loadings that had been used for other systems such as $BIPFeCl_2$ or $IPFeCl_2$.[84] Structurally this system is unique and distinct from other examples due to the fact that one ligating partner is an amide, and this pre-catalyst does not bear two halide substituents. Nevertheless, pre-catalyst activation and successful reactivity had been demonstrated using $NaBHEt_3$. *(n.b Complex **153** was generously provided by Prof. N. Szymczak.)*

In an attempt to enable the same reactivity using NaO^{t}Bu as the activator, 1-octene **142** and pinacolborane **43** were subjected to the set of standard reaction conditions previously used for $BIPFeCl_2$ and $IPFeCl_2$ systems. While catalyst activation was successful, as observed by rapid colour change and consumption of starting materials, the reaction did not form the expected octyl-pinacolboronate ester **143** as the sole product (Scheme 2.6). Only a small quantity of boronic ester **143** was produced, alongside a complex mixture of internal alkenes. The formation of internal alkene, isomerisation, products suggest the presence of a metal-hydride species that is capable of sequential hydrometallation/*β*-hydride elimination for both terminal and internal alkene intermediates. Notably only the presence of terminal/linear boronate ester product was observed, indicating that while hydrometallation of internal alkenes is possible the formation of internal boronic esters was not.



Scheme 2.6. Attempted hydroboration of 1-octene using Szymczak's amide derived *N,N,N*-Fe(II) complex.

2.4 Extension beyond alkene hydroboration reactions

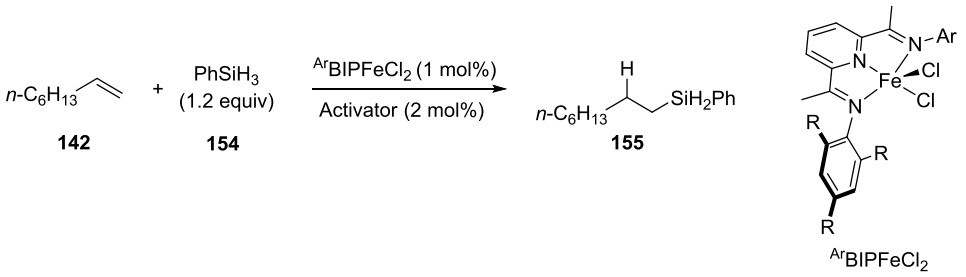
2.4.1 Application of NaO^{t}Bu activation in the iron-catalysed hydrosilylation of alkenes

Given the importance, prevalence and effort allocated to olefin hydrosilylation with both precious and non-precious metals, it was important to assess NaO^{t}Bu as an activator for this reaction class. In a similar manner to that of olefin hydroboration with iron pre-catalysts, organometallic reagents have been used as pre-catalyst activators.[17,31,80,81,83-89] With the BIP-complex class that had been used previously, the same set of complexes could also be trialled for reactivity toward hydrosilylation reactions. Reactivity for isolated low oxidation-state complexes and for *in situ* activation organometallic activated examples had been reported.

Using the standard set of activation conditions found previously for hydroboration reactions, the same methodology was applied to hydrosilylation reactions. In the same way was before, 1-octene **142** was chosen as the model substrate and phenylsilane **154** as the model silane. The choice of reactants was based on prior precedent, whereby successful reactivity had been found using Grignard reagents as pre-catalyst activators.[69] Initially using ^{Mes}BIPFeCl$_2$ **138** (1 mol%) as the pre-catalyst and NaO^{t}Bu (2 mol%) as activator, successful catalyst activation was achieved to give the linear hydrosilylation product **155** in high yield (Table 2.5, entry 1). It was important to check for baseline reactivity in the absence of activator to unequivocally show that successful catalyst activity was reliant on the presence of NaO^{t}Bu. Thus under the same reaction conditions without added NaO^{t}Bu, the reaction was conducted but did not proceed (Table 2.5, entry 2). Similarly the reaction did not proceed in the absence of either pre-catalyst **138**, or in the absence of metal (*i.e* only free ligand ^{Mes}BIP) (Table 2.5, entries 3 & 4).

With reactivity established using ^{Mes}BIPFeCl$_2$ **138**, the reaction conditions were applied to other pre-catalysts with varying steric parameters (Table 2.5, entries 4-7). All pre-catalysts in this family that were assessed showed reactivity, demonstrating that NaO^{t}Bu again worked successfully across multiple sterically distinct pre-catalysts. The most sterically hindered pre-catalyst, ^{iPr}BIPFeCl$_2$ **135**, however performed poorly and only gave the linear silane **155** in modest yield (Table 2.5, entry 7). Less hindered pre-catalysts all performed well, giving high yields of silane **155**. It is interesting to note that all pre-catalysts of this class exhibited the same reactivity to that observed with other activation methods, all generating the anti-Markovnikov product as a single regioisomer.[17,60,69] This may indicate the formation of a common reactive species by all activation methods.

Table 2.5 - Catalyst scope for the 1,2-hydrosilylation of 1-octene



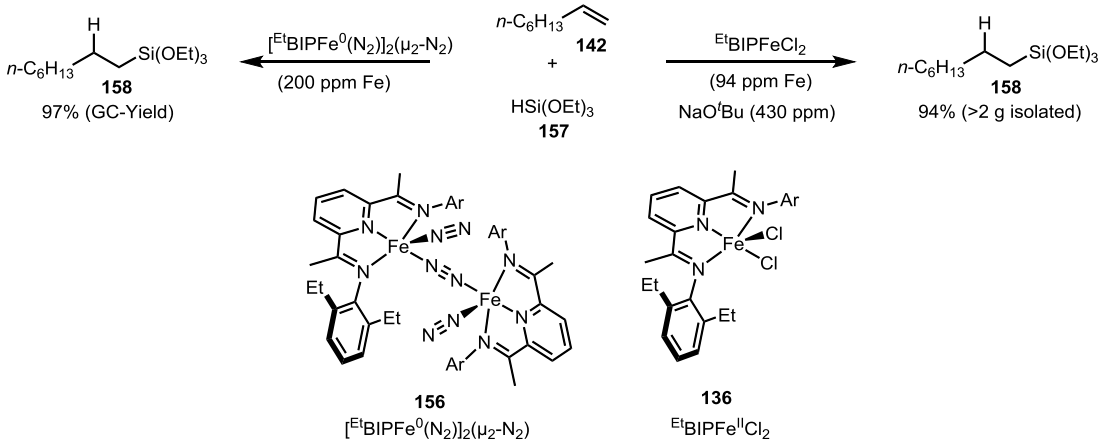
Entry	(pre-)catalyst	Ar	Activator	Yield (%)
1	^{Mes}BIPFeCl$_2$	2,4,6-Me-C$_6$H$_2$	NaO^{t}Bu	87
2	^{Mes}BIPFeCl$_2$	2,4,6-Me-C$_6$H$_2$	-	0
3	none	-	NaO^{t}Bu	0
4	^{Mes}BIP	2,4,6-Me-C$_6$H$_2$	NaO^{t}Bu	0
5	^{Et}BIPFeCl$_2$	2,6-Et-C$_6$H$_3$	NaO^{t}Bu	85
6	$^{2,6\text{-}Me}$BIPFeCl$_2$	2,6-Me-C$_6$H$_3$	NaO^{t}Bu	85
7	^{iPr}BIPFeCl$_2$	2,6-^{i}Pr-C$_6$H$_3$	NaO^{t}Bu	34

[a]Reaction conditions: Following general procedure D; 1-Octene (0.4 mmol), $PhSiH_3$ (0.48 mmol), [Fe] (1 mol%), NaO^{t}Bu (2 mol%), THF (0.5 mL), 25 °C, 60 minutes. [b]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

2.4.2 Scale-up of an iron-catalysed hydrosilylation using NaO^{t}Bu as the activator

With the concept of NaO^{t}Bu activation of BIPFeCl$_2$ pre-catalysts demonstrated for alkene hydrosilylation and the industrial importance of this reaction class, it was meaningful to assess the scalability of this reaction. A relevant comparison using a low oxidation-state iron(0) dinitrogen complex had been reported by Chirik with only 200 ppm Fe.[60] Therefore an analogous iron(II) dichloride complex (^{Et}BIPFeCl$_2$ **136**) activated by NaO^{t}Bu was tested and its reactivity compared (Scheme 2.6). Chirik showed that the isolated iron(0) catalyst **156** could be used effectively at very low catalyst loadings, so it was important to assess if the active catalyst generated by NaO^{t}Bu had a similar activity.[60] It was also necessary in this instance to change the reactant silane to triethoxysilane as phenylsilane had not been used by Chirik. Furthermore, this example using triethoxysilane **157** is industrially relevant as the products of hydrosilylation using this silane are directly used industrially for coatings, sealants and adhesives.

The experiment was conducted using sequentially reduced pre-catalyst loadings until a lower limit was reached at 94 ppm Fe and 430 ppm NaO^{t}Bu. It is important to note that these quantities of pre-catalyst and activator still mirror a 1:2 ratio and the ppm quantities are derived from calculations by mass. In both Chirik's example and this work, activated with NaO^{t}Bu, the product was generated in high yield and with equivalent selectivity for a single anti-Markovnikov regioisomer (Scheme 2.7). As the catalyst loading was lowered from this point, activity was still observed although at much lower levels, as observed by incomplete consumption of starting materials.



Scheme 2.7. Scale-up and comparison of iron-catalysed alkene hydrosilylation reactions.

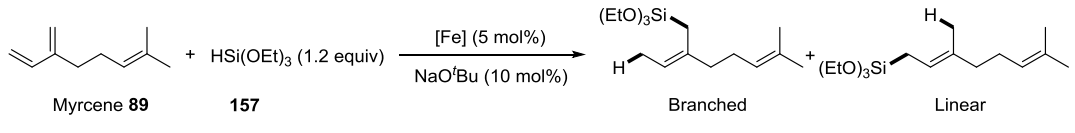
2.4.3 Application of NaO^{t}Bu activation in the 1,4-hydrosilylation of 1,3-dienes

In addition to Ritter's 1,4-hydroboration of 1,3-dienes using iminopyridine-ligated iron complexes, he had also extended the utility of these complexes to the analogous hydrosilylation reactions.[71] However in contrast to 1,4-hydroboration reactions whereby an iron(II) dihalide precursor was necessarily reduced by exogenous added activated magnesium, the related hydrosilylation used a unique activation strategy. Alternatively in this instance, Ritter had shown that a two-step activation strategy could be used to form a catalytically active species which could be isolated and well characterised by X-ray crystallography, together with NMR and Mössbauer spectroscopy (*see chapter 1.51*). Strategically this involved the initial addition of an aryl-lithium reagent to iron(II) chloride followed by addition of iminopyridine ligand. In this method, the added aryl-lithium reagent formed a bis-aryliron(II) species which then underwent a 2-electron reductive elimination in

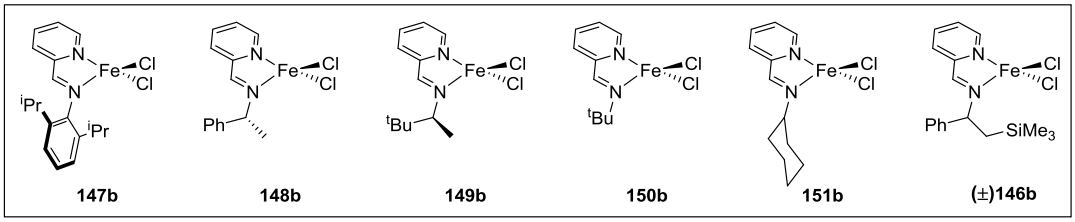
the presence of iminopyridine ligand. The resulting species was isolated and characterised as a formal iron(0) bis-chelate.

Given that the approach taken in this scenario differed from the usual strategy of adding external activators to pre-formed iron(II) dihalide pre-catalysts, it was unclear whether an added external activator would achieve the same reactivity. However when applied to the same iminopyridine iron(II) dichloride pre-catalysts that had been prepared and used for the 1,4-hydroboration of 1,3-dienes, the reactions proceeded in good to excellent yield across the entire spectrum of pre-catalysts (Table 2.6). Myrcene **89** was again chosen as the model substrate and in this instance triethoxysilane as the reacting functionalisation reagent. These choices were taken as both had been used by Ritter.[71] Using the aryl-imino pre-catalyst **147b**, a minor favourability for the branched regioisomer was found however with poor overall selectivity (Table 2.6, entry 1). All other alkyl-imino pre-catalysts showed good selectivity for the linear regioisomer, with **149b** giving an 88:12 ratio and with no observed formation of the (*Z*)-diastereomer. Importantly this compared favourably with the result in which Ritter had used the related ligand **149a** to give the allylsilane products in a ratio of 95:5. On a practical note for these compounds; the allyl-silane products, both linear and branched, displayed no stability when subjected to silica column chromatography and relied on careful distillation for product isolation.

Table 2.6 - Catalyst scope for the 1,4-hydrosilylation of myrcene



Myrcene **89** **157** Branched Linear



147b **148b** **149b** **150b** **151b** **(±)146b**

Entry[a]	(pre-)Catalyst	Overall Yield (%)[b]	Linear: Branched[c]
1	**147b**	88	42:58
2	**148b**	37 (linear)	n.d
3	**149b**	88	88:12
4	**150b**	65	82:18
5	**151b**	81	81:19
6	**(±)146b**	85	86:14

[a]Reaction conditions: Following general procedure B; Myrcene (0.4 mmol), $HSi(OEt)_3$ (0.48 mmol), [Fe] (5 mol%), NaO^tBu (10 mol%), THF (0.5 mL), 25 °C, 60 minutes. [b]Yield determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Regioselectivity determined by ^1H NMR.

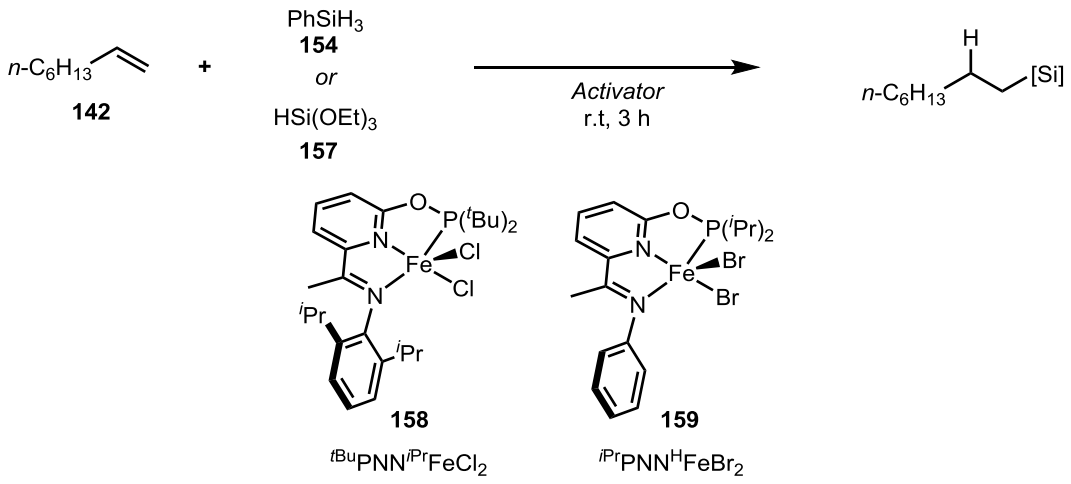
2.4.4 Attempted application to Huang's phosphinite-imino-pyridine iron complex

With successful activation of two pre-catalyst classes for hydrosilylation, it was logical to assess the viability of the activation method for a recently reported next-generation catalyst system. Huang had used less oxo-philic iron phosphinite-iminopyridine complexes which were activated *in situ* by $NaBHEt_3$.[66] The key advantage reported in this next-generation system was a broader substrate scope enabled by increased electron density at the iron centre which disfavoured coordination of polar groups, for example carbonyls or amides.

Applying NaO^tBu in the activation of this pre-catalyst class had very limited success (Table 2.7). Attempts were made with both the $^{tBu}PNN^{iPr}FeCl_2$ **158** and $^{iPr}PNN^{H}FeBr_2$ **159** pre-catalysts, each with unique sterics, and combinations of each of these with 1-octene **142** and phenylsilane **154** or triethoxysilane **157**. However, in all reactions tested the best result was

only formation of small amounts of expected alkylsilane (Table 2.7, entries 5 & 6). Initially this lack of reactivity was attributed to the much higher temperature of activation that was attempted in this work (23°C *vs* −34°C). The conditions set out by Huang used a low temperature activation of the phosphinite-iminopyridine pre-catalysts, while in this work the successful standard conditions operated at room temperature. As a result, it was rational to attempt the activation using NaO^{t}Bu at a reduced temperature, in order to match the conditions used by Huang. Despite this variation in reaction setup, the reactions still did not produce any alkylsilane and only starting materials were recovered (Table 2.7, entries 9 & 10).

Table 2.7 - Phosphinite-iron complex catalysed hydrosilylation of alkenes



Entry	Complex	Activator	Silane	Yield (%)[c]
1[a,b]	$^{t\text{Bu}}$PNN$^{i\text{Pr}}$FeCl$_2$	NaBHEt$_3$	PhSiH$_3$	94[d]
2[a,b]	$^{i\text{Pr}}$PNN$^{\text{H}}$FeBr$_2$	NaBHEt$_3$	HSi(OEt)$_3$	90[d]
3[a,b]	$^{t\text{Bu}}$PNN$^{i\text{Pr}}$FeCl$_2$	NaBHEt$_3$	HSi(OEt)$_3$	0
4[a,b]	$^{i\text{Pr}}$PNN$^{\text{H}}$FeBr$_2$	NaBHEt$_3$	PhSiH$_3$	0
5	$^{t\text{Bu}}$PNN$^{i\text{Pr}}$FeCl$_2$	NaO^{t}Bu	PhSiH$_3$	trace
6	$^{i\text{Pr}}$PNN$^{\text{H}}$FeBr$_2$	NaO^{t}Bu	HSi(OEt)$_3$	5
7	$^{t\text{Bu}}$PNN$^{i\text{Pr}}$FeCl$_2$	NaO^{t}Bu	HSi(OEt)$_3$	0
8	$^{i\text{Pr}}$PNN$^{\text{H}}$FeBr$_2$	NaO^{t}Bu	PhSiH$_3$	0
9[a]	$^{t\text{Bu}}$PNN$^{i\text{Pr}}$FeCl$_2$	NaO^{t}Bu	PhSiH$_3$	0
10[a]	$^{i\text{Pr}}$PNN$^{\text{H}}$FeBr$_2$	NaO^{t}Bu	HSi(OEt)$_3$	0

[a]Pre-catalyst activation conducted at −34 °C in anhydrous toluene. [b]Results taken from previous reports in ref. 66. [c]Yields determined by ^{1}H NMR of the crude reaction. [d]Isolated yield.

2.5 Application to metals beyond iron

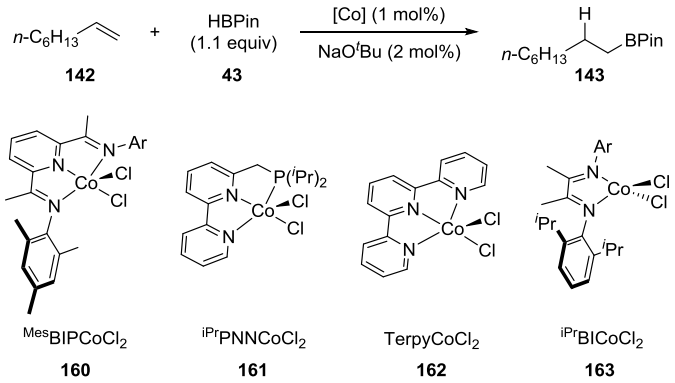
2.5.1 Cobalt-catalysed hydroboration of alkenes

The use of organometallic reagents applies to the activation of both iron(II) and cobalt(II) pre-catalysts and therefore it was potentially possible to apply the newly found NaO^{t}Bu activation strategy to related cobalt(II) systems. The main difference between the analogous iron- and cobalt-catalysed hydrofunctionalisation reactions lies in the operational oxidation states of the active catalysts. For iron, an iron(0)/iron(II) cycle is commonly proposed, whereas by contrast many cobalt examples initially involve generation of cobalt(I) with subsequent σ-bond metathesis pathways are proposed, with no change in oxidation-state of the active catalyst.[29,31,39,74]

If accessible by NaO^{t}Bu assisted reduction, the same cobalt(I) species that have been formed and used previously should also be usable for the hydroboration of alkenes. To this end, cobalt(II) pre-catalysts that had been used previously with organometallic activators, or as their low oxidation-state isolated analogues, were targeted to test NaO^{t}Bu activation. Initially the bisiminopyridine cobalt(II) dichloride pre-catalyst **160** was tested for reactivity under these conditions as Chirik had reported the use of the related cobalt(I)-methyl complex **40**.[86] Application to the standard set of conditions that were found to be broadly applicable for both hydroboration and hydrosilylation using iron(II) pre-catalysts enabled pre-catalyst activation and successful reactivity in this example (Table 2.8, entry 1). The comparable result reported using the isolated ^{Mes}BIPCo(I)-Me analogue **40** gave alkylboronic ester **160** as one regioisomer in >98% yield. Using NaO^{t}Bu and ^{Mes}BIPCo(II)Cl$_2$ **160** as the pre-catalyst, similarly gave the alkylboronic ester **160** as a single regioisomer in >95% yield. With the structurally different ^{iPr}PNN-Co(II)Cl$_2$ **161** pre-catalyst, again the same alkylboronic ester **143** was formed in excellent yield. This is akin to the result reported by Huang using NaBHEt$_3$ as the activator, which gave the same alkylboronic ester **143** as a single regioisomer in >99% yield. The methodology could also be applied to the terpyCo(II)Cl$_2$ **162** pre-catalyst, of which the analogue terpyCo(I)-Me complex had been used by Chirik (Table 2.8, entry 3). The terpyCo(I)-Me complex was reported to give a mixture of regioisomers (59:41, linear/branched) whereas terpyCo(II)Cl$_2$ **162** combined with NaO^{t}Bu gave a mixture which was much greater enriched in linear regioisomer **143** (93:7). Furthermore, ^{iPr}BICoCl$_2$ **163** could be used when activated with NaO^{t}Bu for alkene hydroboration (Table 2.8, entry 4). With this example, the alkylboronic ester **143** was produced as a single regioisomer, albeit in low yield. This result represents an example of catalyst discovery using an entirely

new activation method, that it is not only applicable to previously accessible catalyst manifolds.

Table 2.8 - Cobalt-catalysed 1,2-hydroboration of 1-octene



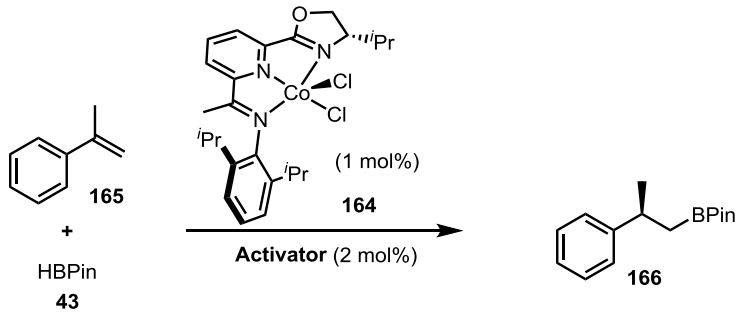
Entry	Complex	Yield (%)
1	^{Mes}BIPCoCl$_2$	>95
2	^{iPr}PNNCoCl$_2$	>95
3	TerpyCoCl$_2$	95[c]
4	^{iPr}BICoCl$_2$	35

[a]Reaction conditions: Following general procedure E; Alkene (0.4 mmol), HBPin (0.44 mmol), [Fe] (1 mol%), NaO^{t}Bu (2 mol%), THF (0.5 mL), 25 °C, 60 minutes. [b]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Ratio of anti-Markovnikov:Markovnikov products was 93:7.

2.5.2 Cobalt-catalysed enantioselective hydroboration of α-methylstyrene

To fully encompass all aspects of cobalt-catalysed hydroboration reactions that had been reported to date, it was significant to assess if this new activation method had scope for use in enantioselective reactions. Given the hypothesis that activation and catalyst reactivity are separate, the activation of a C_1-symmetric enantiopure complex should not interfere with the underlying transformation being performed by the active, low oxidation-state, species. Recently there has been a significant rise in the number of methods for the enantioselective hydroboration of alkenes using iron and cobalt catalysts. A number of these feature the use of an imino-pyridine-oxazoline ligand. Examples have been reported using both isolated cobalt(I) and *in situ* activated cobalt(II) pre-catalysts. A notable early example of this reactivity was reported by Huang and Lu, who used ^{iPr}IPOCoCl$_2$ **164** pre-catalysts in combination with external NaBHEt$_3$ for the efficient hydroboration of 1,1-disubstituted

alkenes.[89] *n.b* Prof. Z. Huang kindly provided a sample of $^{i\text{Pr}}$IPO ligand for use in this work. The exemplar reaction using α-methylstyrene **165** as a test substrate was chosen and the NaO^{t}Bu method applied (Scheme 2.8). This reaction worked exceptionally well, giving the expected alkylboronic ester **166** in high yield and excellent enantioselectivity as determined by analysis using chiral-HPLC.



Activator	%Yield	%ee
NaO^{t}Bu	95	98
$NaBHEt_3$	85	97

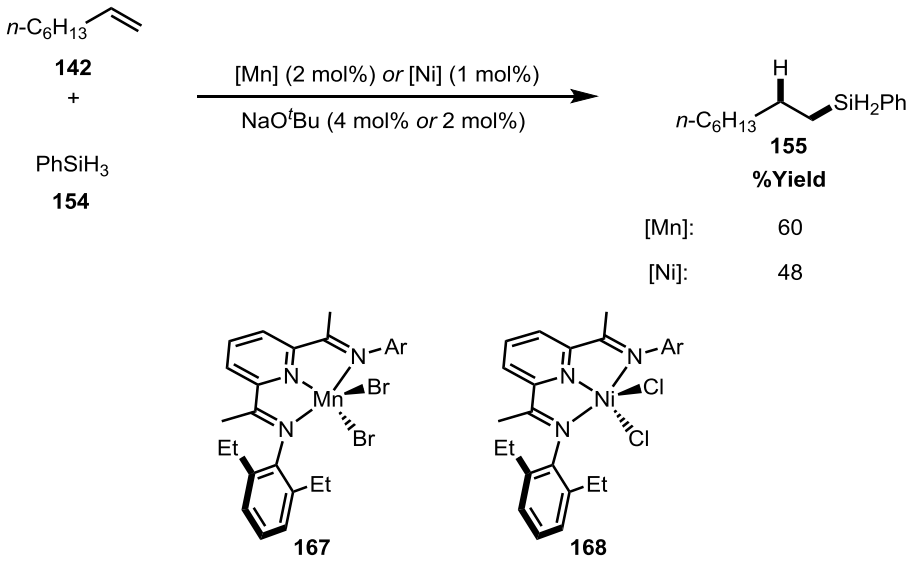
Scheme 2.8. Enantioselective hydroboration of α-methylstyrene

2.5.3 Application to manganese and nickel pre-catalysts

In addition to the known iron and cobalt catalysed hydrosilylation of olefins, a number of nickel-catalysed procedures have also emerged, albeit to a lesser extent.[119-121] While there are a number of nickel catalysts reported for this valuable transformation, examples using manganese were very scarce.[122] This set of facts conveyed the idea that a nickel(II) dihalide pre-catalyst should be amenable to activation using NaO^{t}Bu. Taking this idea forward, a pre-catalyst would be required for assessment, however no easily prepared species could be identified. Therefore an attempt was made to activate and use an unkown $^{\text{Et}}$BIPNiCl$_2$ complex **168** (Scheme 2.9). In this example, 1-octene **142** and phenylsilane **154** were chosen as test reactants and used in combination with $^{\text{Et}}$BIPNiCl$_2$ **168** and NaO^{t}Bu. The reaction worked well and gave the exclusive *anti*-Markovnikov silane **155** exclusively. As this was a previously unknown catalyst for hydrosilylation, this result demonstrates the ability of NaO^{t}Bu to act as a generic activation reagent for catalyst discovery.

Given this ability for catalyst discovery, the same ligand was selected and combined with a manganese salt, in this instance manganese(II) dibromide. Again, the $^{\text{Et}}$BIPMnBr$_2$ **167** complex had never before been used as a catalyst for olefin hydrosilylation, and in fact related complexes have been limited to carbonyl hydrosilylation. Nevertheless, when

subjected to the standard reaction conditions, albeit at slightly higher catalyst loadings (2 mol%), the reaction performed unexpectedly well and generated the exclusive *anti*-Markovnikov regioisomer **155** in good yield (Scheme 2.9).



Scheme 2.9. NaO^{t}Bu enabled hydrosilylation of alkenes with manganese(II) and nickel(II) halide complexes.

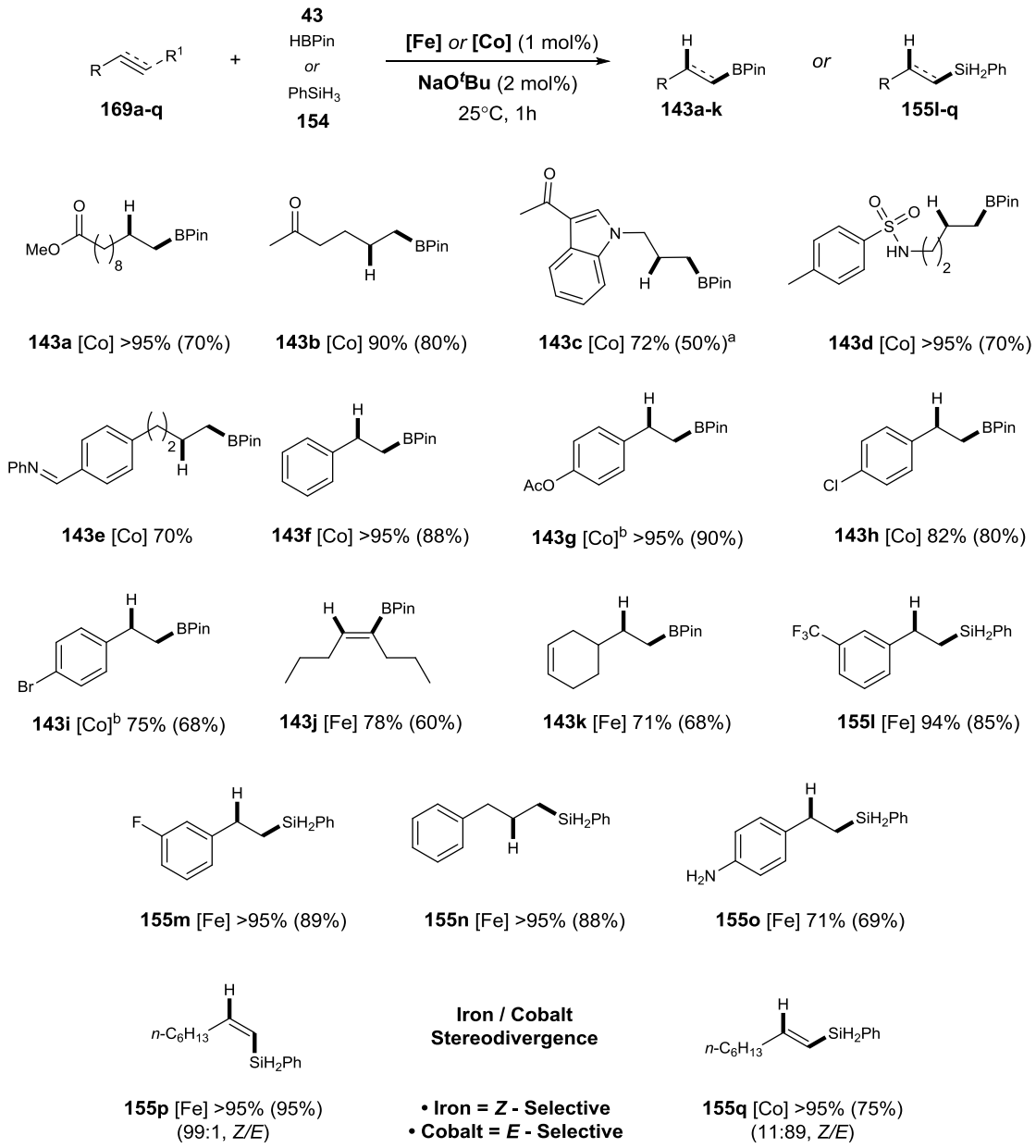
2.6 Substrate scope and tolerance of NaO^{t}Bu activated iron and cobalt complexes

The generality and substrate applicability is key to any synthetic methodology, therefore it was an important step to apply the NaO^{t}Bu activation method to a range of substrates using the established pre-catalysts and reaction condtions. Both iron and cobalt catalysts were tested for the functionalisation of a range of alkene and alkyne substrates, across both hydroboration and hydrosilylation reactions.

For alkene hydroboration, initial reactions used the *N*-mesityl-substituted cobalt(II)dichloride pre-catalyst **160** (^{Mes}BIPCoCl$_2$). Using the NaO^{t}Bu activation methodology, reaction with olefin and pinacolborane **43** for a range of substrates were successful (Scheme 2.10). Notably, ester **143a** and ketone **143b** functionalites remained unreacted during catalysis, which are incompatible using other systems. Furthermore, indole-containing ketone **169c** reacted productively to give the hydroboration product **143c** in reasonable yield, however the product proved unstable on silica and therefore required isolation following oxidation of the intermediate boronic ester. Sulfonamide **169d** could be functionalised in high yield with no reactivity at the sulfonamide group to give the alkylboronic ester **143d** in excellent yield. Imine-substituted **143e** was also formed in good yield, however was unstable to silica

column chromatography due to hydrolysis of the imine group. Vinylarenes (**169f-i**) reacted efficiently under the reaction conditions, including examples containing potentially sensitive halide functional groups. It is important to note that vinylarene substrates **143g** and **143i** required the use of pre-catalyst $^{i\text{Pr}}$PNNCoCl$_2$ **161** for good reactivity, which displayed greater reactivity than the bis(imino)pyridine cobalt(II)dichloride **160** pre-catalyst.

The *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride pre-catalyst $^{\text{Et}}$BIPFeCl$_2$ **136** was selected for exploration of substrate scope with this metal. Initially, internal alkyne **169j** was subjected to hydroboration conditions to give the corresponding product **143j** in high yield and perfect diasteroselectivity. This result and selectivity is equivalent to that reported previously using a Grignard reagent as the activator for the hydroboration of 3-hexyne. Vinylcyclohexene **169k** reacted efficiently using the iron pre-catalyst with selectivity for the terminal alkene over internal alkene. Both vinyl- and allyl-arenes (**143l-o**) underwent functionalisation to give their corresponding boronate ester products (**155l-155o**) in excellent yield. It is important to note the tolerance of a free amine under these reaction conditions (**169o**). Interestingly a stereodivergence was observed in the application of these pre-catalysts to terminal alkyne (**169p-q**); using the *N*-mesityl-substituted cobalt(II)dichloride pre-catalyst **160** $^{\text{Mes}}$BIPCoCl$_2$ the (*E*)-vinylsilane **155q** was the favoured product while the (*Z*)-vinylsilane **155p** was predominant in the reaction using the *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride pre-catalyst $^{\text{Et}}$BIPFeCl$_2$ **136**. In the case of iron, the formation of the thermodynamically unfavoured product may be due to mechanistic rationale proposed by Crabtree and Ojima, whereby an initial silylmetallation is followed by *E/Z* isomerisation of an intermediate metal-silylvinylene or zwitterionic-metallocyclopropene intermediate.[122,123] This mechanistic explanation has also been proposed by Chirik in the cobalt-catalysed (*Z*)-selective hydroboration of alkynes.[124]



Scheme 2.10 - Iron and cobalt catalyst substrate scope for alkene and alkyne hydroboration (**143a-k**) and hydrosilylation (**155l-q**). Yields determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard, and isolated yields are reported in parenthesis. Pre-catalyst used: [Fe] = ^{Et}BIPFeCl$_2$, [Co] = ^{Mes}BIPCoCl$_2$, [Co]^b = ^{iPr}PNNCoCl$_2$. ^{a}Yield of isolated product following oxidative work-up.

2.7 Mechanism and role of NaO^{t}Bu in pre-catalyst activation

The mechanism for organometallic reagents used in the activation of iron(II)- and cobalt(II) precursors is generally well understood. The most well established examples for iron(II) pre-catalyst activation have been extensively studied by Chirik.[27] Similarly Chirik and others have detailed the reactions of several cobalt(II) precursors with organometallic reagents.[18] In many examples, a low oxidation-state species has been isolated and characterised. For the reduction of iron(II) pre-catalysts, formally iron(0) species have been isolated and characterised by a number of methods, including X-ray crystallography and Mössbauer spectroscopy.[27] In the case of cobalt(II) precursors, these have been shown to react with organometallic reagents to form cobalt(I) species; usually cobalt(I)-hydride or cobalt(I)-alkyl complexes, and similarly these have been well-characterised.

The isolation of low oxidation-state iron(0)- and cobalt(I)-complexes has allowed in-depth reactivity studies. Most mechanistic studies imply the necessary formation of these low oxidation-state species before any interaction between catalyst and olefin or catalyst and silane/borane. Therefore this may imply a reductive pathway in the NaO^{t}Bu activation of the pre-catalysts to access productive catalysis. To confirm this hypothesis, or prove otherwise, would require a detailed mechanistic investigation to fully elucidate the likely mechanistic pathway for activation.

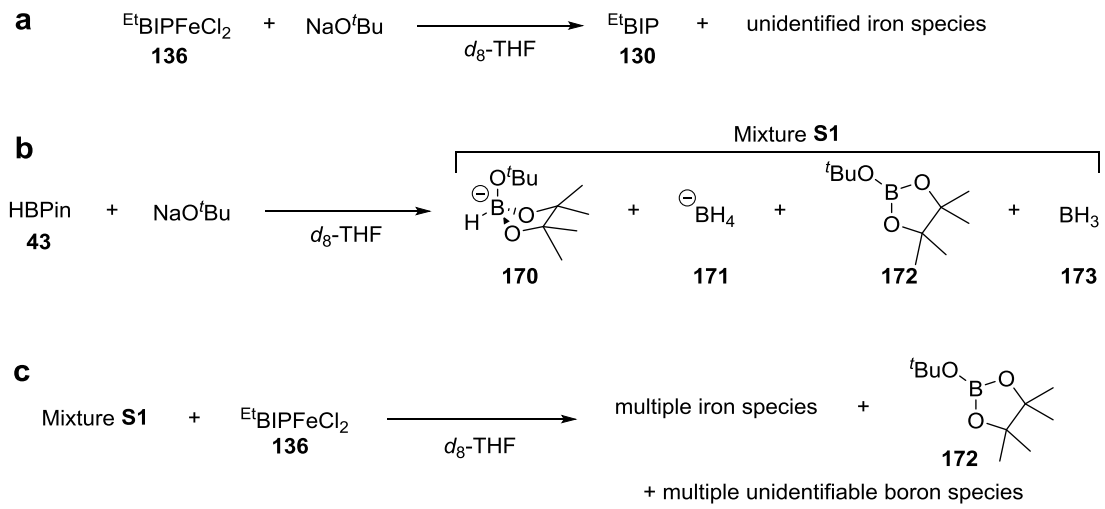
2.7.1 Mechanistic reactions to determine NaO^{t}Bu activation pathways in hydrofunctionalisation reactions using pinacolborane and silane reagents

Initial investigations were based on understanding the role of NaO^{t}Bu with both pre-catalyst and reactants. The reaction conditions that allowed for successful reactivity across a broad range of pre-catalysts involved the use of THF as a solvent. Therefore mechanistic studies used d_8-THF as a solvent to ease reaction analysis and allow the monitoring of reactions by NMR spectroscopy. An exemplar system was required to understand the activation process, therefore ^{Et}BIPFeCl$_2$ was chosen as this catalyst could be used for both hydroboration and hydrosilylation reactions.

To understand the interaction between NaO^{t}Bu and *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride **136** ^{Et}BIPFeCl$_2$, both components were combined and allowed to react in d_8-THF (Scheme 2.10, **a**). The distinct deep-blue colour of the *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride ^{Et}BIPFeCl$_2$ pre-catalyst **136**

quickly changed to yellow in this reaction within minutes. The ^{1}H NMR spectrum of the pre-catalyst exhibited clear broad paramagnetic shifted resonances over the range between δ = −30 ppm to 90 ppm, and following reaction with NaO^{t}Bu, the ^{1}H NMR spectra revealed the disappearance of these signals, and only showed resonances in the standard range (0 to 10 ppm) which corresponded to that of free ligand ^{Et}BIP **130**.[126] It is notable that this resulting mixture was catalytically incompetent for both hydroboration and hydrosilylation. This indicates that the interaction of NaO^{t}Bu with *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride ^{Et}BIPFeCl$_2$ **136** acts to de-metallate ligand from metal to form a catalytically inactive mixture of species.

Having shown that the interaction of NaO^{t}Bu with pre-catalyst did not trigger successful catalyst activation, attention shifted to the interaction of NaO^{t}Bu with substrates. Control reactions of NaO^{t}Bu and alkene showed no change by ^{1}H NMR spectroscopy. However a reaction was observed when NaO^{t}Bu was reacted with pinacolborane **43** (Scheme 2.11, **b**). Analysis of this reaction using ^{11}B NMR spectroscopy revealed the formation of multiple boron containing products; *tert*-butoxyboronate complex **170**, BH_4^- **171**, *tert*-butoxypinacolboronate **172** and BH_3 **173**. These products likely arise from NaO^{t}Bu assisted disproportionation of pinacolborane **43**.[127] This mixture was then tested as a potential pre-catalyst activator. The mixture of multiple boron products, mixture **S1**, was reacted with ^{Et}BIPFeCl$_2$ **136** and the reaction monitored using both ^{1}H and ^{11}B NMR spectroscopy (Scheme 2.10, **c**). This showed the disappearance of *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride ^{Et}BIPFeCl$_2$ **136** resonances (^{1}H NMR), boronate **170**, BH_4^- **171**, BH_3 **173**, alongside concomitant formation of *tert*-butoxypinacolboronate **172**, multiple iron species and a number of unidentifiable boron species. These observations suggest the reduction of *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride ^{Et}BIPFeCl$_2$ **136** by the mixture of NaO^{t}Bu and pinacolborane **43**.

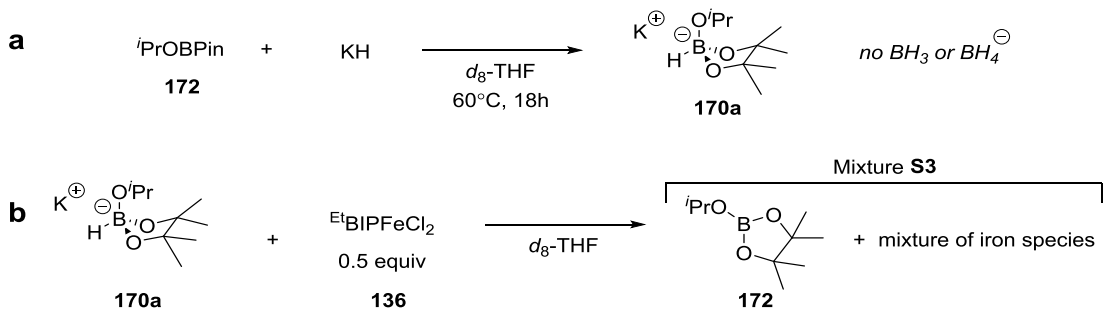


Scheme 2.11 – Mechanistic investigations. **a** reaction of NaO^{t}Bu with an iron(II) pre-catalyst. **b** reaction of NaO^{t}Bu with pinacolborane (1:1). **c** reaction of the mixture from **b** with an iron(II) pre-catalyst. All reactions were monitored and analysed by ^{1}H and ^{11}B NMR spectroscopy.

With the reductive power of the NaO^{t}Bu and pinacolborane mixture **S1** observed, it remained unclear which species was responsible for pre-catalyst reduction. Either boronate complex **170**, BH_4^- **171**, or BH_3 **173** could act as reductants or hydride transfer reagents. BH_4^- has been used as a reductant for a number of synthetic organic transformations, thus it was necessary to determine the activation potential of this species. However, initial studies testing and comparing pre-catalyst activators, the $NaBH_4$ reagent was only a mildly competent activator by comparison to that of $NaBHEt_3$ (45% yield vs 80% yield for 1-octene hydroboration using ^{Mes}BIPFeCl$_2$, *see table 2.1*).

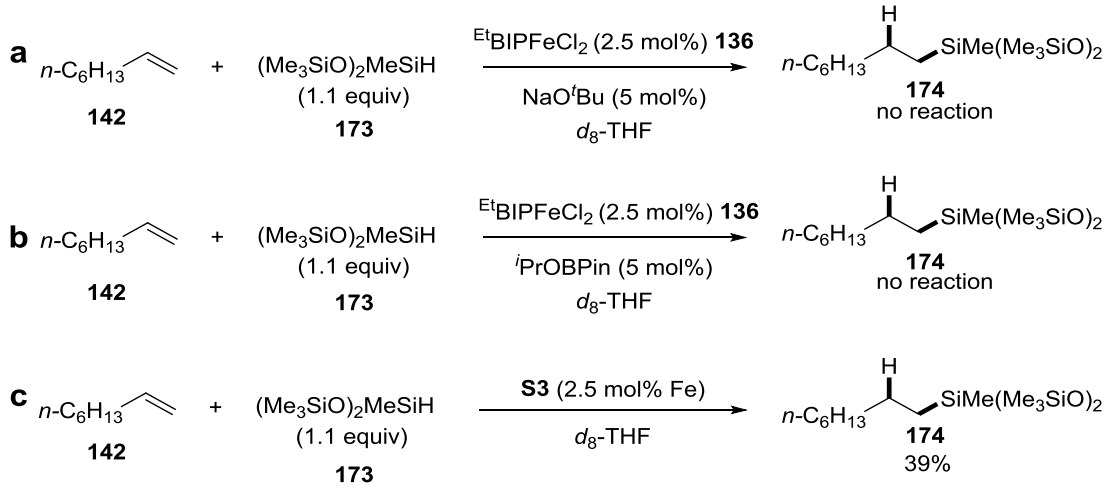
To determine the activation potential of the boronate complex **170**, this or a closely related species would need to be prepared in the absence of any contaminants that could potentially interfere with the activation process. The analogous potassium *iso*-propoxy-hydrido-boronate complex **170a** was prepared from *iso*-propoxy-pinacolboronate and potassium hydride.[127] This reaction cleanly produced the hydride containing boronate complex **170a** without contamination from disproportionation products (BH_4^- **171** *or* BH_3 **173**). Boronate **170a** was then reacted with the *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride pre-catalyst ^{Et}BIPFeCl$_2$ **136** to determine if this could act as a competent activator. Analysis of the resulting mixture **S3** by ^{11}B NMR spectroscopy showed the consumption of boronate **170a**, and ^{1}H NMR spectroscopy showed the disappearance of paramagnetic resonances attributed to *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride pre-catalyst ^{Et}BIPFeCl$_2$ **136**. The formation of *iso*-propoxy-pinacolboronate **172** and a new mixture of

multiple iron-containing species were identified. This example indicates, by analogy, that the boronate complex formed by reaction of NaO^{t}Bu with pinacolborane is competent for the reduction of the *N*-diethylphenyl-substituted bis(imino)pyridine iron(II)dichloride pre-catalyst ^{Et}BIPFeCl$_2$.



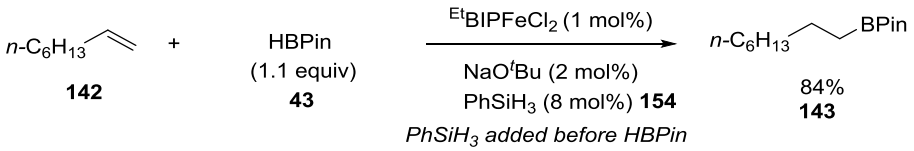
Scheme 2.11 – Evaluation by analogous reaction of boronate complex **170a** as a pre-catalyst reductant for ^{Et}BIPFeCl$_2$. **a** Formation of boronate complex **170a** using isopropoxypinacolboronate and potassium hydride. **b** Application of boronate complex **170a** in the reduction of ^{Et}BIPFeCl$_2$.

Although pre-catalyst reduction had been observed, the ability to initiate catalysis was still needed. Chirik showed that the sterically encumbered silane M'DM ((Me$_3$SiO)$_2$MeSiH) could react productively with BIPFe(0)N$_2$ catalysts and terminal alkenes to give linear alkyl-silanes.[60] The *in situ* activation of the analogous iron(II) pre-catalysts using NaO^{t}Bu could allow access to the same reactivity. However when *in situ* activation was attempted with NaO^{t}Bu no such reactivity was observed (Scheme 2.12, **a**). There was a noticeable lack of colour change in this reaction and therefore it could be considered that pre-catalyst activation had failed under these conditions. The silane reagent in this example is highly sterically hindered, and if required for pre-catalyst activation may be inaccessible to the added NaO^{t}Bu reagent. To avoid this limitation and assess the reactivity of the reduced catalyst mixture produced when using boronate complex **170a**, 1-octene **142** and M'DM **173** were reacted in the presence of pre-reduced catalyst (mixture **S3**, scheme 2.12, **c**). Reactivity in this example was limited but observable and the reaction produced the same alkyl-silane species that had been reported by Chirik (Scheme 2.12, **c**). Importantly the control reaction using isopropoxypinacolborane **172** showed no reactivity, indicating that the hydride equivalent provided by boronate complex **170a** was necessary (scheme 2.12, **b**).



Scheme 2.12 – Assessment of reactivity of reduced pre-catalyst mixtures towards 1-octene hydrosilylation using $(Me_3SiO)_2MeSiH$. **a** Unsuccessful control reaction using NaO^tBu. **b** Control reaction using isopropoxypinacolboronate. **c** Successful 1-octene hydrosilylation using pre-reduced mixture **S3**.

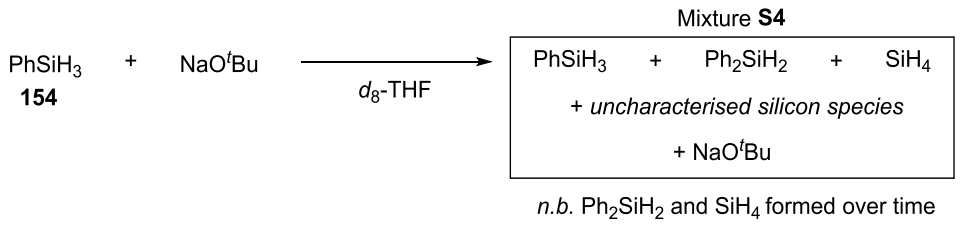
These initial mechanistic implications for hydroboration reactions suggest that the hydride bearing boronate complex **170a** is required for pre-catalyst activation. A related activation mode could be proposed for pre-catalyst activation with silane reagents where a silane reagent would react with NaO^tBu and transfer hydride from silane to pre-catalyst in the same manner as boronate complex **170a**. A mixture containing $^{Et}BIPFeCl_2$ **136**, NaO^tBu and 1-octene **142** was stirred before addition of phenylsilane **154** (8 equivalents wrt. pre-catalyst, Scheme 2.13). Addition of phenylsilane **154** caused an immediate colour change from blue to dark brown. This observation, while only qualitative, suggests that phenylsilane **154** had interacted with the initial reaction components. Following this, pinacolborane was added and, after work-up, the linear alkyl-boronic ester **143** was produced in good yield. Importantly the boronic ester was produced as the sole reaction product as a single regioisomer. This result shows that this pre-catalyst activation strategy produces an active catalyst with identical reactivity to that observed for both the related Fe(0) species and *in situ* activated methods.



Scheme 2.13 – pre-catalyst activation using phenylsilane for 1-octene hydroboration.

As the silane reagent appeared to be involved in pre-catalyst activation, it was significant to explore and identify the interactions between both silane reagent and NaO^tBu. Therefore a

reaction was performed using phenylsilane and NaO^{t}Bu in d^8-THF (Scheme 2.14). The reaction could be monitored by both ^{1}H and ^{29}Si NMR spectroscopy, and using both techniques the formation of diphenylsilane and silane alongside other unidentifiable silicon-containing species was observed. The disproportionation of silane reagents is also known to occur spontaneously in the absence of nucleophile at high temperatures and in the presence of nucleophiles.[128,129] An additional observation by monitoring the reaction over time was the formation of a number of intermediates, which did not correspond to starting material, diphenylsilane or silane. These intermediates could tentatively be assigned as hypervalent silicon species that precede the formation of diphenylsilane and silane. It is important to note that these intermediate species were not *fleeting*, and could be observed on the minute to hour timescale.



Scheme 2.14 – Reaction of equimolar phenylsilane and NaO^{t}Bu monitored over time.

SiH_4 is a pyrophoric gas and therefore it was key to understand the rate of disproportionation, catalyst activation and hydrosilylation as these may have safety implications. By monitoring the reaction by ^{1}H NMR spectroscopy, and specifically the Si-H resonance integration, the rate of reaction was profiled. The half-life of phenylsilane under these conditions was found to be 95 minutes, with 80% peak-conversion observed after 19 hours (Figure 2.1). It is important to note that this investigation was conducted using substoichiometric quantities of NaO^{t}Bu, as this mimics the quantities present in catalytic applications. It is important to note that the rate of catalyst activation and that of the hydrosilylation reactions far exceeds that of disproportionation.

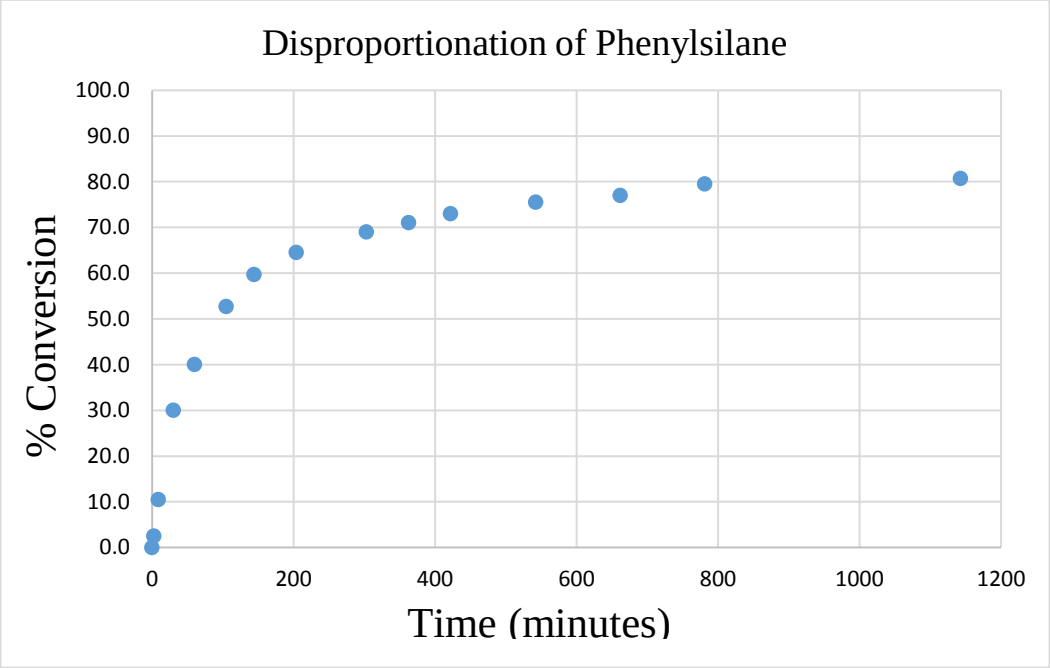
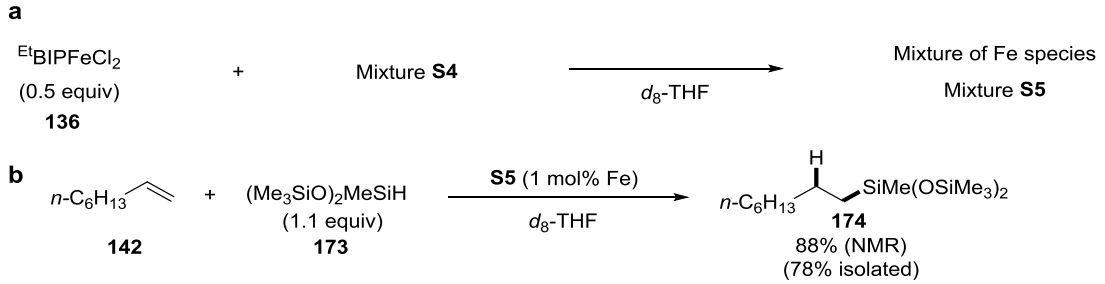


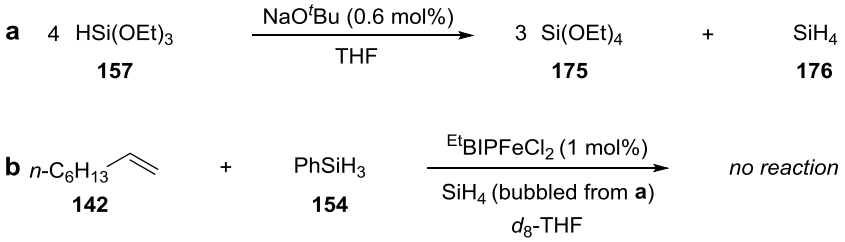
Figure 2.1. Reaction of phenylsilane and NaO^{t}Bu. $PhSiH_3$ $t_{½}$ = 1 hour 35 minutes (0.84 M in d_8-THF, 27°C, 2 mol% NaO^{t}Bu).

To determine the reductive and activation potential of the NaO^{t}Bu/phenylsilane system, these reagents were added to ^{Et}BIPFeCl$_2$ **136** and the reaction monitored by ^{1}H NMR spectroscopy (Scheme 2.15, **a**). As in the analogous experiments using the pinacolborane system, the combination of these reagents reacted with pre-catalyst and the characteristic ^{1}H NMR paramagnetic resonances owing to ^{Et}BIPFeCl$_2$ **136** were consumed. Again a mixture of unidentifiable iron-containing species were produced. The hydrosilylation of 1-octene **136** with M'DM **173** was again targeted for reactivity using this reduced pre-catalyst mixture **S5** (Scheme 2.15, **b**). The regioselectivity observed was identical to that of the related Fe(0) complex and that observed by activation using boronate complex **170a**. In this example the product yield was significantly higher than that observed when using boronate complex **170a**, indicating that the phenylsilane/NaO^{t}Bu combination may be a better *in situ* pre-catalyst activation system.



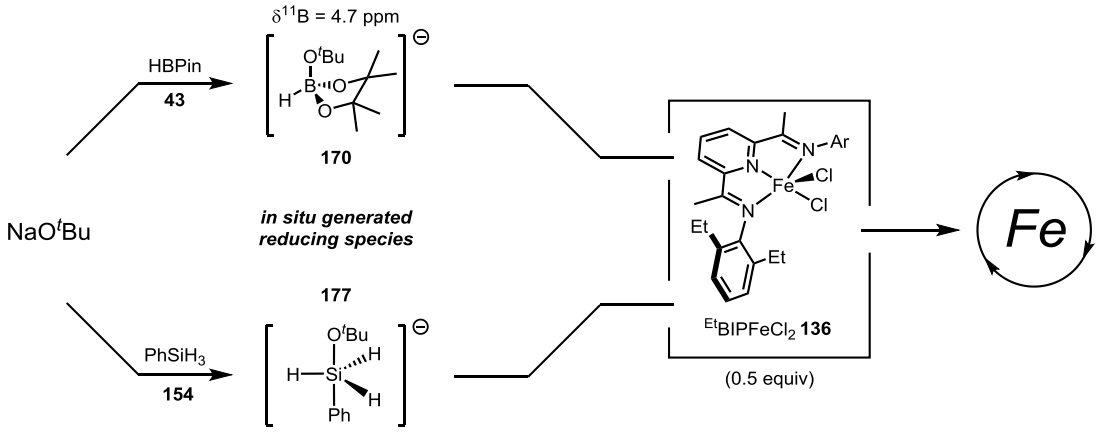
Scheme 2.15 – **a** Reaction of ^{Et}BIPFeCl$_2$ with pre-stirred NaO^{t}Bu and PhSiH$_3$. **b** Reaction of 1-octene with M'DM using pre-activated mixture **S5**.

While the phenylsilane/NaO^{t}Bu combination was clearly an effective pre-catalyst activation system, it was unclear which species was the active reductant. The disproportionation studies revealed that multiple species were produced. Using control reactions from initial activation and pre-catalyst compatibility studies ruled-out phenylsilane as an active reductant. Therefore an intermediate *en route* to diphenylsilane and silane could be responsible for pre-catalyst activation. The potential for SiH$_4$ **176** in pre-catalyst activation was therefore tested. Generation of silane gas **176** could be achieved by NaO^{t}Bu catalysed disproportionation of triethoxysilane **175** (Scheme 2.16, **a**). The rate of disproportionation of triethoxysilane **157** occurs at a much higher rate than that of phenylsilane **154**. Using this reaction, SiH$_4$ **176** gas could be generated and transferred to a mixture containing ^{Et}BIPFeCl$_2$ **136**, phenylsilane **154** and 1-octene **142** which did not show any catalytic activity, including no colour change (Scheme 2.16, **b**).



Scheme 2.16 – **a** Disproportionation of triethoxysilane. **b** Reaction of 1-octene with phenylsilane using ^{Et}BIPFeCl$_2$ as pre-catalyst with attempted activation using SiH$_4$.

Both the boronate **170** and the phenylsilane/NaO^{t}Bu combination suggest a common anionic hypervalent intermediate that is generated *in situ* acting as a pre-catalyst activator. These hydride-bearing intermediates may then act in the same way as organometallic reagents and transfer hydride to the pre-catalyst, which could then undergo reductive elimination of dihydrogen. Such a pathway would allow for the generation of low oxidation-state metal species whose reactivity has been established previously and is in line with the reactivity observed using NaO^{t}Bu as an activator for hydroboration and hydrosilylation reactions.



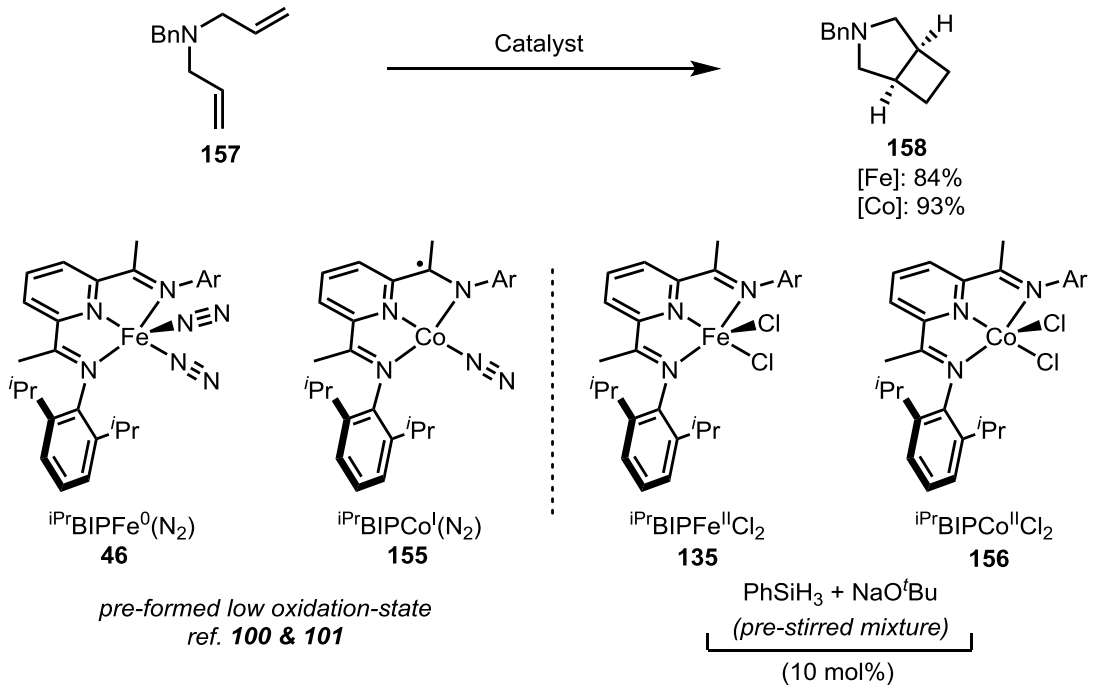
Scheme 2.17 – Proposed pre-catalyst activation pathways: NaO^{t}Bu interacts with pinacolborane to generate tetrahedral boronate complex **170**. Simialrly, NaO^{t}Bu reacts with silane reagents to generate hypervalent silicon intermediates such as **177**. These intermediates may then serve as pre-catalyst reductants.

With this reactivity established and understood, the limitations of this activation method are apparent; a reagent bearing B-H or Si-H bonds would be required for pre-catalyst activation and thus productive reactivity. Consequently access to low oxidation-state metal active catalysts using NaO^{t}Bu would be reliant on added external silane or borane reagent to provide the necessary hydrides required for pre-catalyst activation. Although, while these reagents would be required to initiate reactivity and enable pre-catalyst activation, a small substoichiometric quantity of either silane or borane reagent would be necessary. For example in a reaction with pre-catalyst (1 mol%) and NaO^{t}Bu (2 mol%), only silane or borane (2 mol%) would be required to account for the necessary hydride equivalents. A pre-catalyst activated by either NaO^{t}Bu and pinacolborane **43** *or* NaO^{t}Bu and phenylsilane **154** would then likely act in the same way as previously reported for analogous low-oxidation state catalysts.

2.7.2 Application of NaO^{t}Bu/phenylsilane as an activation system for [2π+2π] cycloaddition

The [2π+2π] cycloaddition of 1,6-dienes has been achieved by Chirik using low oxidation-state Fe(0) and Co(I) complexes and thus would serve as a target reaction to test whether the same reactivity could be accessed from an iron(II) or cobalt(II) precursor.[100-102] It is important to note that only low oxidation-state isolated complexes have been reported for this transformation. Chirik used *N*-di*iso*propylphenyl-substituted bis(imino)pyridine iron(0)dinitrogen $^{i\text{Pr}}$BIPFe(0)$(N_2)_2$ **46** and *N*-di*iso*propylphenyl-substituted

bis(imino)pyridine cobalt(I)dinitrogen ^{iPr}BIPCo(I)N_2 **155** for the [2π+2π] cycloaddition 1,6-dienes.[101,102] Using the analogous Fe(II) **135** and Co(II) pre-catalysts **156**, activation was carried out using NaO^{t}Bu in combination with phenylsilane **154** as this activation system had proved superior in the hydrosilylation of 1-octene using M'DM. Under these activation conditions, the 2π+2π cycloaddition reaction of 1,6-bis-allyl-benzylamine **157** was successful and produced the cyclobutane-containing product **158** in excellent yield for both iron and cobalt catalyst (Scheme 2.18). It is worthy to note that this reaction is very slow when compared to that of alkene hydroboration or hydrosilylation, and is highly sensitive to air and moisture.

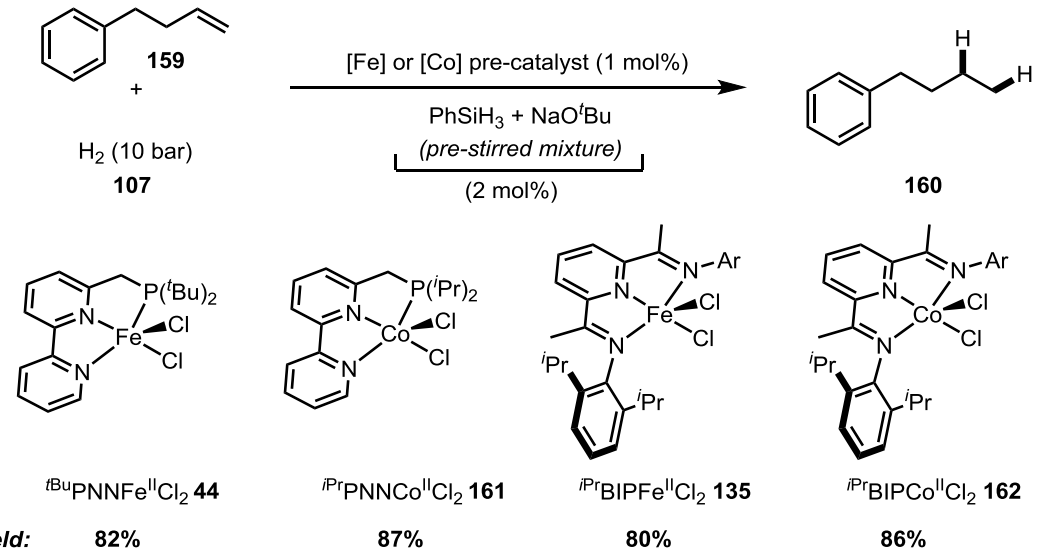


Scheme 2.18 – Iron and cobalt catalysed [2π+2π] cycloaddition reaction using phenylsilane and NaO^{t}Bu activation.

2.7.3 Application of NaO^{t}Bu/phenylsilane as an activation system for alkene hydrogenation

With success found in the [2π+2π] cycloaddition of a 1,6-diene and reactivity akin to Fe(0) and cobalt(I) demonstrated using the NaO^{t}Bu and phenylsilane activation system, it was appealing to attempt further transformations that did not intrinsically contain B-H or Si-H containing reagents. The hydrogenation of alkenes was selected as another reaction class. For this transformation a number of catalysts based on iron and cobalt have been used. The general trend of reactivity remains the same for this reaction class; a low oxidation-state

species is often required for reactivity. To test whether the NaO^{t}Bu and phenylsilane **154** combination could be used in this instance, 4-phenyl-1-butene **159** was selected as an alkene and dihydrogen **107** gas as the necessary stoichiometric reductant (Scheme 2.19). The reaction was applied to both iron and cobalt pre-catalysts and across two ligand classes, both PNN and BIP. As a note regarding reaction setup, phenylsilane **154** (2 mol%) was added to a mixture of pre-catalyst (1 mol%) and NaO^{t}Bu (2 mol%) before pressurising with dihydrogen **107** (10 bar). Across all pre-catalysts tested, all were successful and each produced the reduced alkane product **160** in high yields.



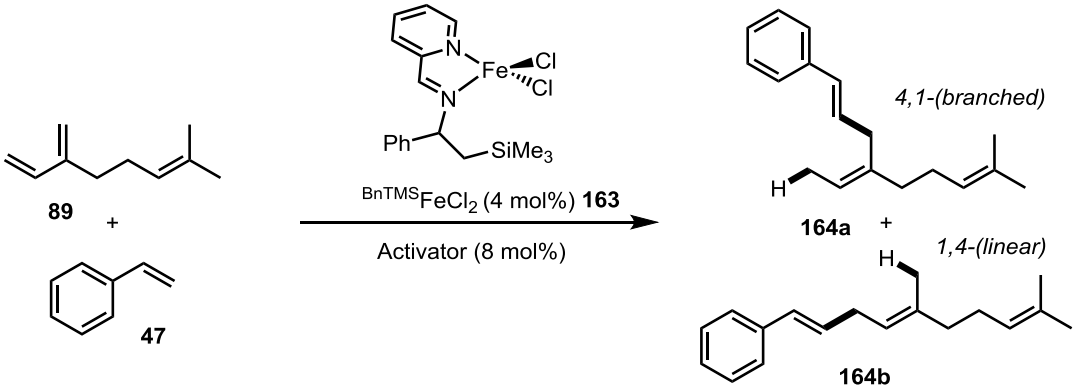
Scheme 2.19 – Iron and cobalt catalysed hydrogenation of 4-phenyl-1-butene using NaO^{t}Bu and phenylsilane as the activator.

2.7.4 Application of NaO^{t}Bu/pinacolborane and NaO^{t}Bu/phenylsilane as an activation system for 1,4-hydrovinylation

The NaO^{t}Bu/phenylsilane combination had demonstrated excellent potential for the activation of a broad range of both iron and cobalt pre-catalysts, although these had exclusively been complexes bearing tridentate ligands. A further extension of this methodology could be demonstrated by application to iminopyridine iron(II) complexes for 1,4-hydrovinylation reactions. Ritter had shown that similar iminopyridine iron(II) pre-catalysts used for 1,4-hydroboration and 1,4-hydrosilylation reactions could be used for the

1,4-hydrovinylation of 1,3-dienes using vinylarenes as a coupling partner with activated magnesium as an activator.[97] To test if the phenylsilane/NaO^{t}Bu combination could activate the same iron(II) pre-catalysts to enable the same reactivity, myrcene **89** and styrene **47** were selected as model substrates. These substrates had been used by Ritter, thus providing a good comparison for any productive reaction (Table 2.9, entry 1). The application of the NaO^{t}Bu/phenylsilane activation system was applied to $^{BnTMS}FeCl_2$ **163** in the presence of myrcene **89** and styrene **47**. At pre-catalyst and activator loadings of less than half that used by Ritter, comparable reactivity was observed and the hydrovinylation products **164a-b** could be easily isolated by distillation with the same regioselectivity observed here (93:7 *vs* 90:10, Table 2.9, entry 2). Furthermore there was no observable erosion of diastereoselectivity at either newly formed alkene. For reactivity and selectivity comparison the activation using NaO^{t}Bu and pinacolborane **43** could also be applied, to generate the same product mixture, in high yield and with the exact same regio- and diastereoselectivity as both NaO^{t}Bu/phenylsilane and magnesium activated methods.

Table 2.9 - Iminopyridine-Iron catalysed 1,4-hydrovinylation of 1,3-dienes



Entry	Activator	Yield (%)[c]	Regioselectivity (1,4/4,1)	4,1-(E/Z)	1,4-(E/Z)
1[a]	Mg*	66	93:7	>99:1	>99:1
2[b]	NaO^tBu + $PhSiH_3$ (pre-stirred)[d]	85	90:10	>99:1	>99:1
3[b]	NaO^tBu + HBPin	75	90:10	>99:1	>99:1

[a]Results from ref 96, reaction in Et_2O (1 M), 10 mol% pre-catalyst and 20 mol% Mg. [b]Reaction conducted *neat* at 23°C. [c]Yields determined by ^1H NMR of the crude reaction mixture. [d]1:1 pre-stirred (for *ca.* 1 minute) mixture of phenylsilane and NaO^tBu in anhydrous THF (0.15 M).

2.8 Summary

Common routes to low oxidation-state catalysis with iron(II) and cobalt(II) pre-catalysts often relied on the use of an organometallic activator to initiate reactivity. The use of sodium *tert*-butoxide parallels this role, and enables activation of a broad range of structurally diverse pre-catalysts. Reactivity was found for hydroboration, hydrosilylation, hydrovinylation, hydrogenation and 2π+2π cycloaddition. The method could be further extended in the discovery of new catalysts with different first-row transition metals, namely nickel and manganese resulting in the first manganese-catalysed alkene hydrosilylation.

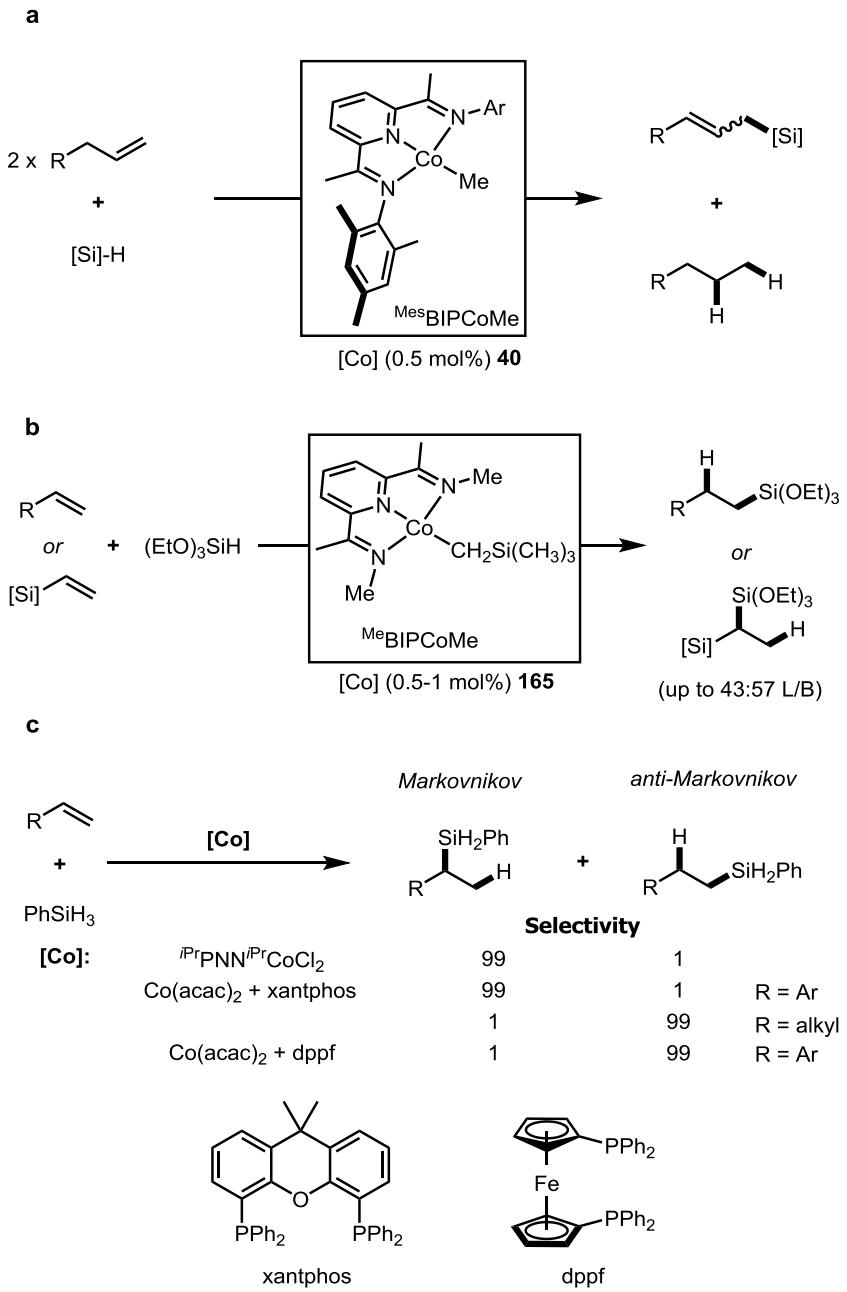
Mechanistic investigations revealed that the alkoxide salt first reacted with a neutral hydride species, either borane or silane, to form an 'ate' complex that could then serve as a hydride donor. The *in situ* generated hydride donor could then transfer hydride to metal and thus

initiate catalysis. Trace metal participation was excluded by assessing the trace metal content of a typical catalytic reaction, showing only minor levels of precious metals. The results presented are suggestive of a generic platform for reactivity and one that is applicable to a broad range of reactivity beyond reductive olefin functionalisation.

3. Regiodivergent cobalt-catalysed alkene hydrosilylation

3.1 State-of-the-art at the outset of the project

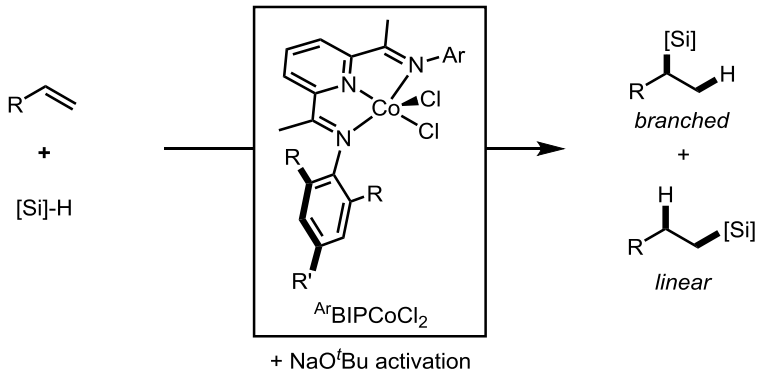
Many examples of cobalt-catalysed alkene hydrosilylation have been reported with the majority showing selectivity for the linear alkyl-silane products. This selectivity mimics that observed with iron and other transition metal catalysts. Chirik showed that isolated BIPCo(I)-alkyl pre-catalysts, *e.g* BIPCo(I)CH_2SiMe_3, could be used for the selective dehydrogenative silylation of terminal alkenes to give allyl-silane products with terminal to internal alkene migration (Scheme 3.1, **a**).[74] The use of alkyl-imino BIPCo(I)-alkyl complexes for the selective hydrosilylation of terminal alkenes to give alkyl-silanes has also been reported.[131] While the majority of reactions using alkyl-imino BIPCo(I)-alkyl complexes gave linear alkylsilanes, substrates bearing an α-silyl group gave mixtures of both linear and branched alkylsilane regioisomers (Scheme 3.1, **b**). These results illustrate a clear influence of the pre-catalyst structure on the selectivity of the reaction, specifically switching from aryl-imino to alkyl-imino sustituted ligands altered reactivity from dehydrogenative silylation to hydrosilylation. Huang showed that the pincer complex $^{i\text{Pr}}$PNN$^{i\text{Pr}}$$CoCl_2$ **42** could be used for the Markovnikov (branched) selective hydrosilylation of terminal alkenes when activated by $NaHBEt_3$ (Scheme 3.1, **c**).[65] This hydrosilylation was shown to be regiodivergent when compared to the catalysis using $^{i\text{Pr}}$PNN$^{i\text{Pr}}$$FeCl_2$ **42a** under the same conditions. Ge demonstrated the hydrosilylation of terminal alkenes using $Co(acac)_2$ and bidentate phosphine ligands, in which xantphos and dppf showed complete regiodivergent reactivity (Scheme 3.1, **c**).[130] Overall, regioselectivity and reactivity in alkene functionalisation reactions were highly dictated by ligand structure.



Scheme 3.1 – State-of-the-art cobalt-catalysed reactions of alkenes with silane reagents. **a** Dehydrogenative alkene silylation to generate allyl-silanes. **b** Substrate derived regiodivergent alkene hydrosilylation. **c** Catalyst derived regiodivergent alkene hydrosilylation.

3.2 Project aims

The aim of this project was to investigate the viability and applicability of using NaO^{t}Bu as an activator for a range of BIP-Co(II) pre-catalysts for alkene hydrosilylation reactions (Scheme 3.2). Following the discovery and optimisation of reaction conditions, an exploration of substrate tolerance and limitations would be investigated. With the regiodivergent reactivity and reaction selectivity reports previously from Chirik, Huang and Ge, it was of interest to examine if choice of activator had any effect on either outcome.[65,74,130] Additionally it would potentially allow mechanistic investigations to establish the cause or determining factors in regiodivergent reactivity and varying reaction selectivity.



Scheme 3.2 – Prospective overview of cobalt-catalysed alkene hydrosilylation.

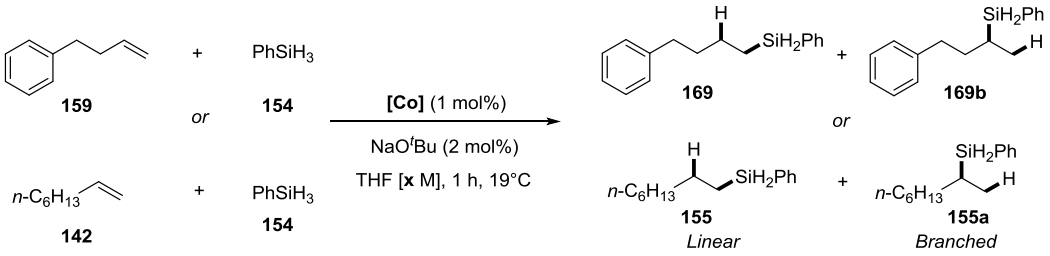
3.3 Reaction discovery and optimisation for cobalt-catalysed alkene hydrosilylation using NaO^{t}Bu as an activator

3.3.1 Reaction discovery and optimisation

The NaO^{t}Bu activation had demonstrated success in the activation of both iron and cobalt pre-catalysts using both solvent-free conditions and in solution. Given the established reactivity in THF for hydroboration reactions using BIPCo(I) complexes, these conditions could also be tested for alkene hydrosilylation reactions. Initially, pre-catalysts with varying steric environments were assessed for their hydrosilylation activity (Table 3.1). This included the testing of ^{H}BIPCoCl$_2$ **166**, ^{Me}BIPCoCl$_2$ **167**, ^{Mes}BIPCoCl$_2$ **160**, ^{Et}BIPCoCl$_2$ **168** and $^{i\text{Pr}}$BIPCoCl$_2$ **162**, each with a progressively more sterically hindered metal centre. These pre-catalysts were activated using NaO^{t}Bu at a 1:2 ratio of pre-catalyst to activator. 4-

Phenyl-1-butene **159** and phenylsilane **154** were used as reactants with the aim of generating either alkylsilanes (by hydrosilylation) or allylsilanes (by dehydrogenative silylation). All pre-catalysts that were tested showed good reactivity giving high yields of a mixture of both linear and branched alkylsilane regioisomers (Table 3.1, entries 1-5). The *N*-mesitylsubstituted pre-catalyst ^{Mes}BIPCoCl$_2$ **160** gave the best selectivity for the branched alkylsilane, while the *N*-phenyl ^{H}BIPCoCl$_2$ gave the best selectivity for linear alkylsilane (Table 3.1, entries 1 & 3). Lowering the reaction temperature from 25 °C to 19 °C showed little change in overall yield but gave observable changes in regioselectivity, particularly when using the *N*-di*iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCoCl$_2$ **162** which showed inverted selectivity for the linear alkylsilane (Table 3.1, entries 6-10). Investigating the change observed when using ^{iPr}BIPCoCl$_2$ **162** at different reaction concentrations showed that a low reaction concentration gave a significant increase in regioselectivity and could be used to generate the linear regioisomer with much greater selectivity (Table 3.1, entries 13 & 15). A similar analysis of the concentration effects using *N*-mesitylsubstituted pre-catalyst ^{Mes}BIPCoCl$_2$ **160** showed a comparable trend with a reaction concentration of 0.5 M in THF being favourable for optimal regioselectivity (Table 3.1, entries 16-23). It is important to note that in all reactions no products of dehydrogenative silylation were observed which is in contrast to the reactivity using the analogous Co(I)-alkyl species.

Table 3.1 – Substituent and concentration effects: Cobalt-Catalysed Hydrosilylation

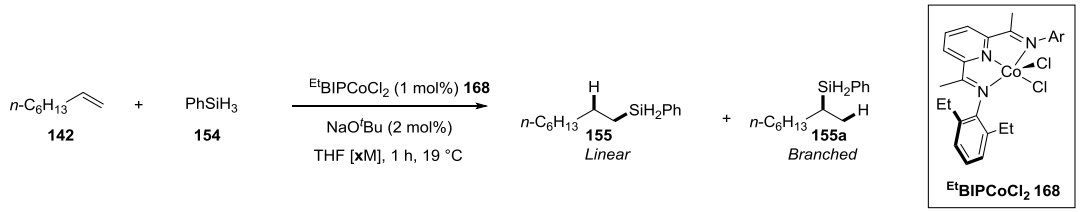


Entry[a]	Catalyst	Concentration	Overall Yield[e] (%)	Linear:Branched
1[b,c]	^{H}BIPCoCl$_2$	1 M	>95	83:17
2[b,c]	^{Me}BIPCoCl$_2$	1 M	88	68:32
3[b,c]	^{Mes}BIPCoCl$_2$	1 M	>95	8:92
4[b,c]	^{Et}BIPCoCl$_2$	1 M	>95	9:91
5[b,c]	^{iPr}BIPCoCl$_2$	1 M	>95	20:80
6[b]	^{H}BIPCoCl$_2$	1 M	90	73:27
7[b]	^{Me}BIPCoCl$_2$	1 M	>95	14:86
8[b]	^{Mes}BIPCoCl$_2$	1 M	>95	9:91
9[b]	^{Et}BIPCoCl$_2$	1 M	>95	14:86
10[b]	^{iPr}BIPCoCl$_2$	1 M	>95	56:44
11[b]	^{iPr}BIPCoCl$_2$	2.5 M	74	79:21
12[b]	^{iPr}BIPCoCl$_2$	0.5	60	93:7
13[b]	^{iPr}BIPCoCl$_2$	0.3	64	94:6
14[b]	^{iPr}BIPCoCl$_2$	0.25	80	89:11
15[b]	^{iPr}BIPCoCl$_2$	0.16	>95	94:6
16[d]	^{Mes}BIPCoCl$_2$	*neat*	>95	14:86
17[d]	^{Mes}BIPCoCl$_2$	0.5	>95	9:91
18[d]	^{Mes}BIPCoCl$_2$	0.3	50	25:75
19[d]	^{Mes}BIPCoCl$_2$	0.25	90	15:85

[a]Reaction conditions: Alkene (1 mmol), $PhSiH_3$ (1.1 mmol), [Co] (1 mol%), NaO^tBu (2 mol%), THF (2.5 mL), 19°C, 60 minutes. [b]Alkene = 4-phenyl-1-butene. [c]Reaction temperature = 25 °C. [d]Alkene = 1-octene. [e]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

To further probe the effects of reducing the overall reaction concentration as a means to enhance regioselectivity, the hydrosilylation reaction using $^{Et}BIPCoCl_2$ **168** was optimised for concentration (Table 3.2). Similarity it was found whereby a common dilute reaction concentration of 0.16 M was optimal for the hydrosilylation reaction using $^{Et}BIPCoCl_2$ **168**. The highest yield and regioselectivity for both $^{Et}BIPCoCl_2$ **168** and $^{iPr}BIPCoCl_2$ **162** pre-catalysts were observed under low reaction concentration.

Table 3.2 - Reaction Concentration: $^{Et}BIPCoCl_2$ Catalysed Hydrosilylation.



Entry[a]	Concentration[b] [M]	Overall Yield[c] (%)	Linear:Branched
1	*neat*	>95	18:82
2	0.5	44	17:83
3	0.3	>95	11:89
4	0.25	<10%	n.d
5	0.2	90	4:96
6	0.16	>95 (>95%)[d]	4:96 (5:95)[d]
7	0.14	>95%	4:96

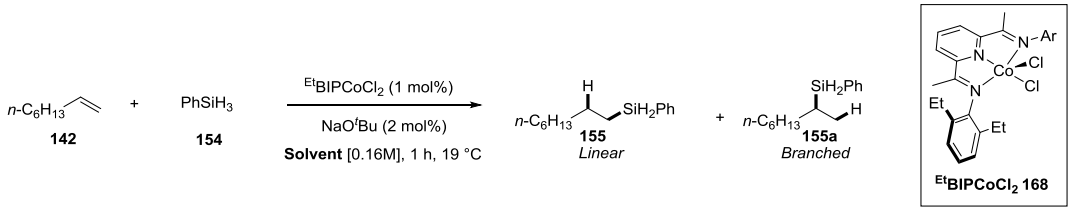
[a]Reaction conditions: 1-octene (1 mmol), $PhSiH_3$ (1.1 mmol), [Co] (1 mol%), NaO^tBu (2 mol%), THF (2.5 mL), 19 °C, 60 minutes. [b]Refers to the initial concentration of 1-octene. [c]Yield determined by ^1H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [d]Repeat reaction.

3.3.2 Reaction solvent selection

The cobalt-catalysed alkene hydrosilylation reactions that have been reported by Chirik, Huang, Ge and others predominantly used THF as the reaction solvent.[18] Solvent-free conditions or apolar alternatives, such as benzene, have been used in only a few examples.

While regiodivergent reactions have been reported by Ge, no examination of solvent effect has been reported.[130] Using the conditions established from pre-catalyst testing, a selection of commonly available solvents were assessed. *N*-Diethylphenyl substituted pre-catalyst ^{Et}BIPCoCl$_2$ **168** was selected as the pre-catalyst for the hydrosilylation reaction. Ethereal solvents showed very comparable reactivity, giving the alkylsilane products in high yields and similar selectivity to that observed in THF (Table 3.3, entries 1-5). Sustainable 'green' alternatives such as ethyl acetate, methyl *tert*-butylether and dimethylcarbonate also performed well, generating the same alkylsilane products in high yields and in good selectivity (Table 3.3, entries 6-8). Apolar and aprotic solvents, specifically toluene and hexane, showed little catalyst activity (Table 3.3, entries 9-10). Chlorinated dichloromethane also showed no reactivity as well as other commonly used solvents (Table 3.3, entries 11-16).

Table 3.3 - Solvent Compatibility: ^{Et}BIPCoCl$_2$ Catalysed Hydrosilylation of 1-Octene.



Entry[a]	Solvent	Overall Yield[b] (%)	Linear:Branched
1	THF	>95	4:96
2	DME	86	10:90
3	Et_2O	>95	4:96
4	2-Me-THF	73	4:96
5	Dioxane	>95	5:95
6	EtOAc	>95	7:93
7	MTBE	>95	5:95
8	Dimethylcarbonate	82	7:93
9	Toluene	4	*n.d*
10	Hexane	trace	*n.d*
11	CH_2Cl_2	0	*n.d*
12	DMF	Trace[c]	*n.d*
13	Acetone	0[c]	*n.d*
14	CPME	6	*n.d*
15	EtOH	0	*n.d*
16	MeCN	0	*n.d*

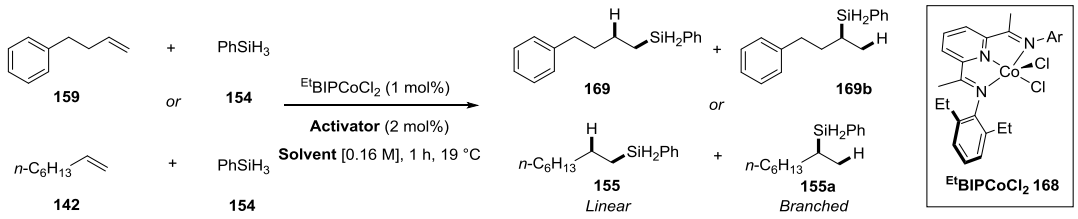
[a]Reaction conditions: 1-octene (1 mmol), $PhSiH_3$ (1.1 mmol), [Co] (1 mol%), Activator (2 mol%), [Solvent] (2.5 mL), 19 °C, 60 minutes. [b]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Complex mixture of unidentified products formed.

3.3.3 Activator selection

With the optimal solvent and reaction concentration established, these parameters could be used to assess and compare different activation methods as a means to benchmark the NaO^{t}Bu activation. Importantly no reaction occurred in the absence of activator (Table 3.4, entry 1). Using LiO^{t}Bu showed observable alkylsilane generation but only in low yield (Table 3.4, entry 2). Using KO^{t}Bu showed comparable reactivity to that of NaO^{t}Bu, generating the alkylsilane products in both high yield and selectivity (Table 3.4, entry 4). Excellent reactivity was also observed using NaOH, which is in contrast to the analogous activation attempted using iron(II) pre-catalysts (Table 3.4, entry 5). The related alkoxides NaOMe and NaOBn showed pre-catalyst activation, however the yields of alkylsilanes produced were significantly lower than that when NaO^{t}Bu was used (Table 3.4, entries 6 & 7). Interestingly Na_2CO_3 also initiated catalysis, albeit in low yield (Table 3.4, entry 8). Unfortunately, while Hünigs base (^{i}Pr$_2$NEt) has been used for the activation of iron(II) pre-catalysts for hydrosilylation, it was not effective for activation in this case (Table 3.4, entry 9).

To compare the NaO^{t}Bu activation method to organometallic reagents, EtMgBr was initially tested in this reaction, however gave only trace quantities of alkylsilanes in EtOAc (Table 3.4, entry 11). The reactions initiated by $NaHBEt_3$ and $LiHBEt_3$ showed good catalyst activity, however the alkylsilane products were produced in lower yields than those generated using NaO^{t}Bu (Table 3.4, entries 12 & 13). Significantly the use of alkyl-lithium reagents was also successful (Table 3.4, entries 14 & 15). In these examples the yields of alkylsilane products was moderate and showed selectivity that was regiodivergent from that produced using NaO^{t}Bu and $NaHBEt_3$. This therefore represents an example of activator derived regiodivergence. The use of EtMgBr in THF, instead of EtOAc, allowed for successful pre-catalyst activation and productive catalysis (Table 3.4, entry 19). These results demonstrate an advantage of using NaO^{t}Bu for generic pre-catalyst activation under a range of reaction conditions.

Table 3.4 – Choice of Activator for ^{Et}BIPCoCl$_2$ Catalysed Hydrosilylation of 1-Octene.

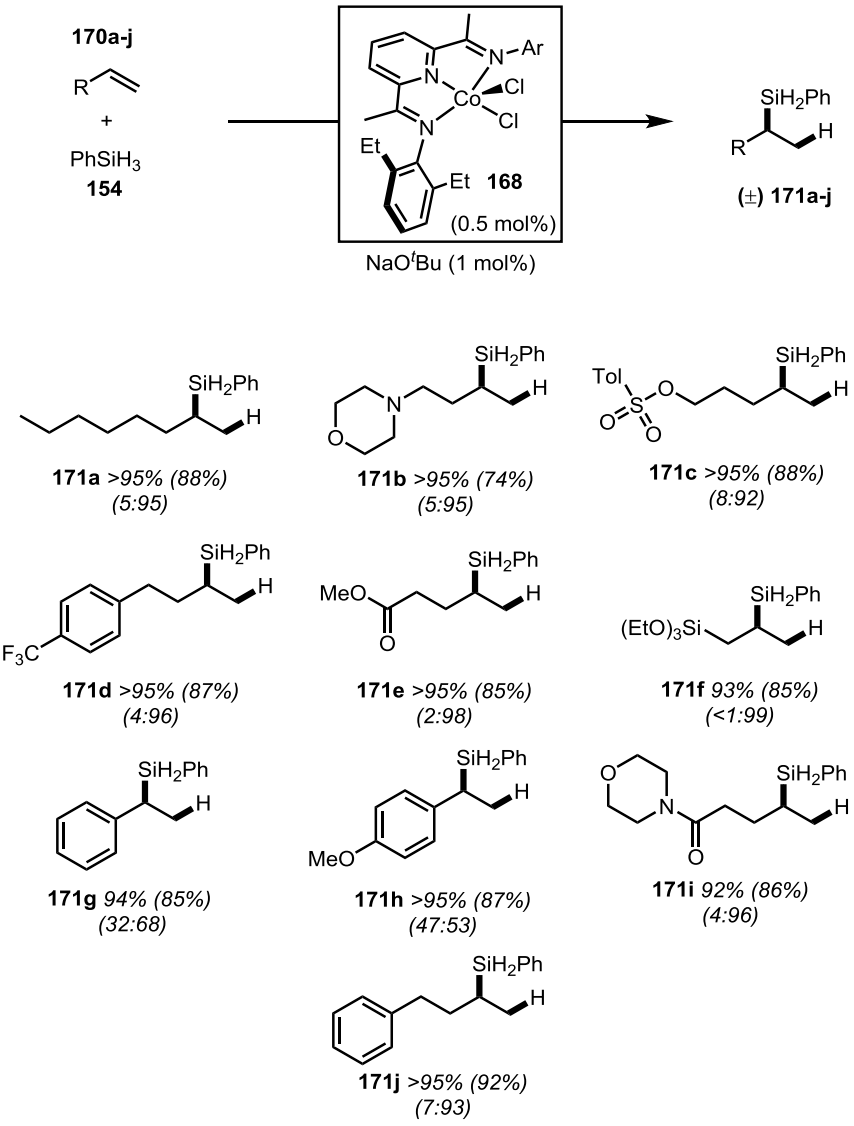


Entry[a]	Activator	Solvent	Overall Yield[d] (%)	Linear:Branched
1[b]	*none*	THF	*trace*	n.d
2[b]	LiO^{t}Bu	THF	10	n.d
3[b]	NaO^{t}Bu	THF	>95	5:95
4[b]	KO^{t}Bu	THF	91	5:95
5[b]	NaOH	THF	95	5:95
6[b]	NaOMe	THF	34	5:95
7[b]	NaOBn	THF	11	n.d
8[b]	Na_2CO_3	THF	26	5:95
9[c]	^{i}Pr$_2$NEt	THF	3	n.d
10[b]	NaO^{t}Bu	EtOAc	>95	5:95
11[b]	EtMgBr	EtOAc	3	n.d
12[b]	$NaBHEt_3$	EtOAc	77	6:94
13[b]	$LiBHEt_3$	EtOAc	58	5:95
14[b]	MeLi	EtOAc	40	87:13
15[b]	^{n}BuLi	EtOAc	50	80:20
16[c]	*none*	THF	0	n.d
17[c]	KO^{t}Bu	THF	71	5:95
18[c]	NaOMe	THF	88	4:96
19[c]	EtMgBr	THF	80	25:75
20[c]	$NaBHEt_3$	THF	50	65:35

[a]Reaction conditions: alkene (1 mmol), $PhSiH_3$ (1.1 mmol), [Co] (1 mol%), activator (2 mol%), solvent (2.5 mL), 19 °C, 60 minutes. [b]Alkene = 4-phenyl-1-butene. [c]Alkene = 1-octene. [d]Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

3.3.4 Substrate scope for the $^{Et}BIPCoCl_2$ catalysed hydrosilylation of alkenes

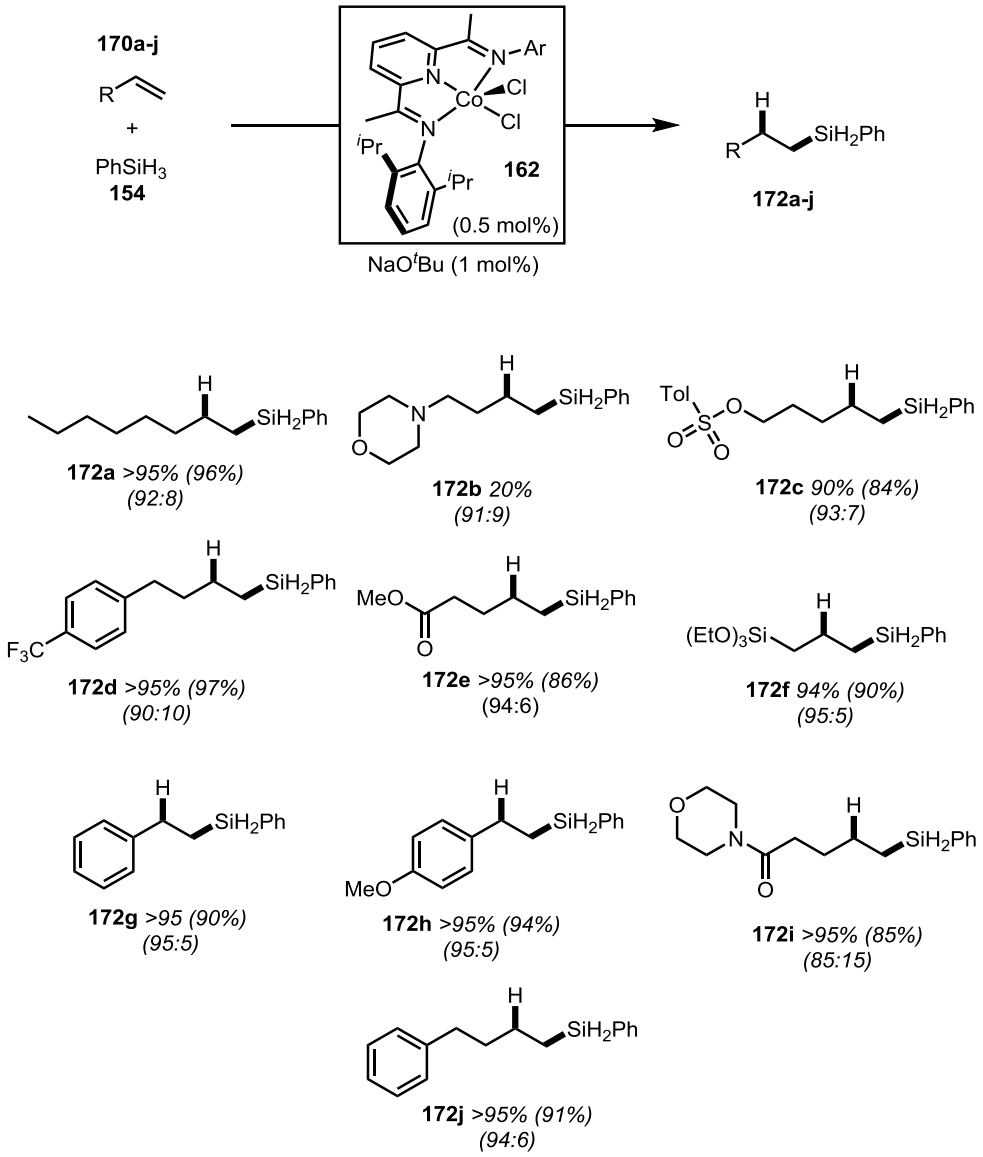
With the optimised reaction parameters for alkene hydrosilylation using *N*-diethylphenyl-substituted bis(imino)pyridine cobalt(II)dichloride $^{Et}BIPCoCl_2$ **168** established, the compatibility of this method for sterically and electronically varied substrates was tested. It was of particular interest to assess whether the Markovnikov selectivity observed in the initial optimisation was a general feature across substrates bearing a range of different functional groups. In these reactions, the terminal alkenes **170a-j** were reacted with phenylsilane to give predominantly the branched alkylsilane products **171a-j**. Using only 0.5 mol% pre-catalyst loading and 1 mol% NaO^tBu, a range of substrates underwent functionalisation (Scheme 3.3). Morpholino-containing alkene **170b** underwent hydrosilylation to give the corresponding branched alkylsilane **171b** in excellent yield and with identical regioselectivity to that found for 1-octene **142** and 4-phenyl-1-butene **159**. Tosyl-protected alcohol **170c** also underwent branched selective hydrosilylation to give the secondary alkylsilane **171c** in high yield without reaction at the tosyl-group. The aryl-trifluoromethyl containing alkene **170d** also underwent successful hydrosilylation to give the expected branched alkylsilane **171d**. Ester **170e** similarly was well-tolerated with no ester hydrosilylation detected. The highest branched selectivity was observed in the hydrosilylation of allyl-triethoxysilane **170f**, which gave the branched alkylsilane **171f** in both high yield and as a single regioisomer. When using vinyl-arenes **170g** and **170h** the reaction was unselective, producing a mixture of regioisomers with only subtle bias for the branched alkylsilanes **171g** and **171h**. Amide **170i** gave the secondary alkyl silane **171i** without reduction or reaction at the amide group in both high yield and regioselectivity.



Scheme 3.3. Substrate scope for the Markovnikov-selective hydrosilylation of terminal alkenes using *N*-diethylphenyl-substituted bis(imino)pyridine cobalt(II)dichloride ^{Et}BIPCoCl$_2$ **168**. Yields determined using 1,3,5-trimethoxybenzene as an internal standard with isolated yields in parenthesis. Selectivities refer to the ratio of linear/branched regioisomers.

3.3.5 Substrate scope for the ^{iPr}BIPCoCl$_2$ catalysed hydrosilylation of alkenes

Having successfully demonstrated the generality of the *N*-diethylphenyl substituted catalyst ^{Et}BIPCoCl$_2$ **168** for the hydrosilylation of alkenes in various different alkenes, the substrate scope of the regiodivergent *N*-di*iso*propylphenyl substituted ^{iPr}BIPCoCl$_2$ **162** catalysed system was investigated to give linear alkylsilanes (Scheme 3.4). The same alkene substrates that had shown reactivity using ^{Et}BIPCoCl$_2$ **168** were assessed using ^{iPr}BIPCoCl$_2$ **162** and under identical reaction conditions. The hydrosilylation of morpholino-containing alkene **170b** reacted poorly, and gave only small quantities of linear alkylsilane **172b**. However catalytic activity was restored in the reaction of tosyl-protected alcohol **170c**, which gave the linear alkylsilane **172c** in high yield and good selectivity. Similarly 4-(4-trifluoromethyl)phenyl-1-butene **170d** gave the alkylsilane **172d** in high yield and with good selectivity for the linear regioisomer. As with the *N*-diethylphenyl substituted catalyst, ester **170e** was chemoselective for hydrosilylation of the alkene to give alkylsilane **172e**. Allyltriethoxysilane **170f** reacted to give alkylsilane **172f** with complete inversion of regioselectivty to that obtained using ^{Et}BIPCoCl$_2$. Vinyl-arenes **170g** and **170h** in this case showed selectivity for the linear alkylsilanes **172g** and **172h**, which was in contrast to the analogous reaction using ethyl-substituted pre-catalyst ^{Et}BIPCoCl$_2$ **168** which was unselective. Amide **170i** reacted productively to give the linear alkylsilane **172i** with good selectivity albeit slightly reduced in comparison to other substrates. Importantly in all examples using ^{iPr}BIPCoCl$_2$ **162** the reactions favourably formed the linear alkylsilane products which is regiodivergent from that observed when using ^{Et}BIPCoCl$_2$ **168**. This represents an example of ligand derived regiodivergence, whereby a change from ethyl-to-*iso*propyl substituent change induces an inversion in regioselectivity.



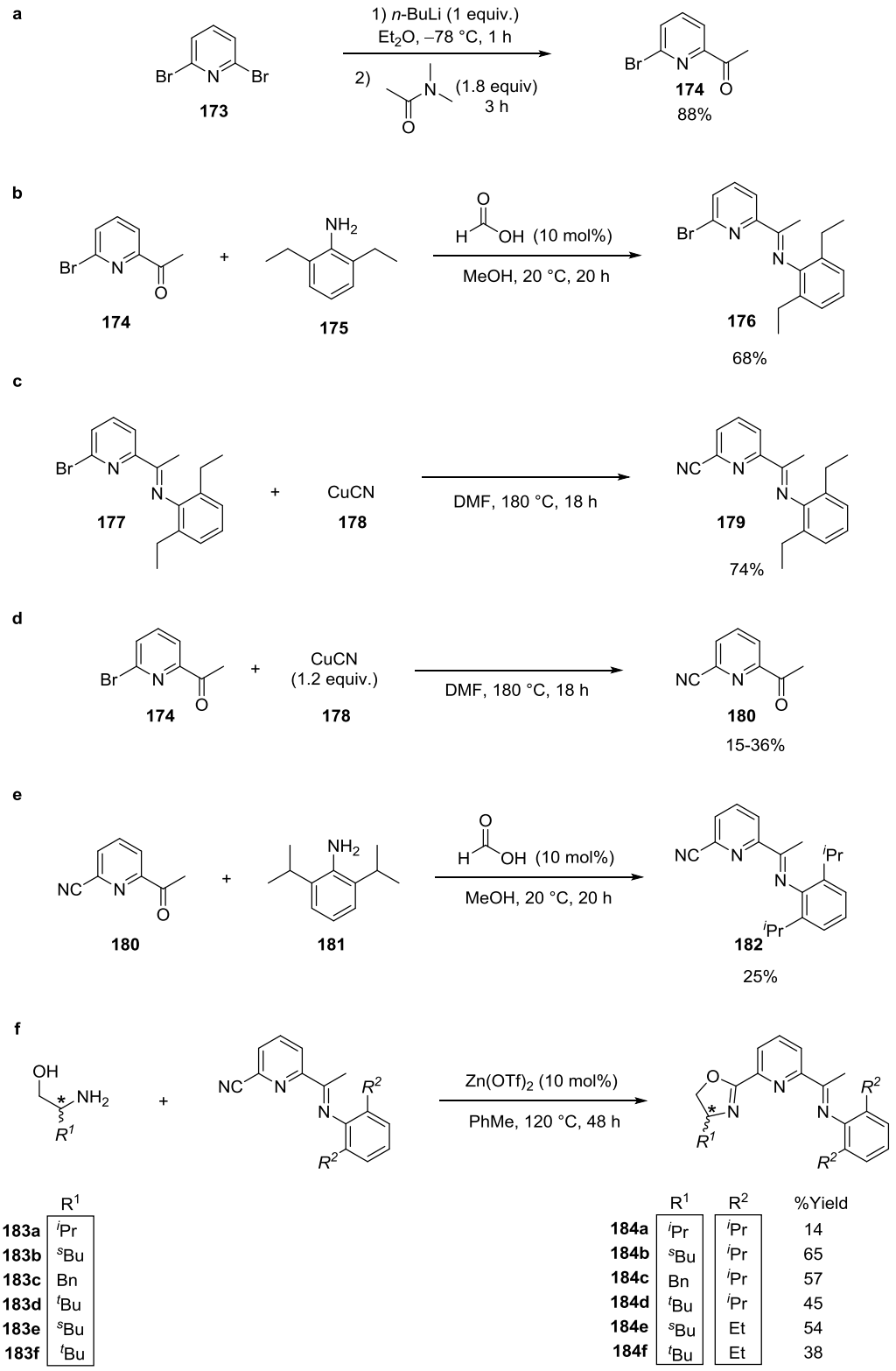
Scheme 3.4. Substrate scope for the *anti*-Markovnikov selective hydrosilylation of terminal alkenes. Yields determined using 1,3,5-trimethoxybenzene as an internal standard with isolated yields in parenthesis. Selectivities refer to the ratio of linear/branched regioisomers.

3.3.6 Attempted enantioselective hydrosilylation of alkenes

Huang and Lu have used enantiopure iminopyridine-oxazoline iron(II) and cobalt(II) complexes for both enantioselective hydroboration and hydrosilylation reactions using a range of substrate classes, including prochiral alkenes and carbonyls. Having found the regiodivergent reactivity of BIPCo(II) complexes activated using NaO^{t}Bu, the formation of branched alkylsilane regioisomers presented the possibility for enantioselective hydrosilylation. In this scenario an enantiopure ligand would be used to induce enantioselectivity, however both reactivity and regioselectivity for the branched regioisomer

would be key for any success. Therefore a number of oxazoline-iminopyridine (IPO) ligands were prepared for assessment (Scheme 3.5).

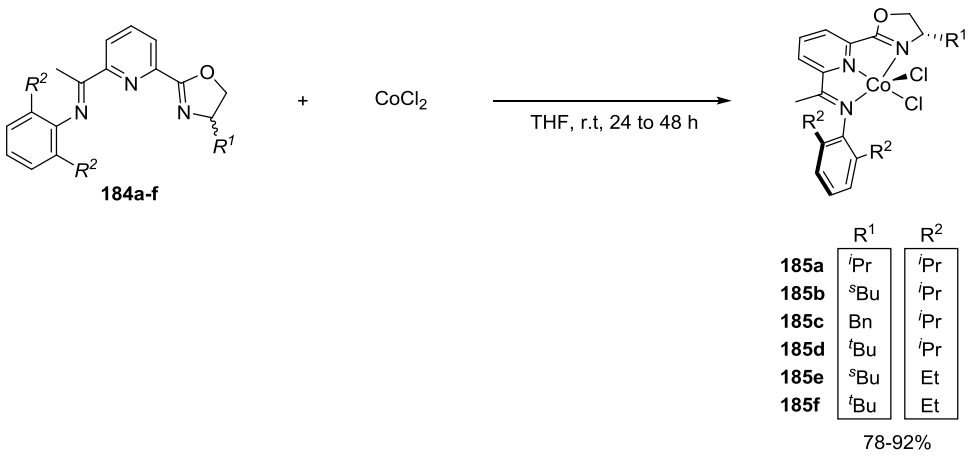
Initially, 2,6-dibromopyridine **173** was used to generate 2-bromo-6-acetylpyridine **174** by lithiation and reaction with dimethylformamide (Scheme 3.5, **a**). A condensation reaction between 2-bromo-6-acetylpyridine **174** and 2,6-diethylaniline **175** gave the imine condensation product **176** in good yield (Scheme 3.5, **b**). Reaction of the imine **176** with super-stoichiometric copper(I) cyanide **178** gave the cyanation product **179** in good yield (Scheme 3.5, **c**). For the analogous *iso*propyl substituted aniline **181**, first the 2-bromo-6-acetylpyridine **174** was cyanated with copper(I) cyanide **178** to give 2-acetyl-6-cyanopyridine **180** in low but useful yields (Scheme 3.5, **d**). The 2-acetyl-6-cyanopyridine **180** was reacted with 2,6-di*iso*propylaniline **181** to give the imine condensation product **182** in low yield (Scheme 3.5, **e**). At this synthetic stage, both *iso*propyl- and ethyl-substituted imines could undergo the same zinc(II)-catalysed oxazoline formation with various enantiopure amino acids (Scheme 3.5, **f**). This final step gave a range of enantiopure IPO ligands with varying steric environments.



Scheme 3.5. Synthesis of iminopyridine-oxazoline (IPO) ligands for attempted enantioselective alkene hydrosilylation.

Following the synthesis of sterically varied enantiopure IPO ligands, the corresponding enantiopure cobalt(II) dichloride complex could be prepared by complexation in THF

(Scheme 3.6). This step gave the expected IPOCo(II)Cl_2 complexes **185a-f** in generally high yields, and each could be easily isolated by filtration from the reaction mixture. It is worthy to note that like tridentate BIPFe(II)Cl_2 and BIPCo(II)Cl_2 complexes, these IPOCo(II)Cl_2 showed good air- and moisture-tolerance for at least one month when exposed to ambient atmosphere.

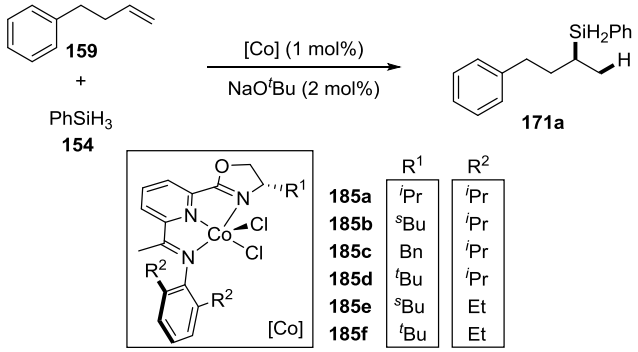


Scheme 3.6. Preparation of IPO-Co(II)Cl_2 complexes for enantioselective alkene hydrosilylation.

To test the ability of enantiopure oxazoline IPOCo(II)Cl_2 complexes **185a-f** to induce stereoselectivity for the hydrosilylation of alkenes, 4-phenyl-1-butene **159** and phenylsilane **154** were selected as reactants, NaO^{t}Bu was used as an activator and the reactions conducted in THF (Table 3.5). Hydrosilylation using $^{i\text{Pr}}$IPO$^{i\text{Pr}}$CoCl$_2$ **185a** proceeded in high yield with excellent regioselectivity for the branched regioisomer and gave a moderate enantiomeric ratio (Table 3.5, entry 1). Using $^{s\text{Bu}}$IPO$^{i\text{Pr}}$CoCl$_2$ **185b** again gave the alkylsilane **171a** in both high yield and excellent regioselectivity and with an improved enantiomeric ratio (Table 3.5, entry 2). A very comparable result was obtained using ^{Bn}IPO$^{i\text{Pr}}$CoCl$_2$ **185c**, which gave the branched alkylsilane **171a** in the same enantiomeric ratio (Table 3.5, entry 3). The same complex was tested at both low temperature (−20 °C) and high temperature (50 °C), however this did not significantly alter the enantiomeric ratio of the alkylsilane (Table 3.5, entries 4 and 5). It is interesting to note that both high yields and excellent regioselectivity were observed at every temperature tested. *tert*-Butyl oxazoline-substituted complex $^{t\text{Bu}}$IPO$^{i\text{Pr}}$CoCl$_2$ **185d** was much less reactive and only gave small quantities of alkylsilane **171a** and with poor regiocontrol (Table 3.5, entry 6). The related ethyl-substituted aryl-imino complex $^{s\text{Bu}}$IPO^{Et}CoCl$_2$ **185e** performed well, generating the alkylsilane product **171a** in high yield, with excellent regioselectivity but with lower enantiomeric ratio than observed for the analogous *iso*propyl substituted analogue (Table 3.5, entry 7). *tert*-Butyl substituted oxazoline $^{t\text{Bu}}$IPO^{Et}CoCl$_2$ **185f** similarly performed poorly, only giving alkylsilane **171a** in

low yield and again as a mixture of regioisomers (Table 3.5, entry 8). Overall, while reactions using this class of pre-catalyst gave high yields and excellent regioselectivity for the branched regioisomer, the maximum enantiomeric excess observed was 50%.

Table 3.5 – Cobalt-catalysed enantioselective hydrosilylation of 4-phenyl-1-butene



Entry	Pre-Catalyst	Overall Yield	Regioselectivity	*e.r*[c]
1	**185a**	92	1:99	34:66
2	**185b**	95	1:99	25:75
3	**185c**	94	1:99	25:75
4[d]	**185c**	>95	1:99	26:74
5[e]	**185c**	>95	1:99	28:72
6	**185d**	12	37:63	n.d
7	**185e**	95	1:99	36:64
8	**185f**	13	40:60	n.d

[a]Reaction Conditions: Alkene (0.5 mmol), $PhSiH_3$ (0.55 mmol), [Co] (1 mol%), NaO^tBu (2 mol%), THF (1.25 mL), r.t, 1 h. [b]Yield determined by ^1H NMR spectroscopy. [c]Determined by HPLC of the silanol following $AgNO_3$ oxidation. [d]Reaction at −20 °C. [e]Reaction at 50 °C.

3.3.7 Mechanistic investigations

In an attempt to understand the regiodivergence between *N*-diethylphenyl-substituted ^{Et}BIPCo(II)Cl_2 **168** and *N*-di*iso*propylphenyl-substituted ^{iPr}BIPCo(II)Cl_2 **162**, mechanistic efforts were made to identify potential reaction intermediates. In the majority of cobalt-catalysed reductive hydrofunctionalisation reactions, either a pre-formed cobalt(I) species or high oxidation state, *i.e* cobalt(II) precursor, that is reduced *in situ* to form a cobalt(I) active

species are used. Both ethyl-substituted ^{Et}BIPCo(II)Cl_2 **168** and *iso*propyl-substituted ^{iPr}BIPCo(II)Cl_2 **162** exhibited paramagnetic ^{1}H NMR behaviour and displayed signals over a wide chemical shift range (−100 to +100 ppm). The related cobalt(I) complexes however are diamagnetic, and are amenable to characterisation by NMR techniques. Therefore to understand and identify intermediates in the hydrosilylation reaction a range of NMR techniques were used. A stoichiometric quantity of ^{Et}BIPCo(II)Cl_2 **168** was reacted with both phenylsilane **154** and NaO^{t}Bu (1:2:2 ratio). As with all catalytic reactions, this mixture quickly turned deep red and produced a diamagnetic cobalt(I) complex which could be observed clearly by both ^{1}H and ^{13}C NMR spectroscopy. Using this data and in combination with 2D-HSQC and HMBC, all proton and carbon resonances could be mapped in the BIP-ligand (Scheme 3.7, upper). The resonances observed were similar to those reported previously for other BIPCo(I) complexes.[132,133] While cobalt(I) complexes bearing the ^{iPr}BIP ligand have been isolated and well characterised, the analogous ethyl-substituted complexes have not. The ethyl-substituted ^{Et}BIPCo(I)Me complex could be prepared independently by reaction of ^{Et}BIPCo(II)Cl_2 with methyllithium for comparison, importantly this reaction proceeds by the chloride intermediate which could be observed in the reaction with a single equivalent of methyllithium (Figure 3.7, **a** and **b**). Analysis of the ^{1}H NMR spectra revealed similar data to that observed for the reported *iso*propyl-substituted complexes. The diagnostic resonances for ^{1}H *para*-pyridine and ^{1}H methyl-ketimine positions did not correspond to that of the cobalt(I) species formed by reduction of ^{Et}BIPCo(II)Cl_2 **168** with phenylsilane **154** and NaO^{t}Bu (Figure 3.6, **c**).

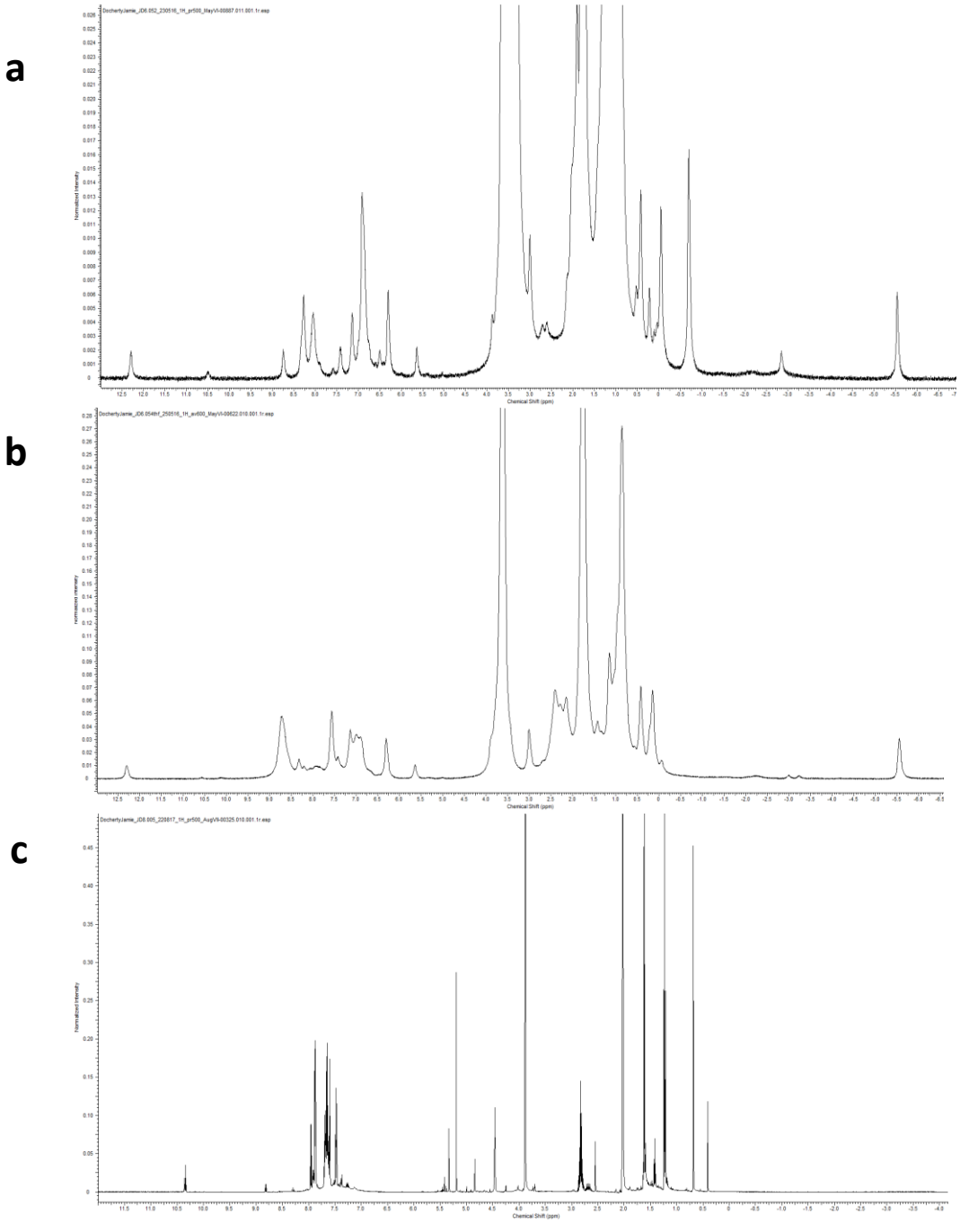
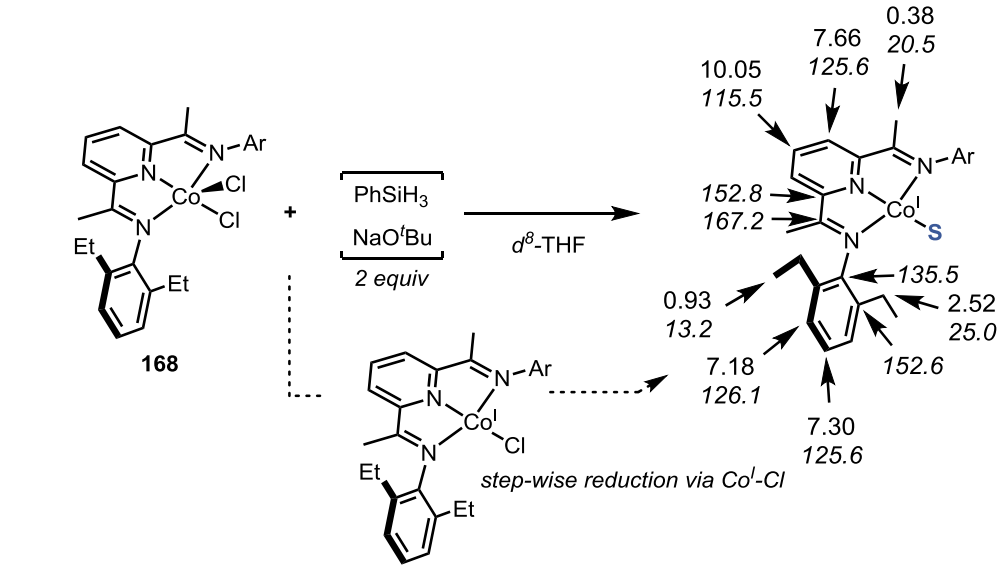
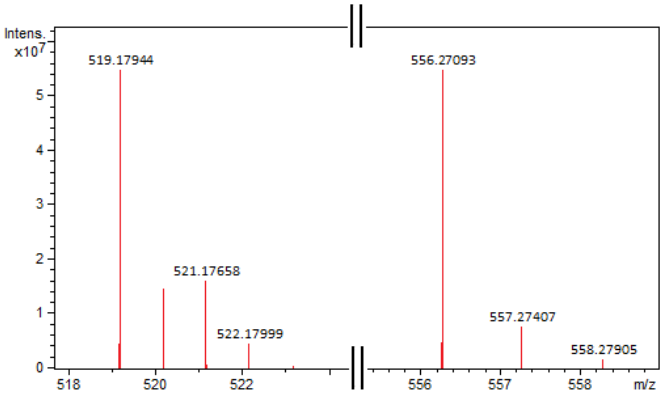


Figure 3.7. **a** Reaction of ^{Et}BIPCoCl$_2$ **168** with MeLi (1 equiv.). **b** Reaction of ^{Et}BIPCoCl$_2$ **168** with MeLi (2 equiv.). **c** Reaction of ^{Et}BIPCoCl$_2$ **168** with phenylsilane and NaO^{t}Bu (1:2:2).

To further elucidate the structure of the species produced on activation of ^{Et}BIPCo(II)Cl$_2$ **168** with phenylsilane and NaO^{t}Bu, the reaction mixture was analysed using atmospheric pressure photoionisation-mass spectrometry (APPI-MS, Scheme 3.7, lower). The data

obtained suggested the formation of ^{Et}BIPCo(I)Cl and the solvent adduct ^{Et}BIPCo(I)(THF). Significantly, no ^{Et}BIPCo(I)H or ^{Et}BIPCo(I)[Si] complex could be identified by either ^{1}H NMR, ^{29}Si NMR or MS methods. Presumably pre-catalyst reduction by phenylsilane and NaO^{t}Bu occurs by successive step-wise hydride transfer and elimination.





Expected m/z:

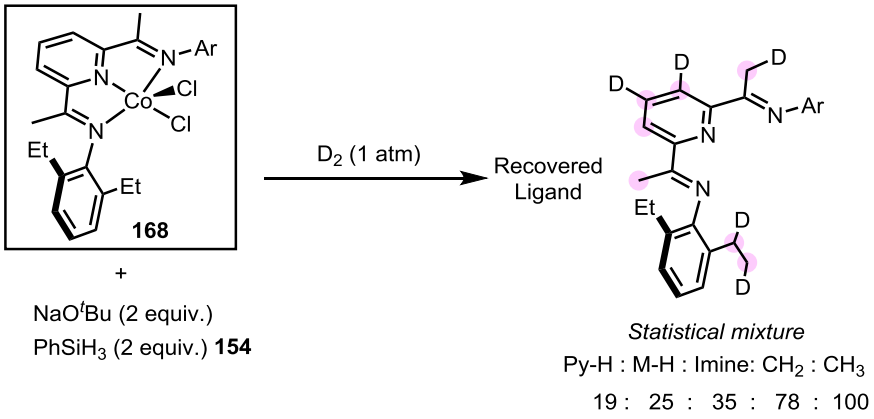
^{Et}BIPCoCl = 519.18515,

^{Et}BIPCo(THF) = 556.27381.

Scheme 3.7. Reduction of ^{Et}BIPCoCl$_2$ using phenylsilane/NaO^{t}Bu in d^8-THF, 'S' denotes the solvent. Chemical shifts for ^{1}H are reported with ^{13}C resonances in italics. APPI-MS detection of reaction intermediates and products.

To gain further insight into the active reduced species produced by the reaction of *N*-ethyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168**, NaO^{t}Bu and phenylsilane **154**, the resulting mixture was subjected to an atmosphere of deuterium gas. The reaction of low oxidation-state cobalt species and C(sp^2)-H bonds has been reported and exploited for C-H borylation

reactions.[134] The Co(I) species produced from the reaction between *N*-ethyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168**, NaO^{t}Bu and phenylsilane **154** interacted productively with deuterium gas and showed that deuterium had been incorporated into the ligand after aqueous work-up (Scheme 3.8). The reaction gave a statistical mixture of deuteration products, with deuterium at both the *meta*- and *para*-pyridyl positions as well as methyl-ketimine and at both methyl- and methine-positions on the aryl-ethyl group. These observations suggest a quick and reversible cyclometallation of the ligand C-H bonds to metal centre. Importantly, free-ligand (^{Et}BIP) was recovered from hydrosilylation reactions without silylation at any position. This may indicate that any cyclometallation is unproductive for catalysis and lies off-cycle for alkene hydrosilylation.

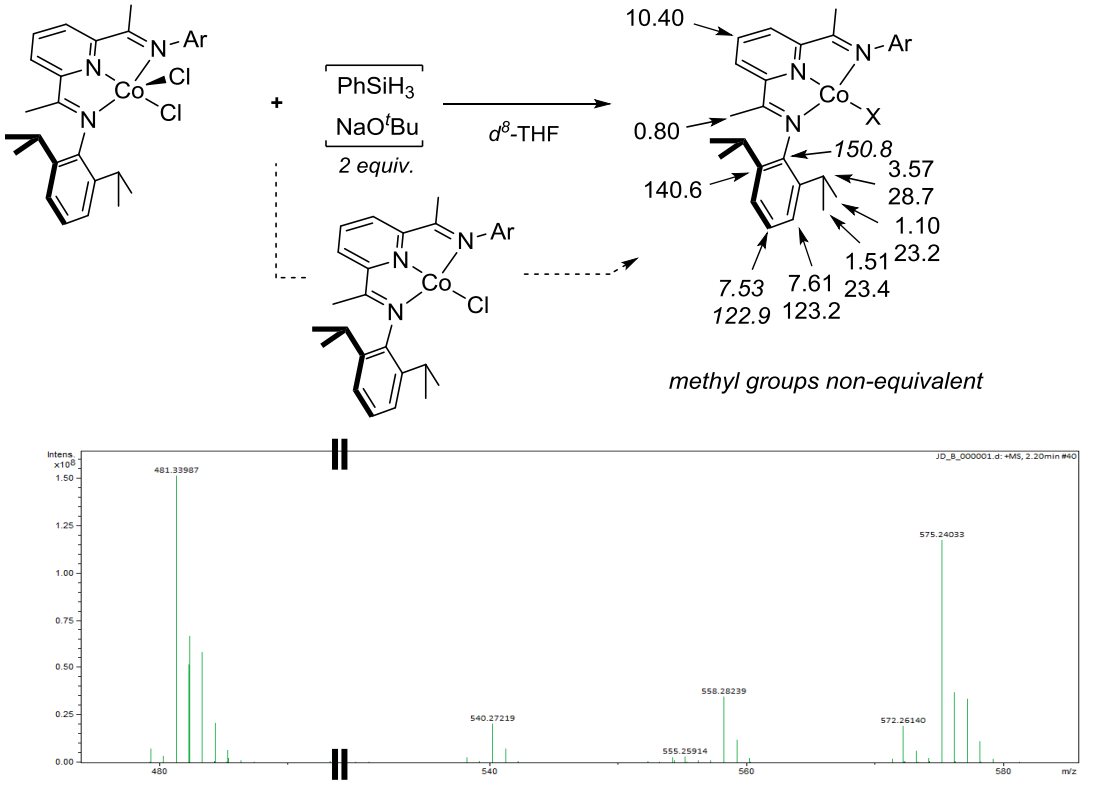


Scheme 3.8. Deuteration of activated cobalt ^{Et}BIPCo(I) species using deuterium gas.

The same analysis was applied to the *N-iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCo(II)Cl$_2$. The ^{1}H NMR spectra exhibited by ^{iPr}BIPCo(II)Cl$_2$ was very similar to that of ^{Et}BIPCo(II)Cl$_2$, both displaying paramagnetic resonances across a broad chemical shift range. However while the related low oxidation-state ^{Et}BIPCo(I) species are unknown, the analogous ^{iPr}BIPCo(I) have been studied and characterised with a number of different coordinating groups.[132,133] The *N-iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCo(II)Cl$_2$ was subjected to pre-catalyst activation by phenylsilane and NaO^{t}Bu with the aim of identifying the identity of a low oxidation-state cobalt(I) species relevant for catalysis. In a similar manner to that of *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$, the solution of *N-iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCo(II)Cl$_2$ underwent a colour change upon activation, forming a deep red solution. The resulting ^{1}H NMR spectra revealed a diamagnetic species with similar resonances to both the ^{Et}BIPCo(I) species produced by the same method and to that of reported cobalt(I) complexes (Scheme 3.9, upper). Although this

reaction produced a diamagnetic species, the NMR data obtained was not clear enough to fully map all chemical shift values for each proton and carbon resonance in the structure. The key resonances at *para*-pyridyl and ketimine protons were identified and had similar, but not identical, values to related cobalt(I) species reported by Budzelaar.[132,133] This indicates that the species produced on reduction with phenylsilane and NaO^{t}Bu is not one that has been previously synthesised and characterised. It should be noted that in both structures of the reduced pre-catalysts, the BIP ligand resonances can be identified however it is unclear in either case if other groups ligate the cobalt centre.

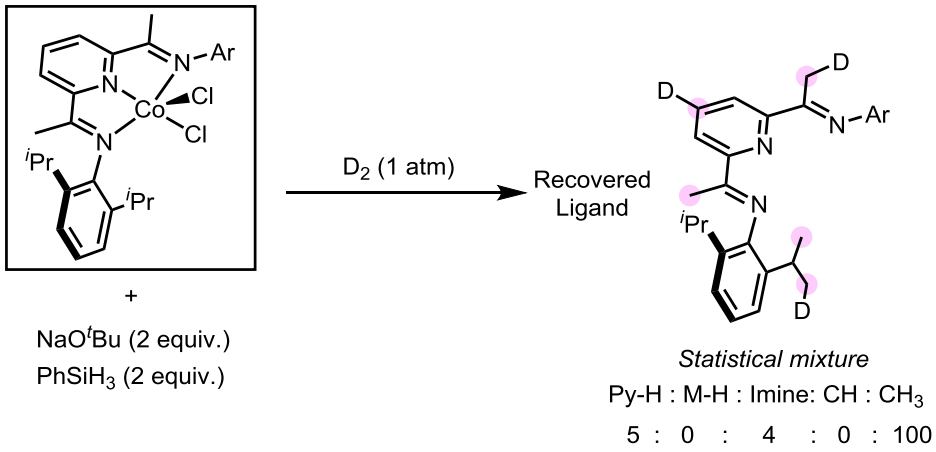
Further insight could be obtained through APPI-MS analysis of the reduced pre-catalyst species (Scheme 3.9, lower). The ions identified included that of $^{i\text{Pr}}$BIP, $^{i\text{Pr}}$BIPCoCl and $^{i\text{Pr}}$BIPCo. In this example, no $^{i\text{Pr}}$BIPCoH, $^{i\text{Pr}}$BIPCo[Si] or $^{i\text{Pr}}$BIPCo(THF) were observed. This may implicate a role of a 'naked' cobalt(I) species, that is only ligated by BIP, for alkene hydrosilylation.



Expected m/z: $^{i\text{Pr}}$BIP = 481.34570, $^{i\text{Pr}}$BIPCoCl = 575.24775, $^{i\text{Pr}}$BIPCo = 540.27890, $^{i\text{Pr}}$BIPCo(H_2O) = 558.28946.

Scheme 3.9. Reduction of $^{i\text{Pr}}$BIPCoCl_2 using phenylsilane/NaO^{t}Bu in d^8-THF. Chemical shifts for ^{1}H are reported with ^{13}C resonances in italics. APPI-MS detection of reaction intermediates and products.

Exposure of the *N-iso*propylphenyl substituted low oxidation-state ^{iPr}BIPCo(I) species by reduction using phenylsilane and NaO^{t}Bu to an atmosphere of deuterium gas gave a similar result to that observed using ^{Et}BIPCo(I) (Scheme 3.10). In this reaction, following work-up and recovery of the BIP ligand, deuterium incorporation could be identified at a mixture of positions, including the *para*-pyridyl, ketimine and at *iso*propyl-methyl groups. This result shows similarity to that of ^{Et}BIPCo(I), and suggests that the low oxidation-state cobalt species in this example can undergo cyclometallation with ligand C-H bonds.



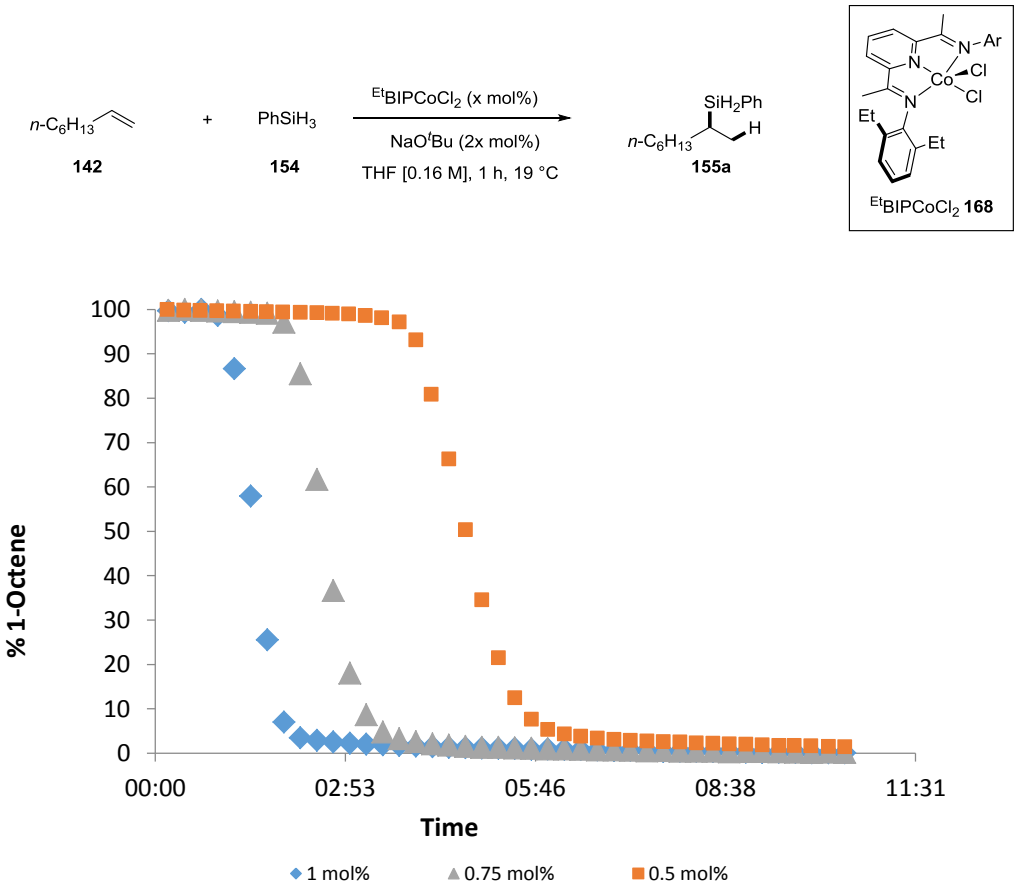
Scheme 3.10. Deuteration of activated cobalt ^{iPr}BIPCo(I) species using deuterium gas.

3.3.8 Reaction progress kinetics

With regiodivergence observed in the reactivity for alkene hydrosilylation using *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168** and *N-iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCo(II)Cl$_2$ **162** it was considered that an investigation of reaction rates may provide mechanistic insight. Using infra-red spectroscopy to measure rates of reaction (ReactIR), the progress of the hydrosilylation reaction could be measured directly *in situ* (Scheme 3.11).

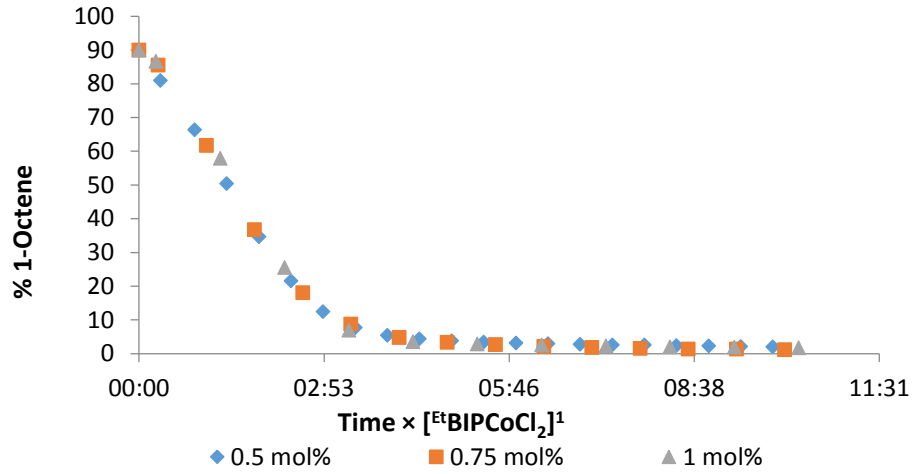
Using the *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168** as the pre-catalyst and activated by NaO^{t}Bu in a 1:2 ratio, the hydrosilylation of 1-octene **142** using phenylsilane **154** could be profiled. The concentration, or catalyst loading, of *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168** was varied from 1 mol% to 0.5 mol%, and always maintaining a 1:2 ratio of pre-catalyst to NaO^{t}Bu. Each reaction displayed similar profiles, always beginning with an induction period of little to no reactivity followed by rapid reaction to form the expected alkylsilane products. The observed induction behaviour was a clear differentiating factor between each reaction, as this was directly associated with the

catalyst loading. Higher catalyst loadings gave reduced induction periods compared to those of lower loadings. Additionally the gradient of each reaction curve (*i.e* reaction rate), once the reaction was beyond induction, varied significantly at each catalyst concentration. This was suggestive of a rate dependence with respect to catalyst. Importantly, it was clarified that an increased loading of NaO^{t}Bu (1:10) with respect to catalyst had no rate enhancement nor did it affect the induction period.



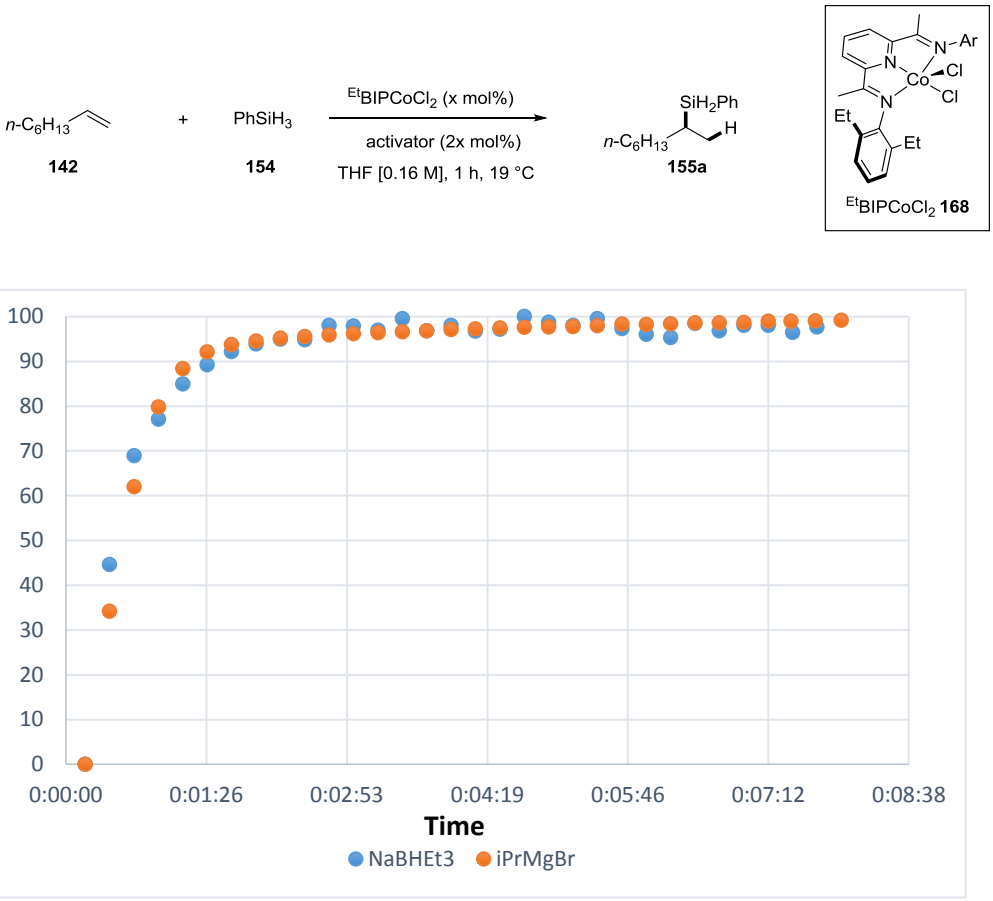
Scheme 3.11. Reaction progress kinetics of 1-octene reacting with phenylsilane using ^{Et}BIPCoCl$_2$ **168** pre-catalyst, followed by IR absorbance of 1-octene.

To determine the reaction order with respect to catalyst, the method of Burés was used (Scheme 3.12). This method allows for order in catalyst to be found from a normalised time scale, t[cat]^n, which adjusts the entire reaction profile based on concentration data. To use this method, it was essential to exclude the induction period observed in each reaction and only use data beyond this point. When calculated and plotted for each concentration at n = 0, 0.5, 1, 2, the best overlay was found at n = 1 and clear mismatching was identified at the other values, indicating an order of reaction with respect to *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ of 1.



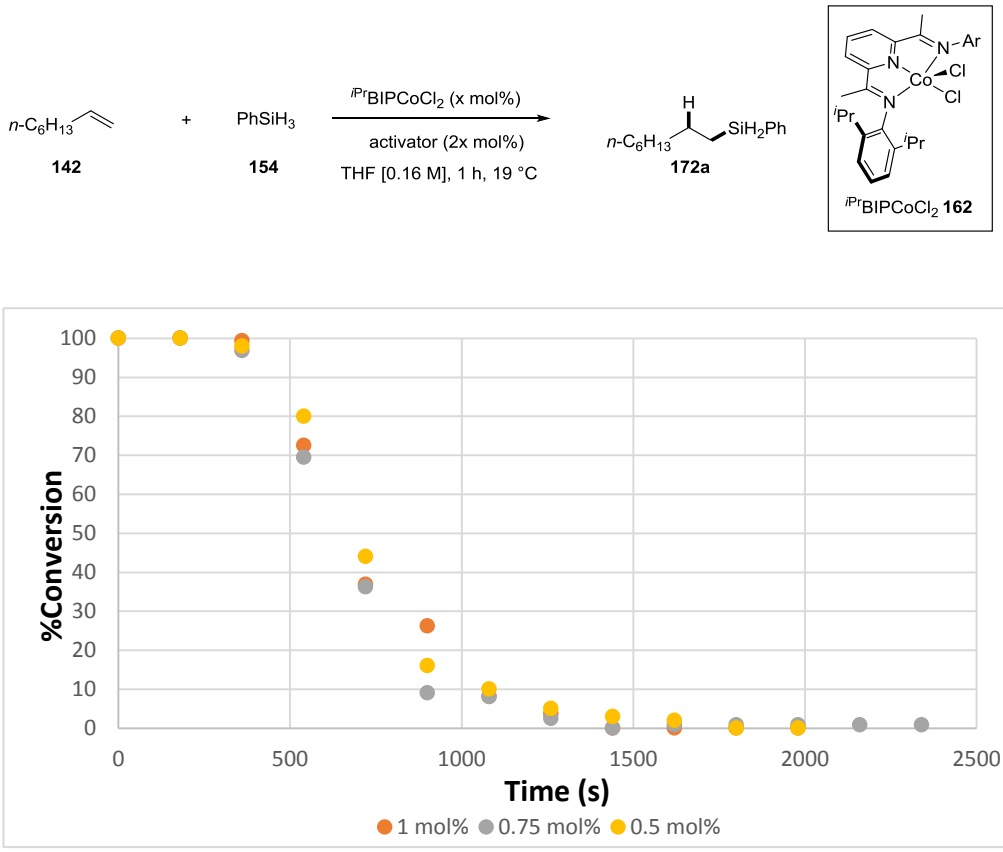
Scheme 3.12. Graphical plot of 1-octene *vs.* normalised time t[Catalyst]^{1} (Induction period omitted). Catalyst = ^{Et}BIPCoCl$_2$ **168**.

To probe the cause of the induction period observed in these reactions, the same process was monitored using organometallic reagents as the activator (Scheme 3.13). These reactions displayed no such induction, rapidly forming the alkylsilane product **155a**. This may suggest that the induction period observed when using NaO^{t}Bu as an activator is due to a slow interaction of NaO^{t}Bu with phenylsilane and therefore delayed pre-catalyst activation.



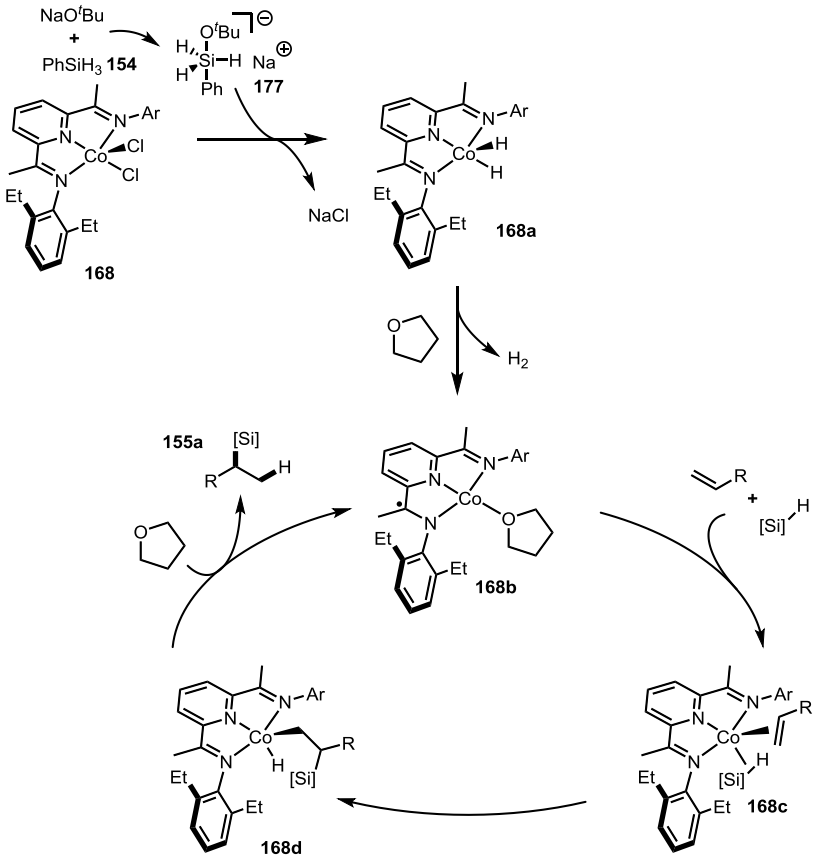
Scheme 3.13. Reaction progress monitoring for ^{Et}BIPCoCl$_2$ **168** catalysed hydrosilylation of 1-octene using organometallic reagents as activators.

The same reaction progress kinetic analysis could be undertaken for the analogous *N-iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCo(II)Cl$_2$ **162** (Scheme 3.14). The reaction progress followed much of the same characteristics exhibited by *N*-ethylphenyl substituted pre-catalyst ^{Et}BIPCo(II)Cl$_2$ **168**, with a similar induction period followed by reaction progress. It is notable that the reaction rates for reactions using ^{iPr}BIPCo(II)Cl$_2$ **162** are significantly slower than that of ^{Et}BIPCo(II)Cl$_2$ **168**. Overlay of reaction rates in this example showed identical rate of reaction regardless of catalyst loading. This would suggest that the rate of reaction is independent of catalyst concentration, and hence an order with respect to catalyst is 0. A zero order in catalyst implied that the catalyst is not involved in the rate-determining step for the reaction. However this result may be due to a limited solubility of pre-catalyst in the reaction solvent and therefore limiting the overall rate of reaction by the soluble quantity of catalyst.



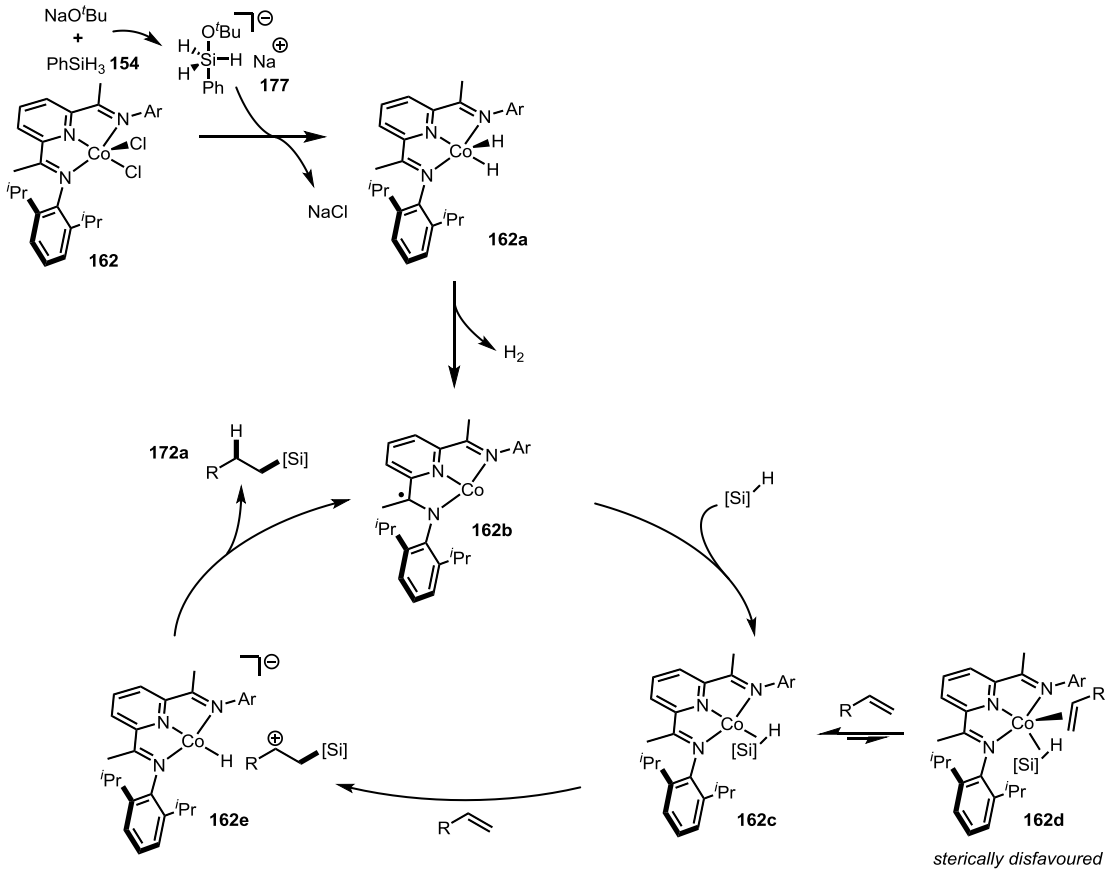
Scheme 3.14**.** Reaction progress kinetics – 1-octene reacting with phenylsilane using ^{iPr}BIPCoCl$_2$ **162**.

The branched selective alkene hydrosilylation using *N*-diethylphenyl-substituted cobalt pre-catalyst ^{Et}BIPCoCl$_2$ **168**, may proceed by formation of siliconate **177**, with hydride transfer to the pre-catalyst followed by reductive elimination of dihydrogen. This would give a low oxidation-state cobalt(I) species. The ^{1}H NMR studies indicate the formation of a diamagnetic cobalt complex, presumably a low-spin d^8 complex. The analogous cobalt(II) or cobalt(0) species would possess d^7 and d^9 electronic stuctures respectively and therefore would exist as paramagnetic complexes. As the THF-adduct **168b** was observed by APPI-MS, this could serve as an initial on-cycle catalyst for alkene hydrosilylation. Alkene and silane coordination to the cobalt-centre with THF displacement could generate the ternary inner-sphere structure **168c**. This may then undergo silicon-group addition to the *β*-position of the alkene and form an alkyl-hydrido-cobalt species **168d** that, following reductive elimination, generates the branched alkylsilane **155a** and reforms the catalyst.



Scheme 3.15. Proposed mechanism for the Markovnikov-selective hydrosilylation of alkenes using ^{Et}BIPCoCl$_2$.

Using the *N*-di*iso*propylphenyl substituted pre-catalyst ^{iPr}BIPCoCl$_2$ **162** the mechanism of pre-catalyst activation may be similar but catalytic turnover and product generation must differ. Siliconate complex **177** would transfer hydride from silicon to cobalt(II) pre-catalyst **162**, followed by reductive elimination of dihydrogen. The cobalt species bearing BIP ligand and no other ligating groups **162b**, such as THF, was observed by APPI-MS and would therefore serve as the low oxidation-state active catalyst to initiate hydrosilylation. The silane reagent may coordinate to the 'naked' cobalt species **162c**, and sterically the formation of ternary species **162d** with both silane and alkene coordinated may be disfavoured. This inability to form ternary inner-sphere complex **162d** could be the regioselectivity determining factor. Following silane coordination, direct siliylation of the alkene to give the cobalt(I)-hydride and β-silyl cation may occur. The hydride could then be trapped on reaction with the β-silyl cation to give the observed linear alkylsilane product that is experimentally observed which would regenerate the on-cycle catalyst.



Scheme 3.16. Proposed mechanism for the *anti*-Markovnikov-selective hydrosilylation of alkenes by ^{iPr}BIPCoCl$_2$.

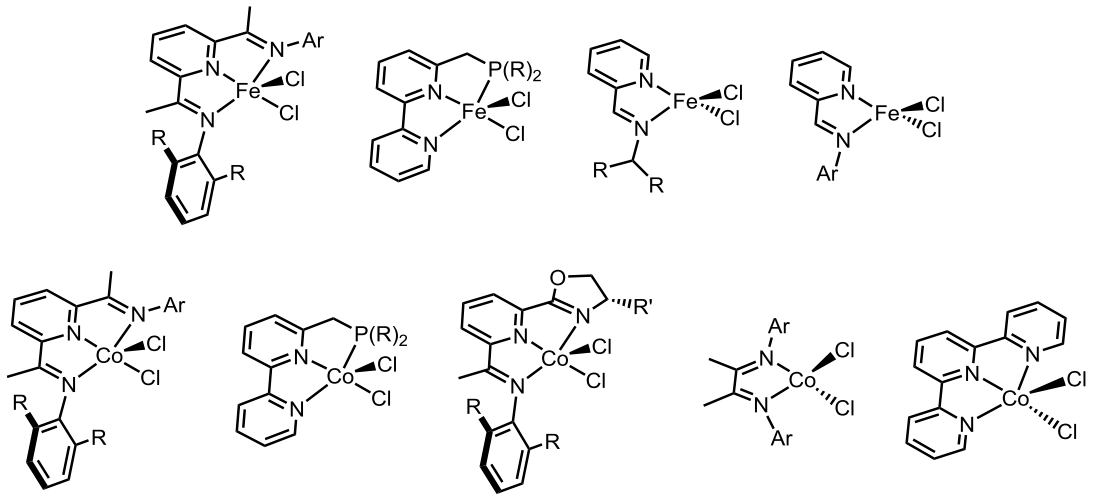
3.4 Summary

Regiodivergent cobalt-catalysed alkene hydrosilylation was found to be possible using structurally similar ligand frameworks. Sodium *tert*-butoxide was shown to be an efficient activator for cobalt(II) pre-catalysts for alkene hydrosilylation. This reactivity was demonstrated across a range of electronically and structurally differentiated alkenes. With the exception of styrene derivatives, the regiodivergent reactivity of the cobalt pre-catalysts with unique *N*-aryl substitutents was found to apply to all substrates tested. Mechanistic investigations show a 1st order dependence on catalyst for the *N*-diethylphenyl substituted cobalt(II) complex while the *N*-di*iso*propylphenyl substituted cobalt(II) complex exhibits zero order kinetics with respect to catalyst concentration. These results are indicative of unique mechanistic pathways which will require further interrogation to determine the definitive mechanism of regiodivergent hydrosilylation.

4.0 Conclusions and outlook

At the outset of this project the majority of iron and cobalt catalysed methods for low oxidation-state catalysis required the use of strongly reducing metals or organometallic reagents at either the catalyst preparation step or for *in situ* activation. These complexes had proven to be powerful synthetic methods for the construction of carbon-carbon and carbon-heteroatom bonds. Significantly the reactivity exhibited by these methods could compare well with analogous precious metal catalysed procedures. The use of air- and moisture tolerant higher oxidation-state pre-catalysts that could be reduced in situ using organometallic reagents provided a new level of practicality which allowed for use of these methods by the non-specialist practitioner. Nevertheless these methods often used highly reactive reagents, such as Grignards or alkyl-lithiums. The necessity of using strongly reducing reaction components has hindered the widespread adoption of these otherwise powerful synthetic methods.

The overarching aim of the project was to overcome practicality limitations, and allow for easier use of low oxidation-state iron and cobalt methods. An investigation of activation reagents led to the discovery and development of NaO^{t}Bu as a potent pre-catalyst activator for alkene hydroboration and hydrosilylation reactions. Using NaO^{t}Bu, a range of iron and cobalt pre-catalysts were activated for alkene hydroboration and hydrosilylation reactions (Scheme 4.1). A number of different ligand classes were among the operational catalysts, hosting unique steric and electronic structures.

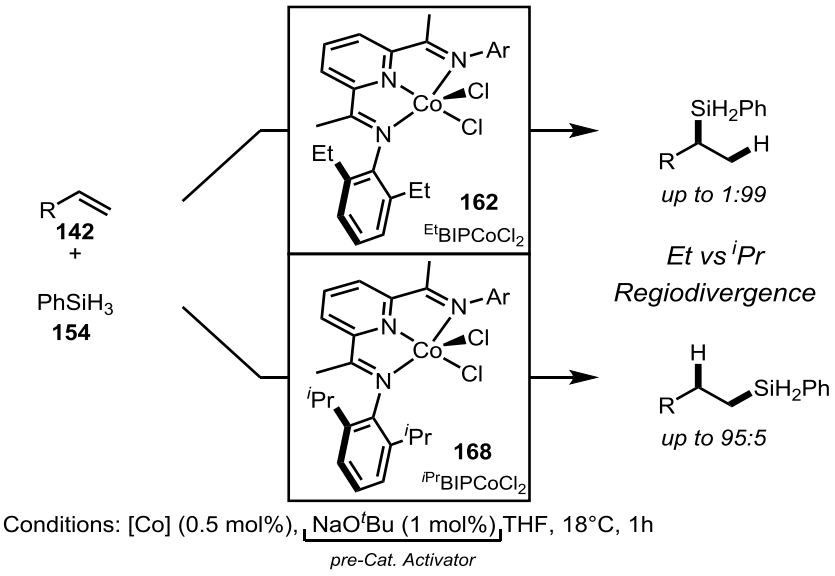


Scheme 4.1. Iron and cobalt pre-catalysts that underwent successful activation uing NaO^{t}Bu.

Mechanistic investigations suggest a role of the hydrofunctionalisation reagent (HBPin or $HSiR_3$) in the activation of both iron and cobalt pre-catalysts, whereby NaO^{t}Bu acts as a nucleophile towards these reagents. The intermediate adduct formed from the reaction between NaO^{t}Bu and hydrofunctionalisation reagent serves as a hydride donor, which enables generation of metal-hydride species that can initiate catalysis.

Understanding the role of alkoxide and hydrofunctionalisation reagent enabled the expansion of the activation method beyond alkene hydroboration and hydrosilylation. Using substoichiometric quantities of added borane or silane reagent triggered catalyst activation for reactions that did not inherently contain a hydrofunctionalisation reagent. Therefore the applicability of low oxidation-state catalysis could be used for alkene hydrovinylation, hydrogenation and [2π+2π] alkene cycloaddition reactions.

The NaO^{t}Bu activation method was applied in cobalt-catalysed hydrosilylation where regiodivergent reactivity was observed between two structurally analogous pre-catalysts. The *N*-diethylphenylsubstituted bis(imino)pyridine cobalt(II)dichloride pre-catalyst was selective for the Markovnikov-addition products, whereas the *N*-di*iso*propylphenylsubstituted bis(imino)pyridine cobalt(II)dichloride was selective for the anti-Markovnikov regioisomer (Scheme 4.2). Regioselectivity was further divergent when using different pre-catalyst activators, for example alkyl-lithium reagents gave different regioselectivity from borohydride reagents. Mechanistic investigations show that pre-catalyst reduction using NaO^{t}Bu and phenylsilane produce low oxidation-state cobalt(I) species. These species could be identified using mass spectroscopy and NMR methods.



Scheme 4.2. Regiodivergent cobalt-catalysed alkene hydrosilylation using NaO^{t}Bu as an activator.

The outlook for alkoxide pre-catalyst activation is broad and promising. NaO^{t}Bu has broad commercial availability, low hazards and can be used without specialist equipment. All of these traits are required for high throughput robotic discovery platforms, and therefore serves as an apt method for rapid reaction discovery and optimisation in both academic and industrial settings. Advancing operational practicality is essential for the mass adoption of any synthetic method. Alkoxide activation fills this requirement and enables access to synthetically powerful low oxidation-sate catalysts to the non-expert.

Future work on this topic may include expansion to further pre-catalyst classes for the development of reductive synthetic transformations, such as alkene hydrosilylation. In this context, the development of operationally simple alkene hydrosilylation protocols with tertiary silanes using Earth-abundant metals would be industrially valuable.[17,60] Similarly, extension of the NaO^{t}Bu activation method to metals beyond nickel, cobalt, iron and manganese could be possible.

In the context of cobalt-catalysed regiodivergent alkene hydrosilylation, further work is required to delineate the mechanism and cause of regiodivergence. Crystallisation and X-ray crystallographic characterisation of the reduced species from activation by NaO^{t}Bu and phenylsilane would prove useful in confirming the identity of the catalyst resting state. Further kinetic information would supplement the already measured data, and allow for construction of diverging catalytic cycles. Specifically, it would be important to assess the order of each reacting species, *i.e* alkene and silane, and determine the reversibility of any hydrometallation or silylmetallation through use of d^3-phenylsilane ($PhSiD_3$).

5.0 Experimental

5.1 General experimental

Reaction Setup: All reactions were performed in oven (185 °C) and/or flamed-dried glassware under an atmosphere of anhydrous nitrogen or argon, unless otherwise indicated. All air- and moisture sensitive reactions were carried out using standard vacuum line and Schlenk techniques, or in a glovebox with a purified argon atmosphere. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to external bath temperatures. Room temperature (r.t) was approximately 22 °C. "Brine" refers to a saturated solution of sodium chloride in H_2O.

NMR Spectroscopy: ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker AVI 400 MHz; Bruker Avance I 600 MHz spectrometers at 27°C unless otherwise specified. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual deuterated solvent peak ($CHCl_3$: 7.27 ppm, 77.00 ppm; CH_2Cl_2: 5.32 ppm, 54.00 ppm; d_8-THF: 1.73 ppm, 25.37; CD_3CN: 1.94 ppm, 1.39 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet). Coupling constants, *J*, are reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided and assignments are indicated. ^{1}H and ^{13}C assignments are corroborated through 2-D NMR experiments (COSY, HSQC, HMBC).

Infrared Spectroscopy: Infra-red (IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (serial no. A213749) spectrometer. Relevant peaks are reported in cm^{-1}.

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Ionisation (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Chemical Ionization (CI^+) spectra were performed with methane reagent gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Electrospray Ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Melting Points: Melting points (mp) were determined on a Stuart Scientific SMP10,

or Griffin Gallankamp, melting point apparatus in capillary tubes and are uncorrected.

Chromatography: Analytical thin-layer chromatography was performed on aluminium-backed silica plates (Merck 60 F_{254}). Pet. ether refers to petroleum ether 40-60. Product spots were visualised by UV light at 254 nm, and subsequently developed using potassium permanganate solution if appropriate. Flash column chromatography was performed on silica gel (Merck Kielselgel 60, 40-63 μm) unless otherwise stated.

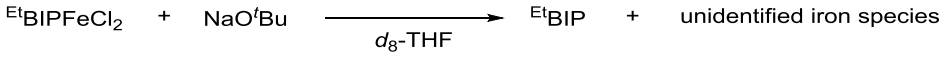
Solvents: All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Anhydrous d_8-tetrahydrofuran was distilled from sodium/benzophenone. Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et_2O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH_2Cl_2) (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvent toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Reaction solvent ethanol (absolute, VWR) was used as received. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH_2Cl_2) (ACS grade, amylene stabilized), diethylether (Et_2O) (Fisher, BHT stabilized ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

Chemicals: All reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, Fluorochem and Apollo Scientific or synthesised within the laboratory.

Iron (II) chloride was purchased from Strem Chemicals Inc. (UK); anhydrous iron chloride, 98% (product number 93-2631. Lot 19226800, 44.00000% Fe, expect 44.059%). Cobalt (II) chloride was purchased from Strem chemicals Inc. (UK); anhydrous cobalt chloride 99%+ (product number 93-2721. Lot A6262018). Nickel (II) chloride ethylene glycol dimethyl ether complex 98% (product number 696668. Lot BGBC3892V) was purchased from Sigma Aldrich (UK). Cobalt (II) chloride was purchased from Strem chemicals Inc. (UK); anhydrous cobalt chloride 99%+ (product number 93-2721. Lot A6262018). Sodium *tert*-butoxide (97%) was purchased from Sigma Aldrich (UK). Sulfate buffer refers to aqueous sulfate buffer solution which was prepared by dissolving Na_2SO_4 (1.5 mol) in H_2SO_4 (0.5 mol) and adding water to give a total volume of 2 L.

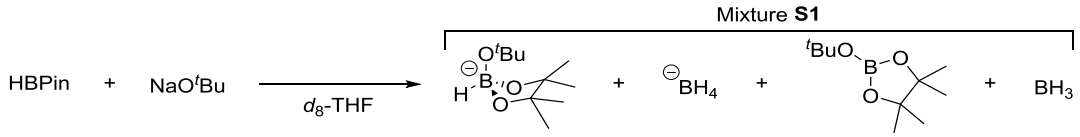
5.2 Mechanistic studies and relevant spectra

R1| Reaction of ^{Et}BIPFeCl$_2$ with sodium *tert*-butoxide



Anhydrous d_8-tetrahydrofuran (0.5 mL) was added to a mixture of sodium *tert*-butoxide (1.0 mg, 10.0 µmol) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (2.8 mg, 5.0 µmol). The blue colour of ^{Et}BIPFeCl$_2$ quickly turned yellow and there was a lack of paramagnetic resonances observed by ^{1}H NMR spectroscopy which was suggestive of ligand de-metallation. This phenomenon has also been observed by Byers and co-workers.[125] Furthermore, the resulting mixture was catalytically unreactive towards either alkene hydrosilylation or hydroboration.

R2| Reaction of pinacolborane with sodium *tert*-butoxide



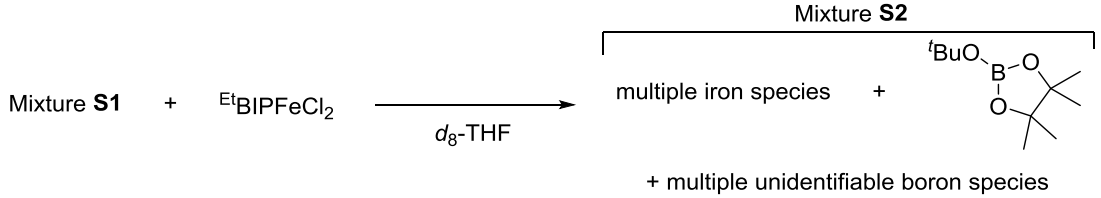
Pinacolborane (52 µL, 0.36 mmol) was added to a suspension of sodium *tert*-butoxide (35 mg, 0.36 mmol) in anhydrous d_8-tetrahydrofuran (0.5 mL) to give mixture **S1**.

^{11}B NMR (160 MHz, d_8-THF)

21.5 (br. s), 8.4 (s), 4.4 (br. m), −14.8 (br. m), −43.0 (quin., J = 80.4 Hz).

Data for all species were consistent with those reported previously.[127]

R3| Reaction of mixture S1 with ^{Et}BIPFeCl$_2$

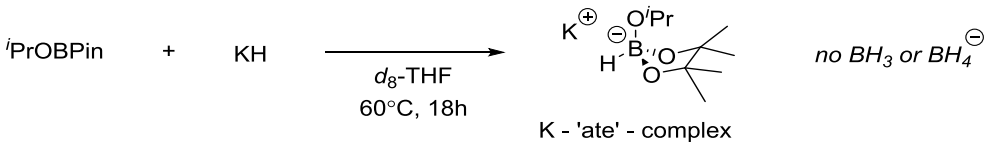


Mixture **S1** (100 µL, 0.072 mmol wrt. NaO^{t}Bu) was added to a suspension of ^{Et}BIPFeCl$_2$ (20 mg, 0.036 mmol) in anhydrous d_8-tetrahydrofuran (0.5 mL). The blue suspension quickly turned into a dark brown solution (mixture **S2**) which contained multiple iron species as indicated by the appearance of several new ^{1}H NMR resonances.

^{11}B NMR (160 MHz, d_8-THF)

27.3 (d, *J* = 154 Hz), 23.3 (br. s), 17.7 (br. s), 10.9 (br. s), 6.4 (br. m).

R4| Reaction of 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane with potassium hydride

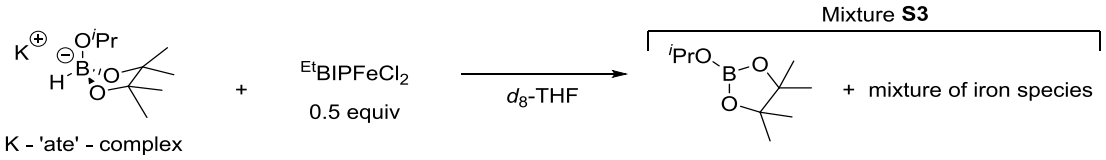


2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (~18 µL, 0.1 mmol) was reacted with potassium hydride (8 mg, 0.2 mmol) in anhydrous d_8-tetrahydrofuran (0.5 mL) to give K-ate-complex.

^{11}B NMR (160 MHz, d_8-THF)

21.2 (br. s), 8.5 (br. s) 5.7 (br. s).

R5| Reaction of K-ate-complex with ^{Et}BIPFeCl$_2$

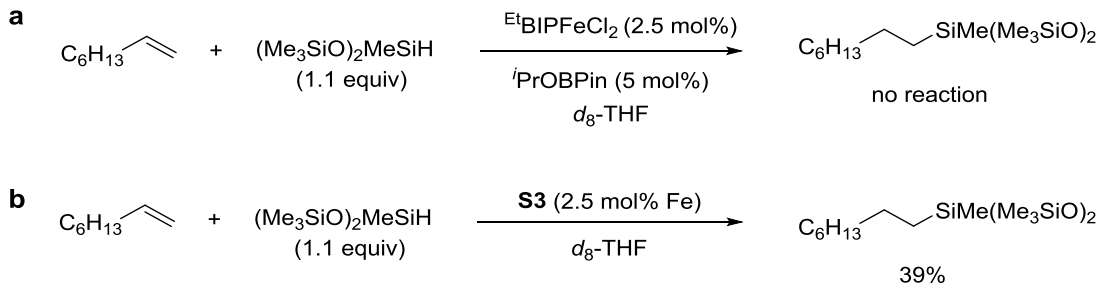


Following filtration of remaining potassium hydride, K-ate-complex (100 µL of a 500 µL solution, 25 µmol) was added to a suspension of (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (6.9 mg, 13 µmol) in anhydrous d_8-tetrahydrofuran (0.5 mL) to give 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane and a mixture of iron species (Mixture **S3**).

^{11}B NMR (160 MHz, d_8-THF)

21.2 (br. s), 8.5 (br. s) 5.7 (br. s).

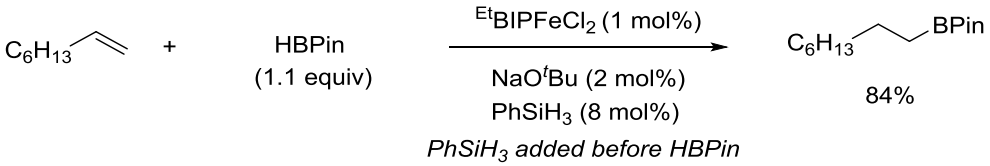
R6| Reaction of 1-octene and MD'M using mixture S3 as a catalyst



(**a**) 1-Octene (78 µL, 0.5 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (150 µL, 0.55 mmol) 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (5 µL, 25 µmol, 5 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (6.9 mg, 13 µmol, 2.5 mol%) were reacted in anhydrous d_8-tetrahydrofuran (0.5 mL). After 20 hours, no hydrosilylation products were observed by ^{1}H NMR spectroscopy.

(**b**) 1-Octene (78 µL, 0.5 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (150 µL, 0.55 mmol) were added to mixture **S3** (500 µL, 2.5 mol%). The mixture was stirred for 20 hours at room temperature, diluted with diethylether (2 mL) and sulfate buffer (1 mL). 1,3,5-Trimethoxybenzene (2 mM solution in diethylether, 2 mL, 8 µmol), as an internal standard, was added and the organic phase of the mixture sampled. The yield was determined by integration of ^{1}H NMR resonances. See below for product characterisation.

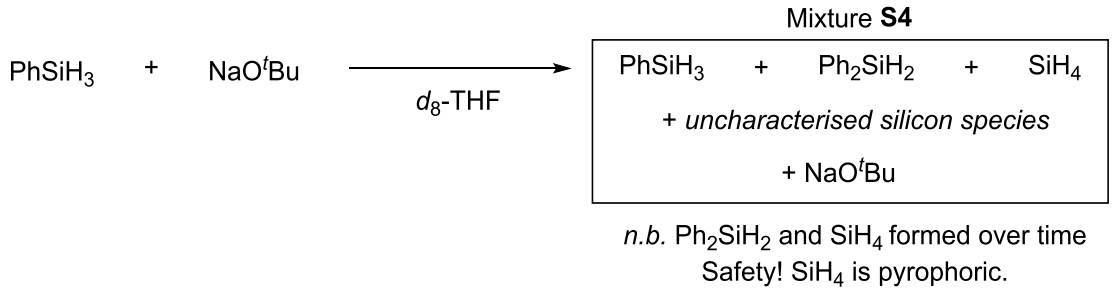
R7| pre-Catalyst activation using *trace* silane for hydroboration



Phenylsilane (1 drop, *ca.* 5 µL, 8 mol%) was added to a mixture of ^{Et}BIPFeCl$_2$ (2.8 mg, 5.0 µmol, 1.0 mol%) and sodium *tert*-butoxide (1.0 mg, 5.0 µmol, 1.0 mol%). The mixture quickly turned brown (over 5-10 seconds), 1-octene (78 µL, 0.50 mmol) and pinacolborane (80 µL, 0.55 mmol) was added. The resulting mixture was stirred at 25°C for 1 hour, diluted with diethylether (2 mL) and water (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

N.b. The reaction proceeds in the absence of phenylsilane, however the colour change may be suggestive of a catalyst activation that preceeds addition of HBPin. In this case, phenylsilane is used to generate an active species that is catalytically active for alkene hydroboration.

R8| Reaction of phenylsilane with sodium *tert*-butoxide



Phenylsilane (40 µL, 0.32 mmol) was added to a suspension of sodium *tert*-butoxide (31 mg, 0.32 mmol) in anhydrous d_8-tetrahydrofuran (0.5 mL) to give a mixture of silicon species (Mixture **S4**).

n.b Caution should we taken when handling silanes. Practitioners should be aware of potential disproportionation and formation of flammable SiH_4 gas (b.p −112°C). See: Buchwald, S. L. Silane Disproportionation Results in Spontaneous Ignition. *Chemical & Engineering News* **71**, 2 (1993).

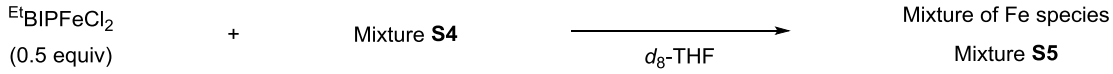
^{29}Si NMR (100 MHz, d_8-THF, after 13 minutes)

−33.6, −44.7, −60.8, −77.0, −86.3, −96.5.

^{29}Si NMR (100 MHz, d_8-THF, after 36 minutes)

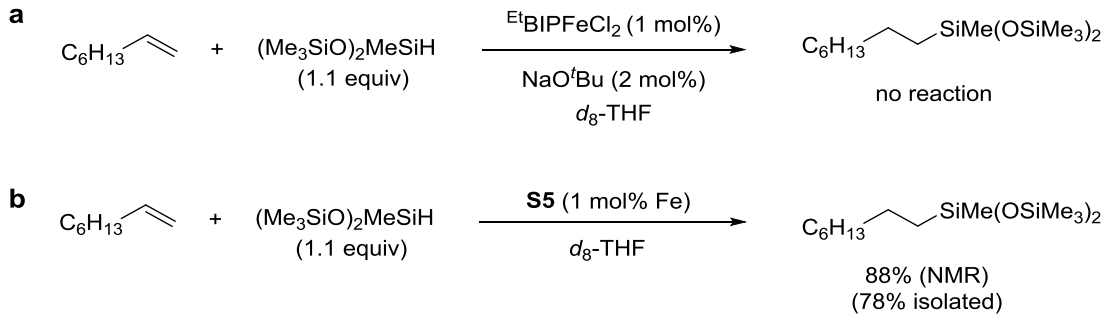
−33.9, −60.8, −67.2, −96.7, −109.5.

R9| Reaction of mixture S4 with ^{Et}BIPFeCl$_2$



Mixture **S4** (55 µL, 0.036 mmol wrt. NaO^{t}Bu) was added to a suspension of ^{Et}BIPFeCl$_2$ (10 mg, 0.018 mmol) in anhydrous d_8-tetrahydrofuran (0.6 mL). The blue suspension quickly turned into a dark brown solution (mixture **S5**) which contained multiple iron species as indicated by the appearance of several new ^{1}H NMR resonances.

R10| Reaction of 1-octene and MD'M using mixture S5 (1 mol%) as a catalyst



(**a**) 1-Octene (78 µL, 0.5 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (150 µL, 0.55 mmol) sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL). After 20 hours, no hydrosilylation products were observed by ^{1}H NMR spectroscopy.

(**b**) 1-Octene (78 µL, 0.5 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (150 µL, 0.55 mmol) were added to mixture **S5** (180 µL, 5.0 µmol [Fe], 1.0 mol%). The mixture was stirred for 2 hours at room temperature, diluted with diethylether (2 mL) and sulfate buffer (1 mL). 1,3,5-Trimethoxybenzene (2 mM solution in diethylether, 2 mL, 8 µmol), as an internal standard, was added and the organic phase of the mixture sampled. The yield was determined by integration of ^{1}H NMR resonances, and the crude product mixture purified by flash column chromatography (60 g SiO_2, 40 mm Ø, petroleum ether/diethylether 99:1) to give 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane (131 mg, 0.39 mmol, 78%) as a colourless oil.

^{1}H NMR: ($CDCl_3$, 500 MHz)

1.44-1.12 (m, 12H), 0.89 (t, J = 7.1 Hz, 3H), 0.50-0.42 (m, 2H), 0.10 (s, 18H), 0.01 (s, 3H).

^{13}C NMR: ($CDCl_3$, 125 MHz)

33.3, 31.9, 29.3, 29.2, 23.0, 22.7, 17.6, 14.1, 1.9, −0.3.

^{29}Si NMR: ($CDCl_3$, 99 MHz)

6.8, −21.3.

Data for all species were consistent with those reported previously.[135]

R11| Assessing the ability of SiH_4 to activate the iron pre-catalyst ($^{Et}BIPFeCl_2$)

a 4 $HSi(OEt)_3$ $\xrightarrow[THF]{NaO^tBu\ (0.6\ mol\%)}$ 3 $Si(OEt)_4$ + SiH_4

b C_6H_{13} + $PhSiH_3$ $\xrightarrow[SiH_4\ (bubbled\ from\ \mathbf{a})\ d_8\text{-THF}]{^{Et}BIPFeCl_2\ (1\ mol\%)}$ *no reaction*

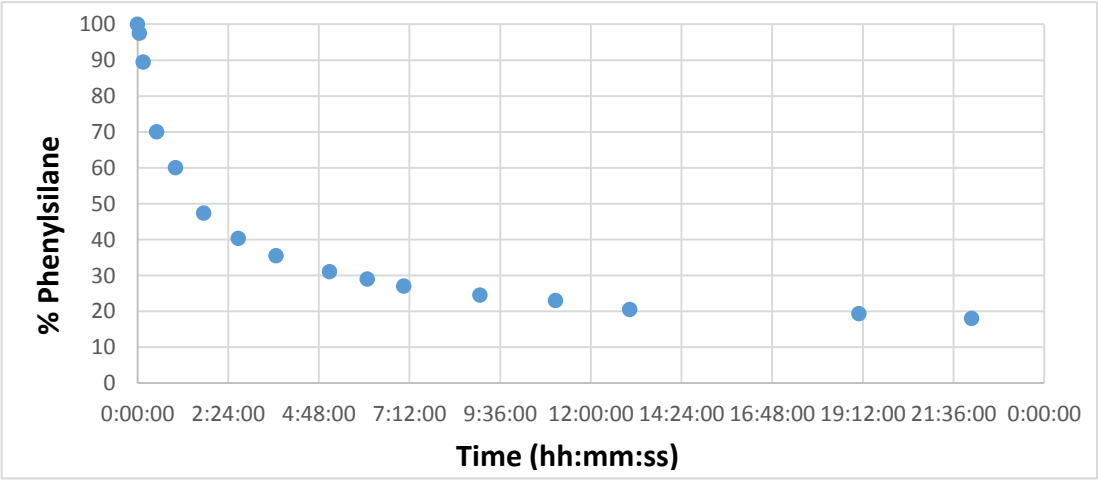
(**a**) Triethoxysilane (5.1 mL , 34.8 mmol) was added dropwise (over 15 minutes) to a stirred mixture of sodium *tert*-butoxide (20 mg, 0.2 mmol, 0.6 mol%) in anhydrous tetrahydrofuran (4 mL) to liberate SiH_4 gas from solution.

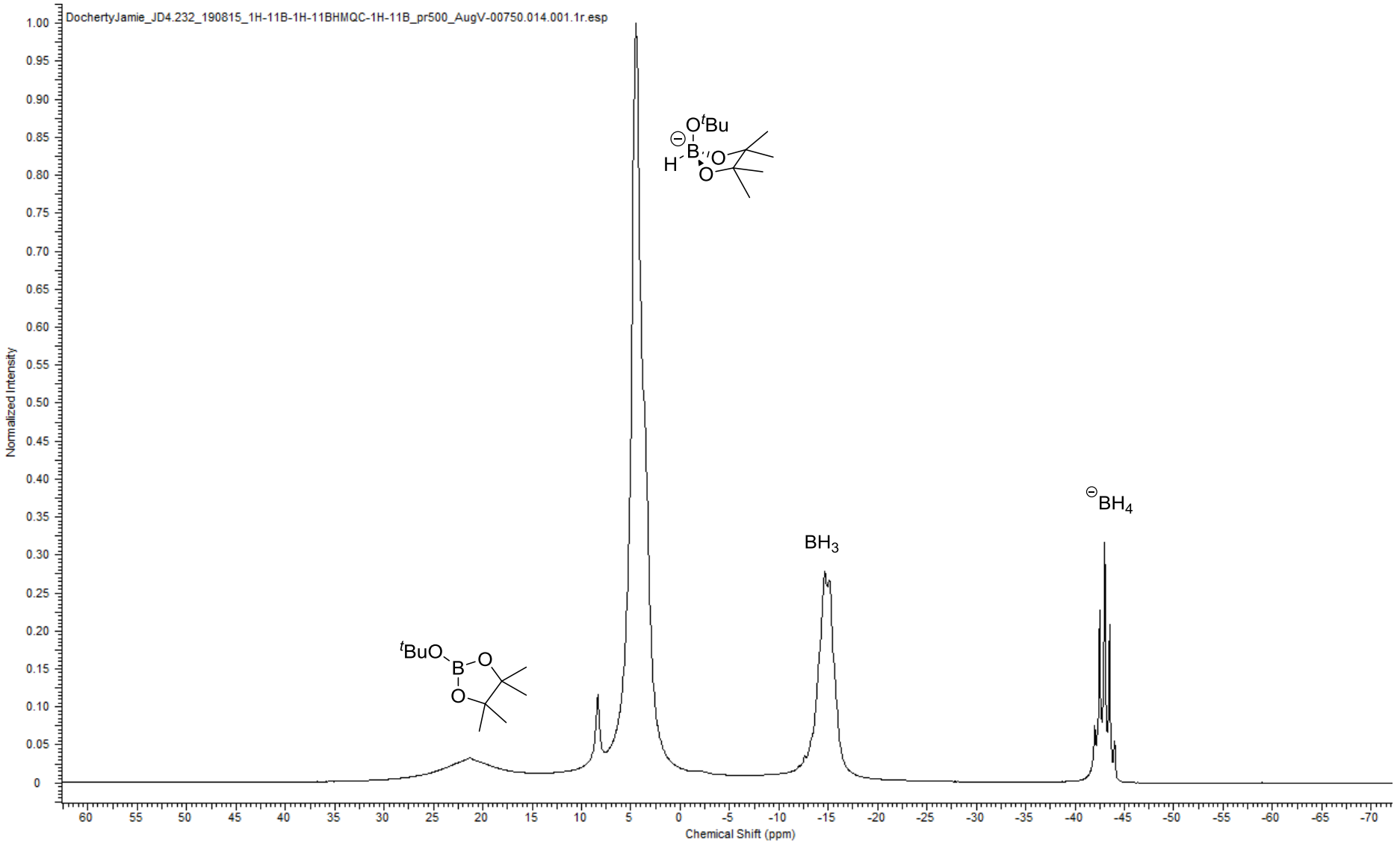
(**b**) 1-Octene (78 µL, 0.5 mmol), phenylsilane (67 µL, 0.55 mmol) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [$^{Et}BIPFeCl_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were stirred in anhydrous d_8-tetrahydrofuran (1 mL). The SiH_4 generated in reaction (**a**) was transferred and passed through the reaction solution by cannula. No colour change was observed nor any catalyst activity, even though SiH_4 was observed in the reaction mixture (by ^1H & ^{29}Si NMR spectroscopy *vide infra*).

R12| Rate of disproportionation of phenylsilane

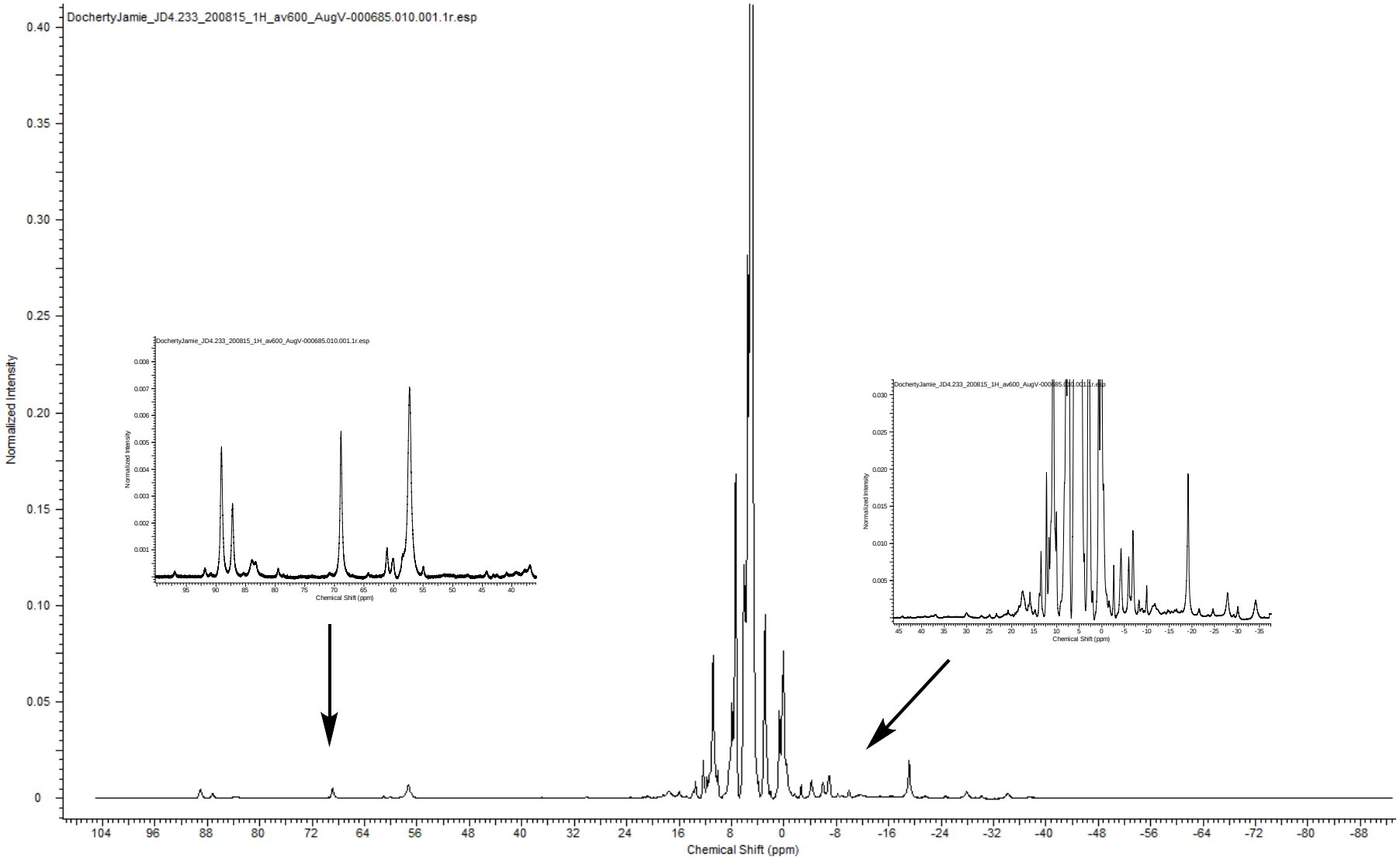
$PhSiH_3$ $\xrightarrow[d_8\text{-THF}]{NaO^tBu\ (2\ mol\%)}$ Ph_2SiH_2 + SiH_4

Phenylsilane (51 µL, 0.42 mmol) was added to a J-Young's NMR tube containing sodium *tert*-butoxide (0.8 mg, 8.4 µmol) and anhydrous d_8-tetrahydrofuran (0.5 mL). The disapperance of phenylsilane was monitored by ^1H NMR spectroscopy, following $PhSi\mathbf{H}_3$ (δ 4.17 ppm, s, 3H) and overall aromatic integration (δ 7.73-7.14 ppm, m, 5H). $PhSiH_3$ $t_{½}$ = 1 hour 35 minutes (0.84 M in d_8-THF, 27°C, 2 mol% NaO^tBu)

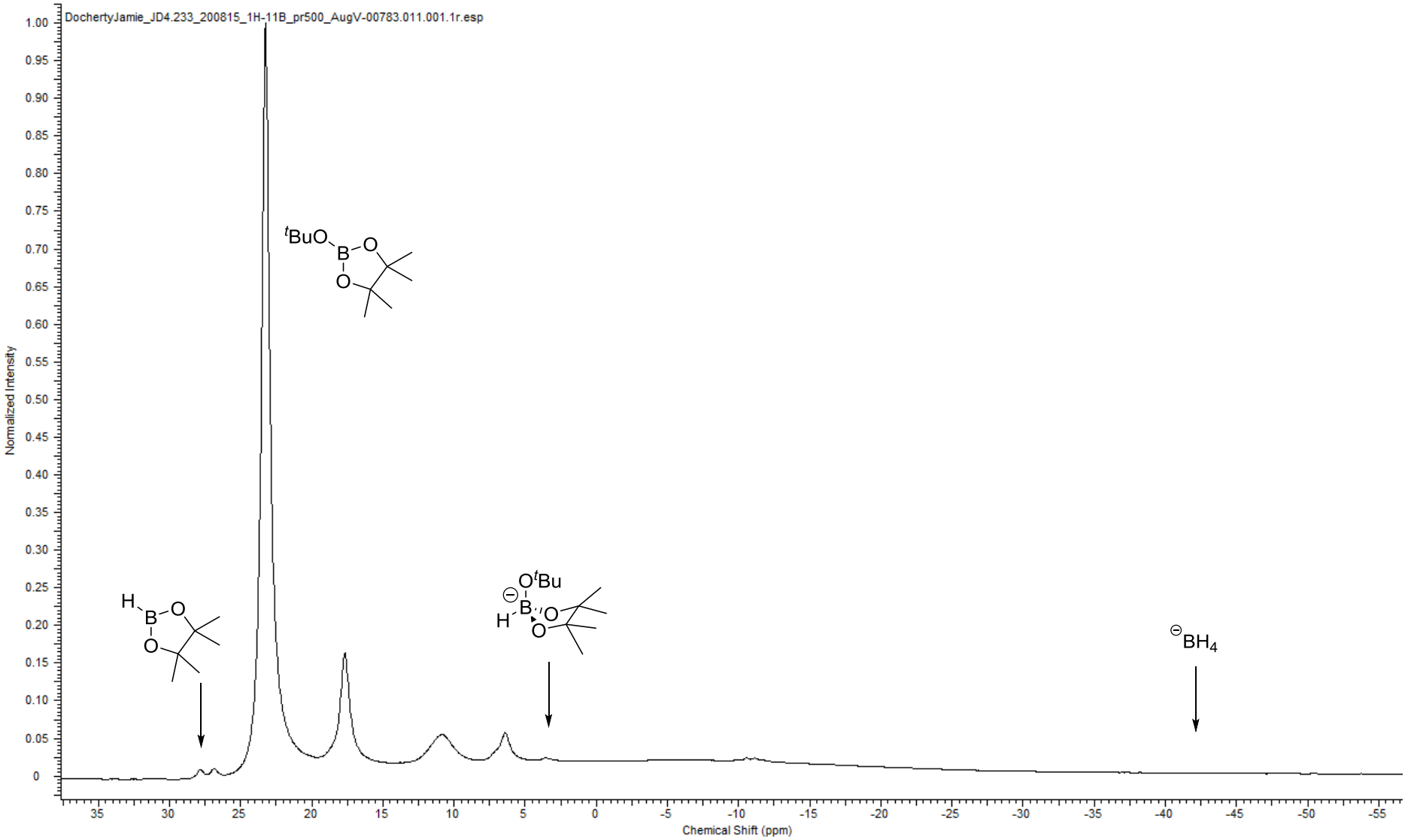




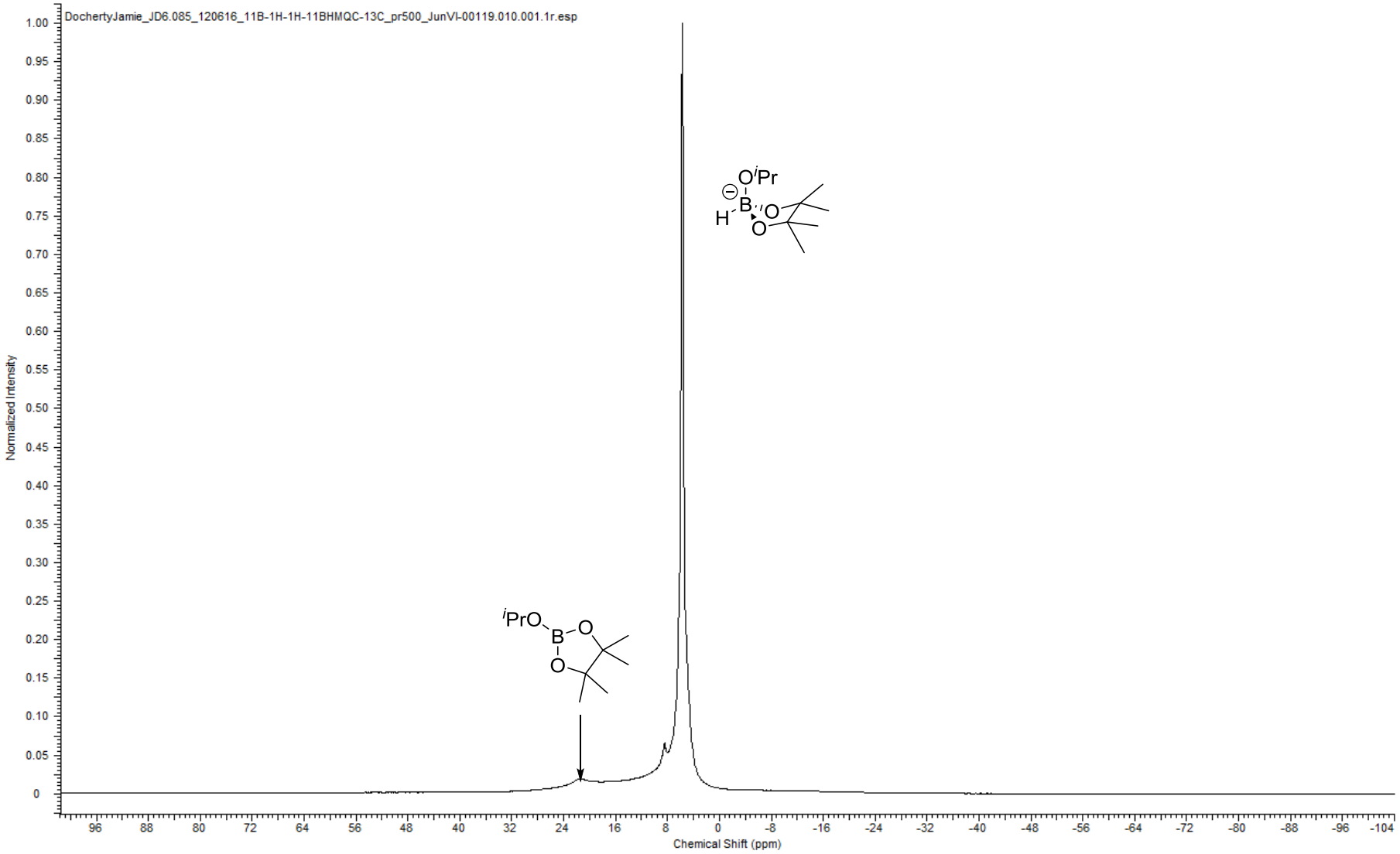
^{11}B NMR (160 MHz, d_8-THF) of pinacolborane + sodium *tert*-butoxide (1:1).



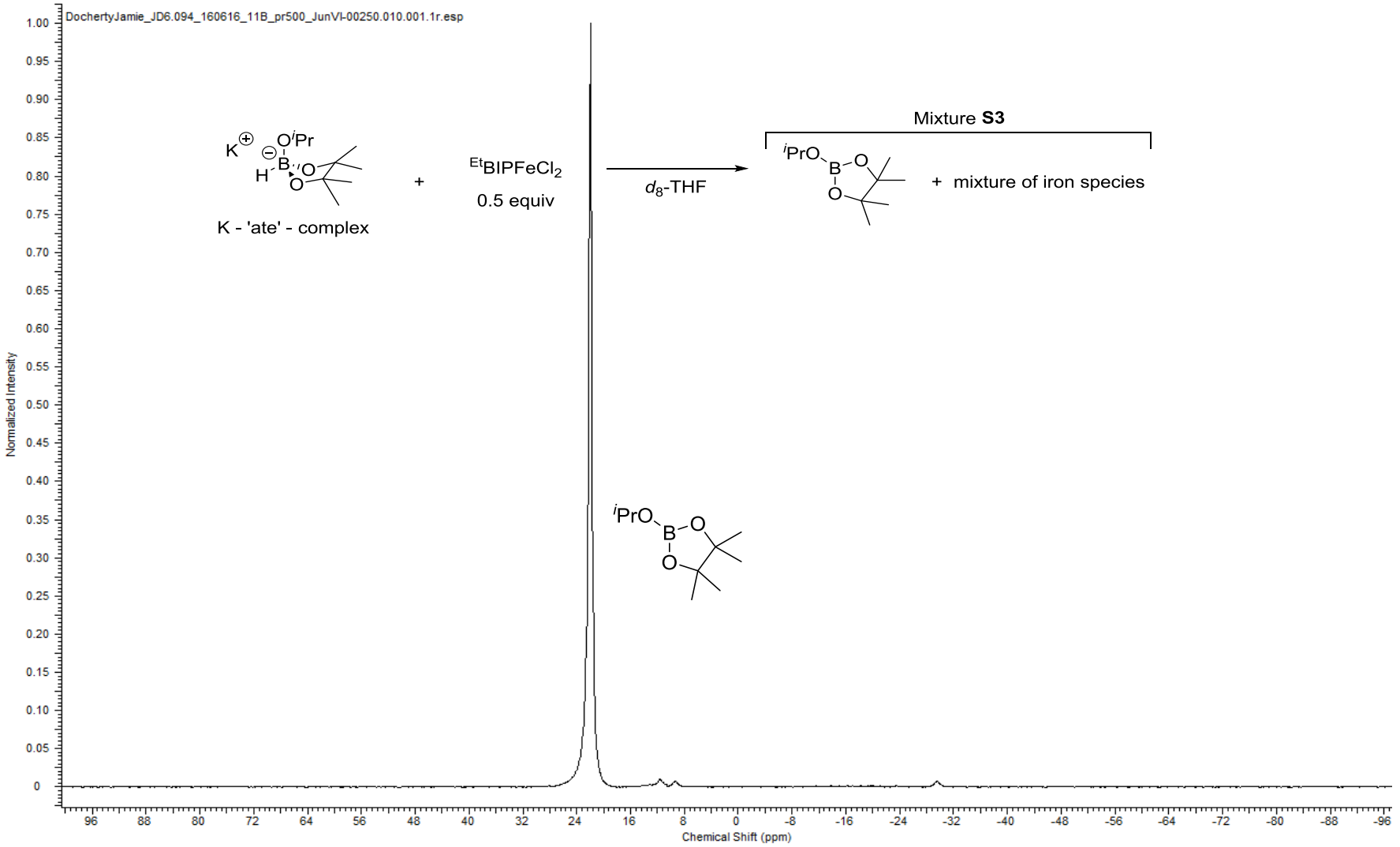
^{1}H NMR (600 MHz, d_8-THF) of **S1** + ^{Et}BIPFeCl$_2$ (0.5 equiv).



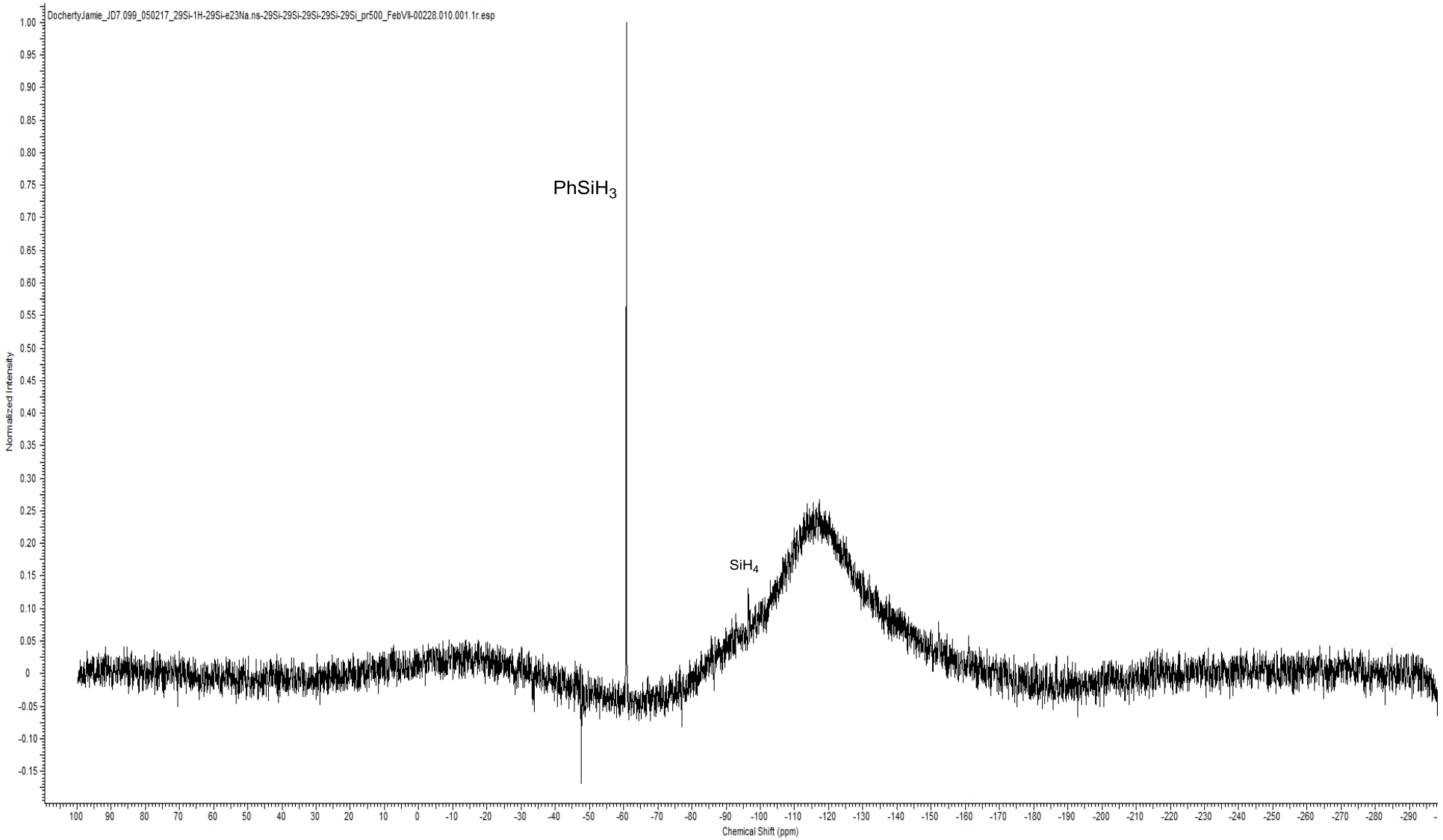
^{11}B NMR (160 MHz, d_8-THF) of **S1** + ^{Et}BIPFeCl$_2$ (0.5 equiv).



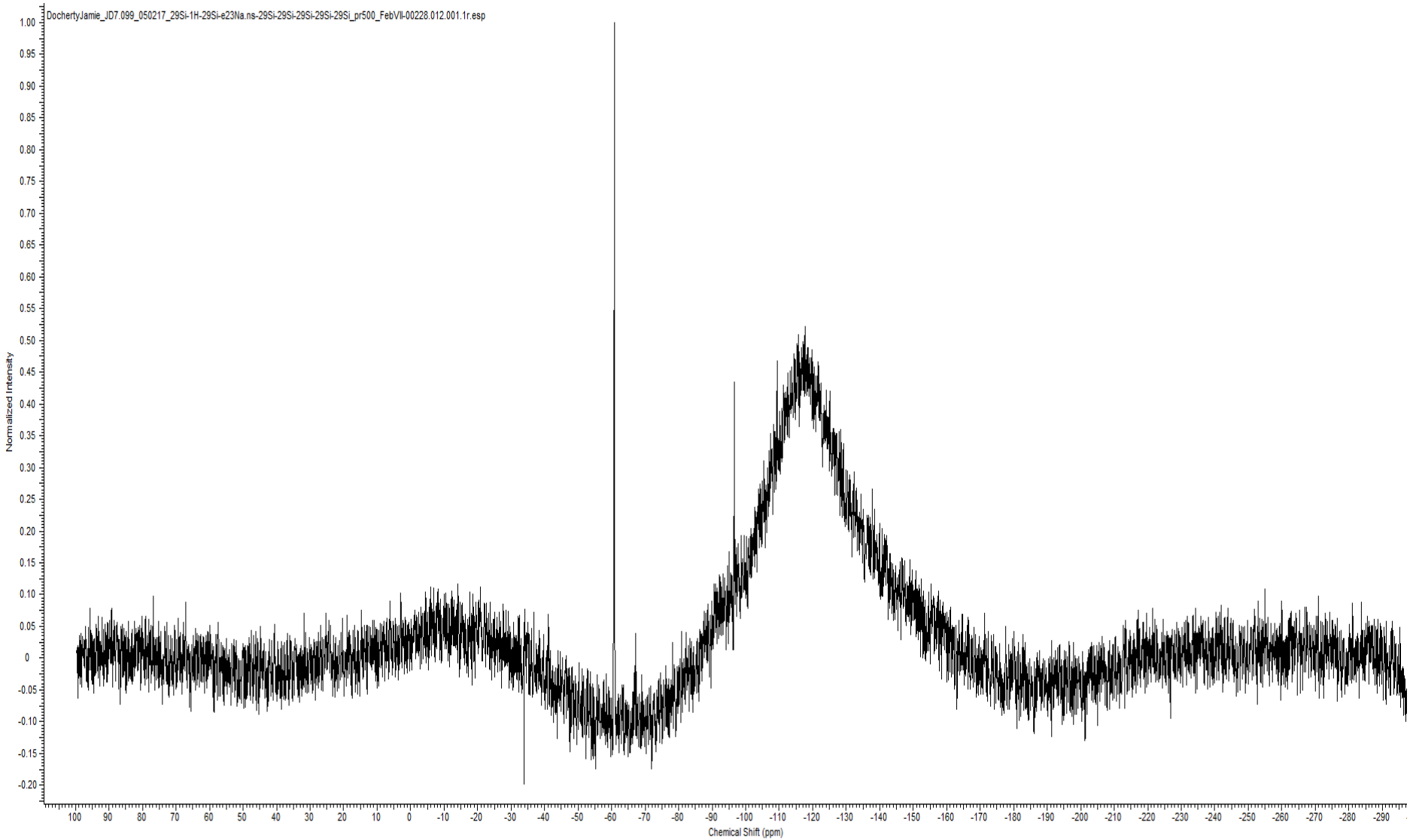
^{11}B NMR (160 MHz, d_8-THF) of 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane + potassium hydride (1:1).



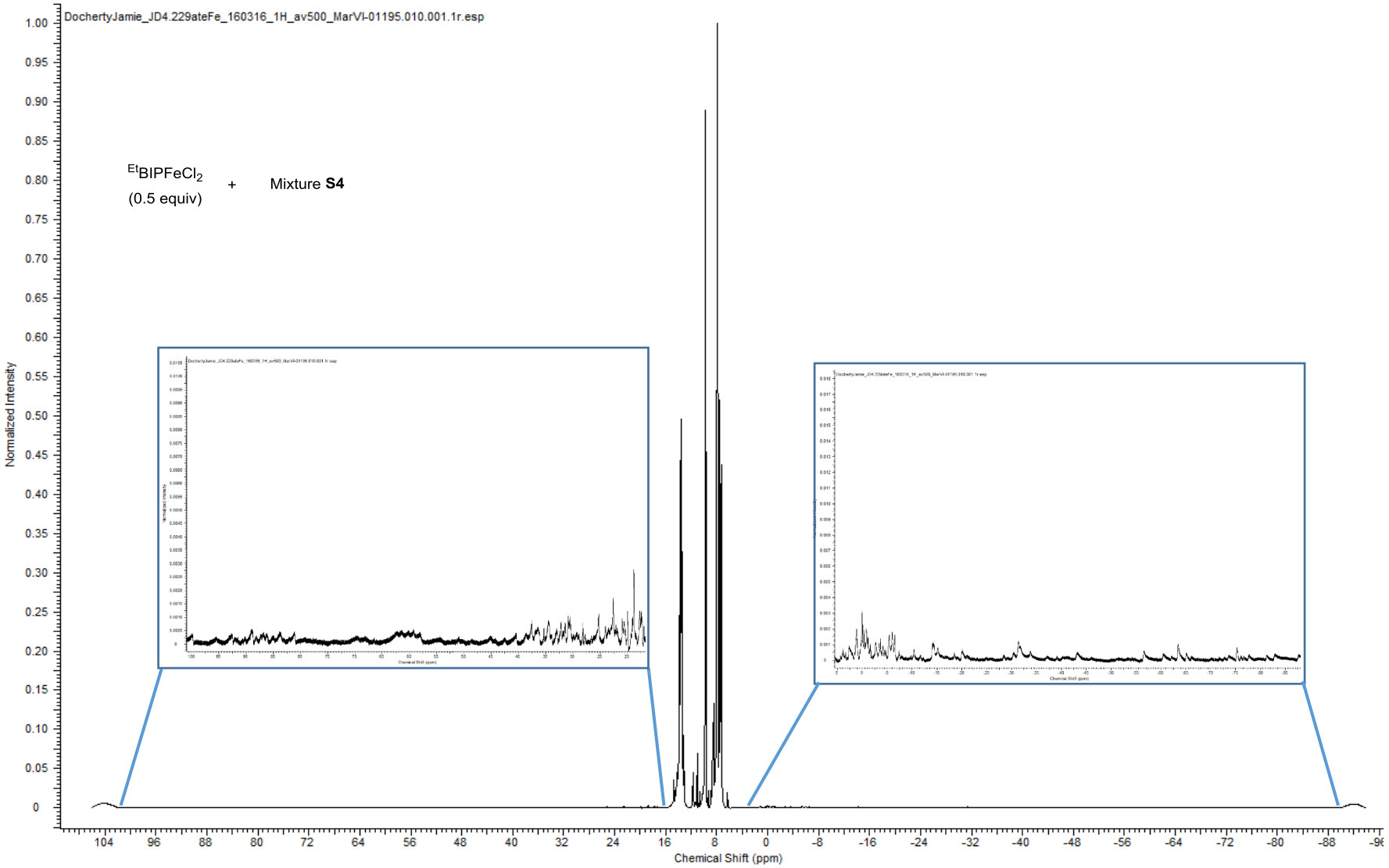
^{11}B NMR (160 MHz, d_8-THF) of 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane.



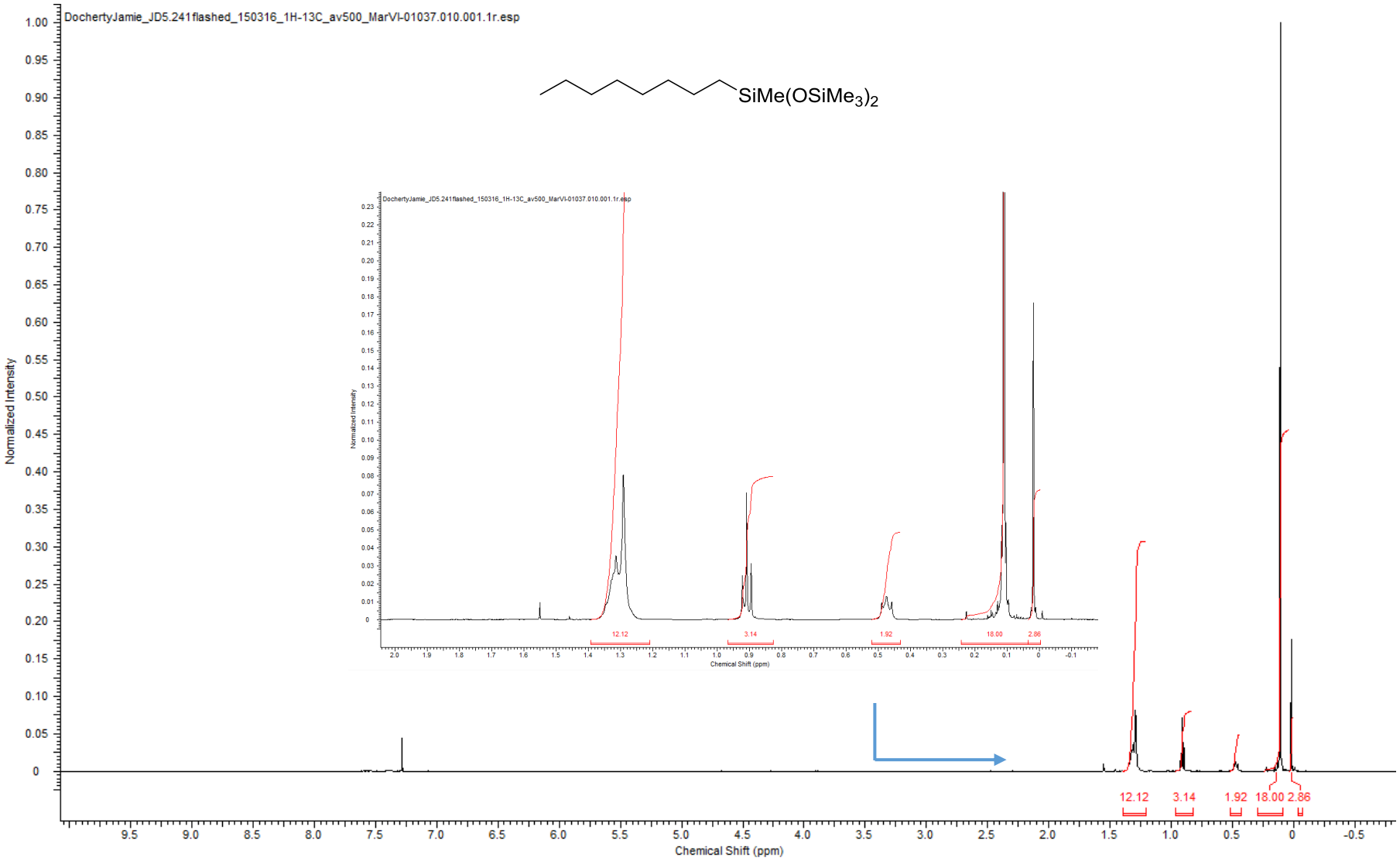
^{29}Si NMR (99 MHz, d_8-THF, after 13 minutes) of phenylsilane + sodium *tert*-butoxide (1:1) **S4**.



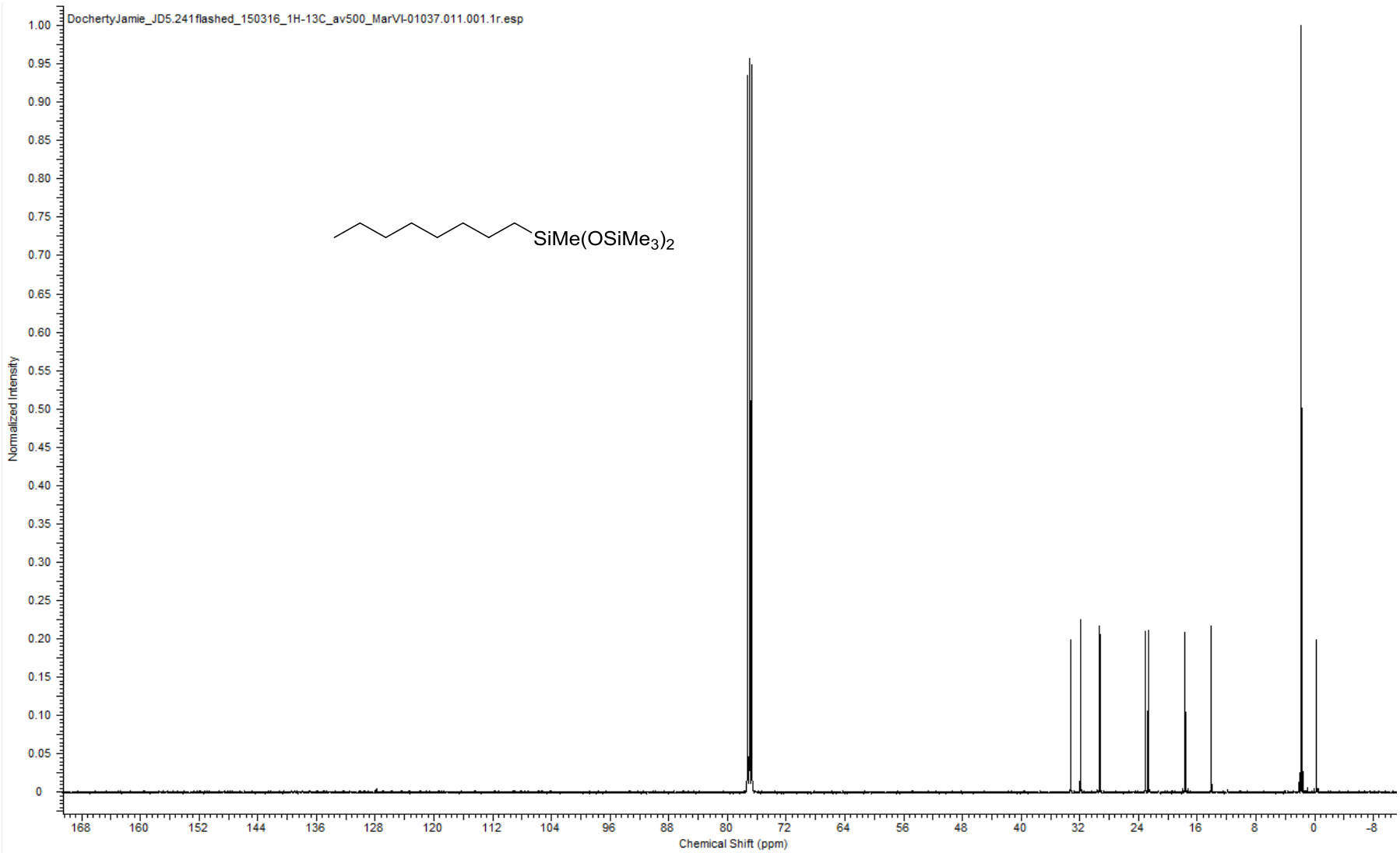
^{29}Si NMR (99 MHz, d_8-THF, after 36 minutes) of phenylsilane + sodium *tert*-butoxide (1:1) **S4**.



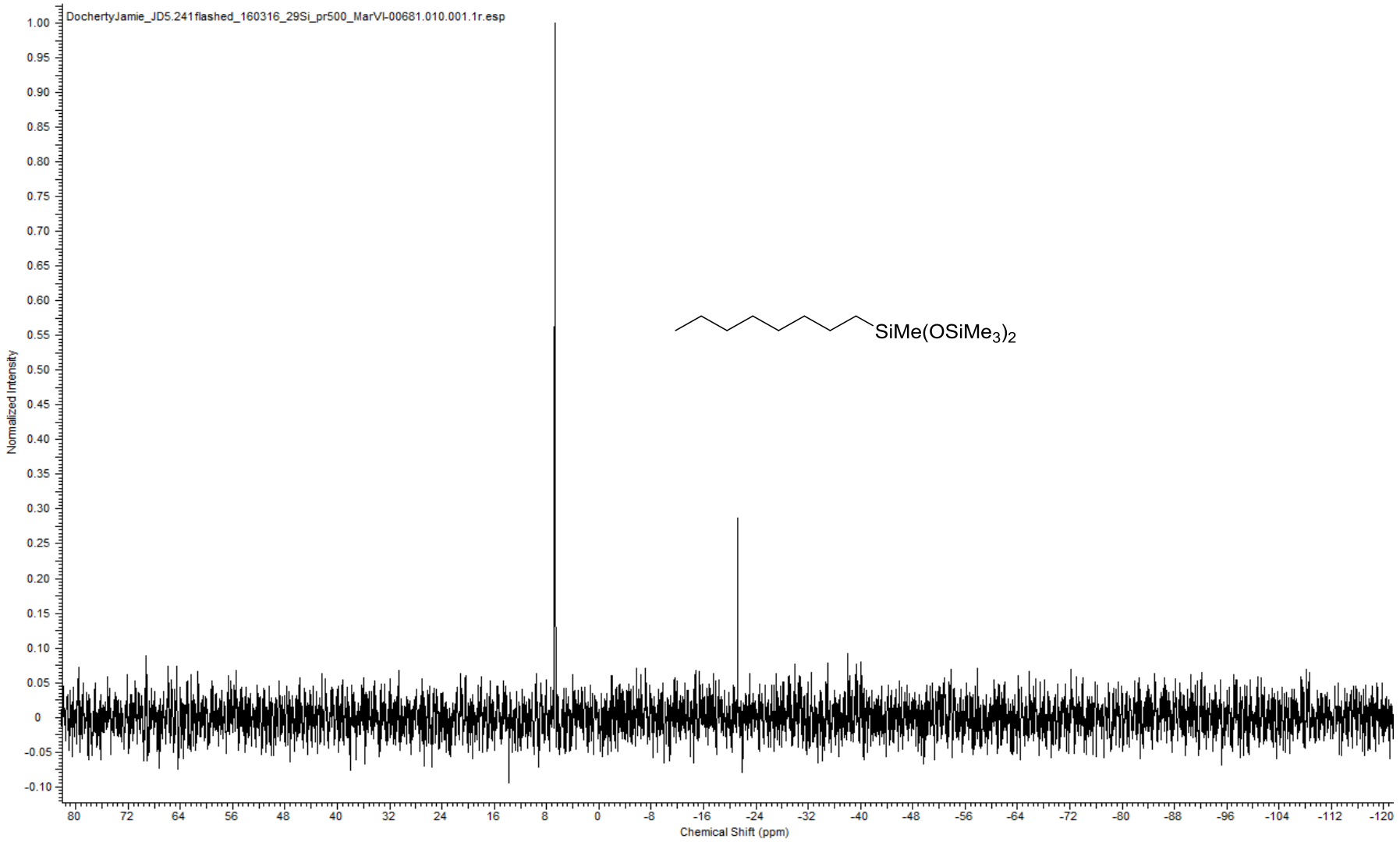
^{1}H NMR (500 MHz, d_8-THF) of **S4** + ^{Et}BIPFeCl$_2$ (0.5 equiv).



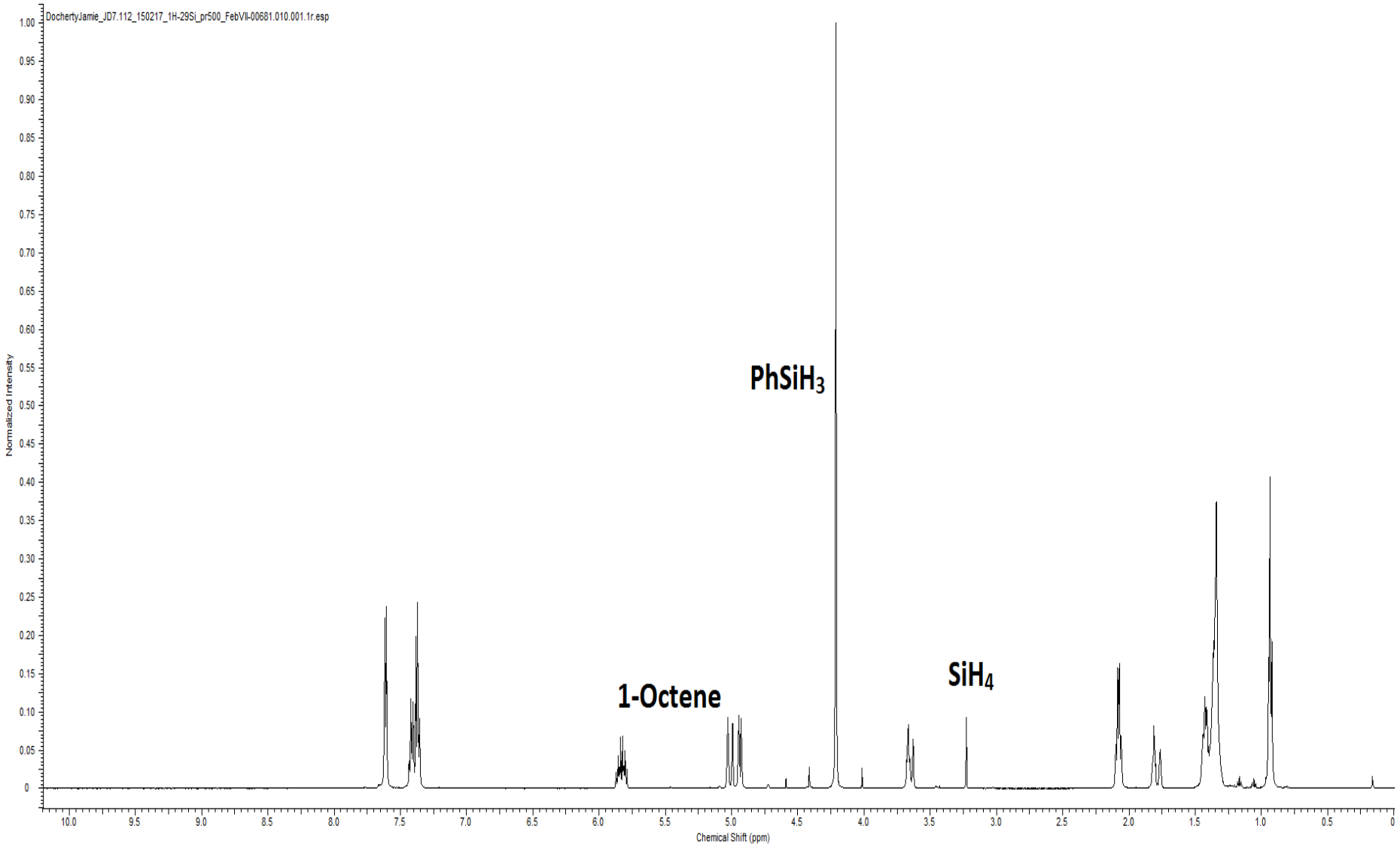
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane.



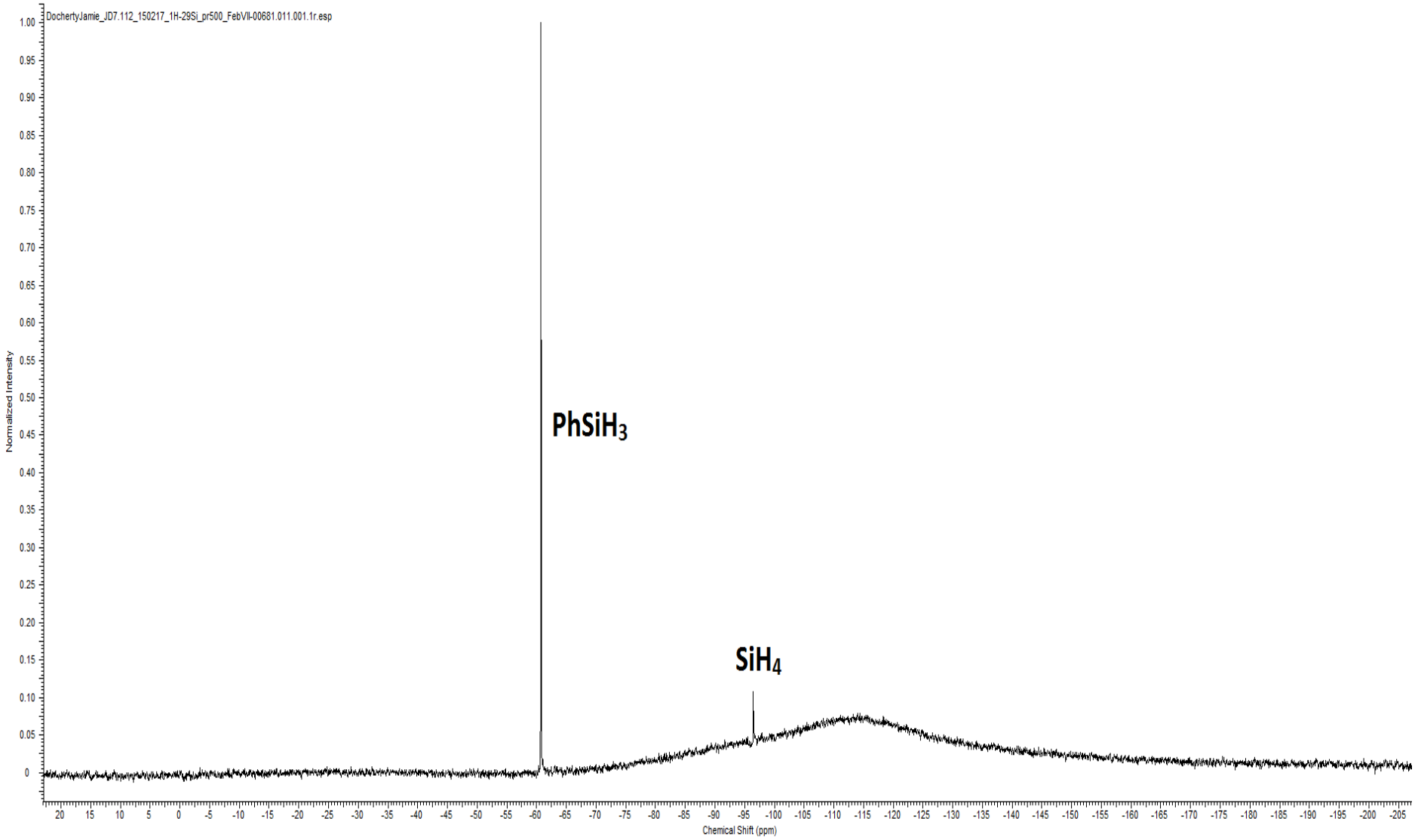
^{13}C NMR (125 MHz, $CDCl_3$) of 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane.



^{29}Si NMR (99 MHz, $CDCl_3$) of 1,1,1,3,5,5,5-heptamethyl-3-octyltrisiloxane.



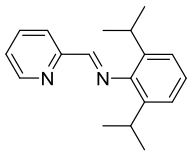
^{1}H NMR (500 MHz, d_8-THF) of reaction R11 (**b**) – attempted SiH_4 pre-catalyst activation.



^{29}Si NMR (99 MHz, d_8-THF) of reaction R11 (**b**) – attempted SiH_4 pre-catalyst activation.

5.3 Ligand and Substrate Synthesis

2,6-Di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline



Di*iso*propylaniline (0.60 mL, 3.2 mmol) was added dropwise (over ca. 30 seconds) to a stirred solution of 2-pyridinecarboxaldehyde (0.30 mL, 3.2 mmol) and *p*-toluenesulfonic acid monohydrate (94 mg, 0.5 mmol) in anhydrous toluene (40 mL). The mixture was heated at reflux under Dean-Stark conditions for 23 hours. After cooling to room temperature, the solvent was removed *in vacuo* and the brown residue purified by column chromatography (120 g SiO_2 , 30 mm Ø, pet ether/diethylether 20:1) to give a yellow amorphous solid which was recrystallised from petroleum ether (10 mL) to give 2,6-di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline (2 crops, 751 mg, 2.8 mmol, 88%) as yellow cuboidal crystals.

TLC: R_f (SiO_2) = 0.53 (petroleum ether/diethylether 1:1)

m.p 66-68°C (petroleum ether)

^{1}H NMR: (500 MHz, $CDCl_3$)

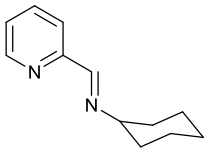
8.74 (dq, *J* = 4.9, 1.0 Hz, 1H), 8.32 (s, 1H), 8.28 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89-7.74 (m, 1H), 7.43 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.20-7.12 (m, 3H), 2.98 (sept, *J* = 6.9 Hz, 2H), 1.19 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR: (125 MHz, $CDCl_3$)

163.0, 154.4, 149.7, 148.4, 137.3, 136.8, 125.3, 124.5, 123.1, 121.4, 28.0, 23.5.

The spectroscopic data were consistent with those reported.[85]

(*E*)-*N*-(Pyridin-2-ylmethylene)cyclohexylamine



Cyclohexylamine (1.14 mL, 10.0 mmol) was added dropwise to a stirred suspension of 2-pyridine carboxaldehyde (0.95 mL, 10.0 mmol) and potassium carbonate (2.40 g, 17.4 mmol) in diethylether

(30 mL). The resulting mixture was stired at room temperature for 19 hours. The reaction mixture was directly filtered through a silica plug (5 g SiO_2, 10 mm Ø, diethylether) and the solvent removed *in vacuo*. The crude product was purified by vacuum distillation (90 °C, 0.9 mbar) to give (*E*)-*N*-(pyridin-2-ylmethylene)cyclohexylamine (1.82 g, 9.80 mmol, 97%) as a yellow oil.

^{1}H NMR: (600 MHz, $CDCl_3$)

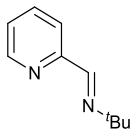
8.66 (app. d, *J* = 4.3 Hz, 1H), 8.42 (s, 1H), 8.01 (app. d, *J* = 7.9 Hz, 1H), 7.75 (app. td, J = 7.7, 1.4 Hz, 1H), 3.37-3.28 (m, 1H), 1.92-1.75 (m, 4H), 1.75-1.67 (m, 1H), 1.68-1.57 (m, 2H), 1.41 (qt, *J* = 12.8, 3.2 Hz, 2H), 1.30 (tt, *J* = 12.3 Hz, 3.2 Hz, 1H).

^{13}C NMR: (150 MHz, $CDCl_3$)

159.5, 155.0, 149.4, 136.5, 124.5, 121.4, 69.6, 34.2, 25.6, 24.7.

The spectroscopic data were consistent with those reported.[136]

(*E*)-*N*-(Pyridin-2-ylmethylene)*tert*-butylamine



tert-Butylamine (1.05 mL, 10.0 mmol) was added dropwise to a stirred suspension of 2-pyridine carboxaldehyde (0.95 mL, 10.0 mmol) and potassium carbonate (2.24 g, 16.2 mmol) in diethylether (20 mL). The resulting mixture was stirred at room temperature for 21 hours. The reaction mixture was directly filtered through a silica plug (5 g SiO_2, 10 mm Ø, diethylether) and the solvent removed *in vacuo*. The crude product was purified by vacuum distillation (65 °C, 0.9 mbar) to give (*E*)-*N*-(pyridin-2-ylmethylene)*tert*-butylamine (1.59 g, 9.80 mmol, 98%) as a yellow oil.

^{1}H NMR: (600 MHz, $CDCl_3$)

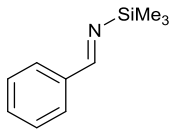
8.64 (dq, *J* = 4.83, 0.95 Hz, 1H), 8.38 (s, 1H), 8.04 (dt, *J* = 7.86, 0.85 Hz, 1H), 7.76-7.71 (m, 1H), 7.30 (ddd, *J* = 7.48, 4.83, 1.23 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR: (150 MHz, $CDCl_3$)

156.4, 155.6, 149.3, 136.5, 124.4, 120.1, 57.8, 29.6.

The spectroscopic data were consistent with those reported.[137]

(*E*)-*N*-Benzylidene-1,1,1-trimethylsilanamine



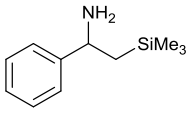
n-Butyllithium solution (1.6 M in hexane, 21.0 mL, 33.6 mmol) was added dropwise (over *ca.* 5 minutes) to *neat* hexamethyldisilazane (4.80 g, 3.0 mmol) at 0°C. The resulting solution was warmed to room temperature and stirred for 15 minutes before dropwise addition (over ca. 5 minutes, exothermic) of benzaldehyde (3.05 mL, 30.0 mmol) at 0°C. The reaction mixture was stirred at room temperature for 30 minutes, the volatiles removed *in vacuo* and the crude product distilled (60°C, 0.9 mbar) to give (*E*)-*N*-benzylidene-1,1,1-trimethylsilanamine (3.54 g, 20.0 mmol, 60%) as a yellow oil. All manipulations were conducted using inert Schlenk technique, and the product used immediately.

^{1}H NMR: (400 MHz, $CDCl_3$)

9.04 (s, 1H), 7.86-7.80 (m, 2H), 7.52-7.45 (m, 3H), 0.29 (s, 9H).

The spectroscopic data were consistent with those reported.[138]

(±)-1-Phenyl-2-(trimethylsilyl)ethanamine



(Trimethylsilyl)methyllithium solution (1 M in pentane, 7.2 mL, 7.2 mmol) was added dropwise (over ca. 10 minutes) to a stirred solution of (*E*)-*N*-benzylidene-1,1,1-trimethylsilanamine (1.06 g, 6.0 mmol) in tetrahydrofuran (10 mL) at 0°C. The reaction mixture was stirred at 0°C for 2 hours and quenched with aqueous HCl solution (1 M, 20 mL). The aqueous phase was washed with diethylether (3 x 20 mL) and the organic phase washed with aqueous HCl solution (1M, 2 x 10 mL). Aqueous NaOH solution (6M, 40 mL) was added to the aqueous extracts, and this was extracted with diethylether (3 x 20 mL) and the combined organic extracts washed with brine (20 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to give (±)-1-phenyl-2-(trimethylsilyl)ethanamine (920 mg, 4.76 mmol, 79%) as a yellow oil. The product was used without further purification.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.33-7.29 (m, 4H), 7.25-7.20 (m, 1H), 4.06 (t, *J* = 7.6 Hz, 1H), 1.14-1.07 (m, 2H), −0.10 (s, 9H).

^{13}C NMR: (125 MHz, $CDCl_3$)

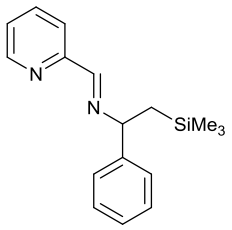
148.7, 128.5, 126.8, 126.0, 53.8, 28.7, −1.1.

^{29}Si NMR: (100 MHz, $CDCl_3$)

−0.3.

The spectroscopic data were consistent with those reported.[97]

(±)-1-Phenyl-*N*-[(*E*)-pyridin-2-ylmethylene]-2-(trimethylsilyl)ethanamine



1-Phenyl-2-(trimethylsilyl)ethanamine (608 mg, 3.14 mmol) was added dropwise to a stirred suspension of 2-pyridine carboxaldehyde (0.30 mL, 3.10 mmol) and potassium carbonate (693 mg, 5.0 mmol) in diethylether (10 mL). The resulting mixture was stirred at room temperature for 24 hours. The reaction mixture was directly filtered through a silica plug (5 g SiO_2, 10 mm Ø, diethylether) and the solvent removed *in vacuo*. The crude product was purified by vacuum distillation (170 °C, 0.9 mbar) to give (±)-1-phenyl-*N*-((*E*)-pyridin-2-ylmethylene)-2-(trimethylsilyl)ethanamine (853 mg, 3.02 mmol, 97%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

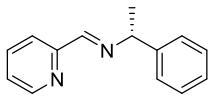
8.63 (dq, *J* = 4.9, 1.0 Hz, 1H), 8.41 (s, 1H), 8.08 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.75-7.70 (m, 1H), 7.44-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.29 (ddd, *J* = 7.5, 4.9, 1.3 Hz, 1H), 7.24 (tt, *J* = 7.3, 1.3 Hz, 1H), 4.64 (t, *J* = 7.4 Hz, 1H), 1.46-1.34 (m, 2H), −0.08 (s, 9H).

^{13}C NMR: (125 MHz, $CDCl_3$)

159.6, 155.0, 149.3, 145.1, 136.4, 128.5, 127.1, 127.0, 124.5, 121.3, 72.2, 27.5, −0.9.

The spectroscopic data were consistent with those reported.[139]

(*R*)-1-Phenyl-*N*-[(pyridin-2-yl)methylene]ethanamine



(*R*)-Methylbenzylamine (0.51 mL, 4.0 mmol) was added dropwise to a stirred suspension of 2-pyridine carboxaldehyde (0.38 mL, 4.0 mmol) and potassium carbonate (1.0 g, 7.2 mmol) in diethylether (20 mL). The resulting yellow mixture was stirred at room temperature for 26 hours. The reaction mixture was directly filtered through a silica plug (5 g SiO_2, 10 mm Ø, diethylether) and the solvent removed *in vacuo*. The resulting orange oil was purified by vacuum distillation (135 °C, 0.3 mbar) to give (*R*)-1-phenyl-*N*-[(pyridin-2-yl)methylene]ethanamine (603 mg, 2.9 mmol, 73%) as a pale yellow oil.

^{1}H NMR: (600 MHz, $CDCl_3$)

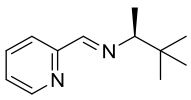
8.65 (dq, *J* = 4.8, 1.0 Hz, 1H), 8.48 (s, 1H), 8.11 (dt, J = 8.0, 1.0 Hz, 1H), 7.76-7.73 (m, 1H), 7.47-7.43 (m, 2H), 7.38-7.33 (m, 2H), 7.31 (ddd, *J* = 7.5, 4.9, 1.3 Hz, 1H), 7.28-7.24 (m, 1H), 4.65 (q, *J* = 6.6 Hz, 1H), 1.63 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR: (150 MHz, $CDCl_3$)

160.5, 154.9, 149.4, 144.6, 136.5, 128.5, 127.0, 126.7, 124.7, 121.5, 69.6, 24.6.

The spectroscopic data were consistent with those reported.[139]

(*S*)-3,3-Dimethyl-*N*-(pyridin-2-ylmethylene)butan-2-amine



(*S*)-3,3-Dimethyl-2-butylamine (0.54 mL, 4.0 mmol) was added dropwise to a stirred suspension of 2-pyridine carboxaldehyde (0.38 mL, 4.0 mmol) and potassium carbonate (1.0 g, 7.2 mmol) in diethylether (20 mL). The resulting yellow mixture was stirred at room temperature for 20 hours. The reaction mixture was directly filtered through a silica plug (5 g SiO_2, 10 mm Ø, diethylether) and the solvent removed *in vacuo*. The resulting orange oil was purified by vacuum distillation (85 °C, 0.3 mbar) to give (*S*)-3,3-dimethyl-*N*-(pyridin-2-ylmethylene)butan-2-amine (649 mg, 0.7 mmol, 85%) as a pale yellow oil.

^{1}H NMR: (600 MHz, $CDCl_3$)

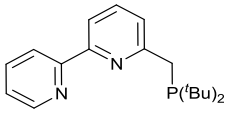
8.64 (dq, *J* = 4.8, 1.0 Hz, 1H), 8.34 (s, 1H), 8.06 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.75-7.71 (m, 1H), 7.30 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 3.08 (q, *J* = 6.6 Hz, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.94 (s, 9H).

^{13}C NMR: (150 MHz, $CDCl_3$)

159.6, 155.2, 149.3, 136.4, 124.4, 121.1, 75.2, 34.3, 26.6, 17.3.

The spectroscopic data were consistent with those reported.[71]

6-[(Di-*tert*-butylphosphino)methyl]-2,2'-bipyridine



Lithium di*iso*propylamide solution (1.8 M in tetrahydrofuran/heptane/ethylbenzene, 1.0 mL, 1.76 mmol) was added dropwise (over 15 minutes) to a stirred solution of 6-methyl-2,2′-dipyridine (250 mg, 1.47 mmol) in anhydrous diethylether (10 mL) at 0°C. The mixture was stirred at 0°C for 1 hour, cooled to −78°C and a solution of di-*tert*-butylchlorophosphine (336 µL, 1.76 mmol) in anhydrous diethylether (6 mL) was added dropwise (over 15 minutes). The mixture was stirred at −78°C for 1 hour, slowly warmed to room temperature (over *ca.* 2 hours) and stirred for 48 hours before the addition of degassed water (15 mL) at room temperature. The solution was extracted with diethylether (3 *x* 20 mL), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give an orange oil that was purified by flash column chromatography (20 g neutral Al_2O_3, 30 mm Ø, hexane/diethylether 9:1 to 2:1) to give 6-((di-*tert*-butylphosphino)methyl)-2,2'-bipyridine (112 mg, 0.36 mmol, 24%) as a colourless amorphous solid.

TLC: R_f (neutral Al_2O_3) = 0.27 (hexane/diethylether 1:1)

^{1}H NMR: (500 MHz, CD_2Cl_2)

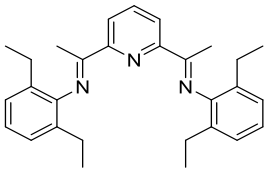
8.63 (dq, *J* = 4.7, 1.0 Hz, 1H), 8.44 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.19-8.16 (m, 1H), 7.80 (td, *J* = 7.6, 1.7 Hz, 1H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.41-7.38 (m, 1H), 7.28 (ddd, *J* = 7.4, 4.7, 1.3 Hz, 1H), 3.13 (d, $^{2}J_{PH}$ = 3.0 Hz, 2H), 1.18 (d, $^{3}J_{PH}$ = 10.7 Hz, 18H).

^{31}P NMR: (200 MHz, CD_2Cl_2)

37.1

The spectroscopic data were consistent with those reported.[140]

2,6-Bis{1-[(2,6-diethylphenyl)imino]ethyl}pyridine



2,6-Diethylaniline (3.2 mL, 19.3 mmol) was added to a stirred suspension of 2,6-diacetylpyridine (1.45 g. 8.8 mmol) and para-toluenesulfonic acid mono-hydrate (101 mg, 0.53 mmol) in toluene (40 mL). The resulting mixture was heated at reflux under Dean-Stark conditions for 20 hours. After cooling to room temperature, the solvent was removed *in vacuo* and the solid recrystallised from dichloromethane (20 mL) to give 2,6-bis[1-((2,6-diethylphenyl)imino)ethyl]pyridine (5 crops, 2.34 g, 5.51 mmol, 63%) as yellow needles.

m.p: 195-196°C (dichloromethane); Lit[12] 185−186°C (dichloromethane)

^{1}H NMR: (500 MHz, $CDCl_3$)

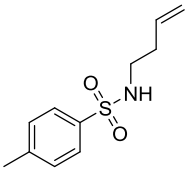
8.49 (d, *J* = 7.8 Hz, 2H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.17-7.14 (m, 4H), 7.08-7.03 (m, 2H), 2.49-2.32 (m, 8H), 2.26 (s, 6H), 1.17 (t, *J* = 7.6 Hz, 12H).

^{13}C NMR: (125 MHz, $CDCl_3$)

166.9, 155.2, 147.8, 136.9, 131.2, 126.0, 123.3, 122.2, 24.6, 16.8, 13.7.

The spectroscopic data were consistent with those reported.[81]

***N*-Tosyl-3-butenylamine**



In a sealed tube, 4-bromobut-1-ene (2.0 mL, 20 mmol) was added to a stirred suspension of tosylamine (3.10 g, 18.2 mmol) and potassium carbonate (5.50 g, 40 mmol) in acetone (20 mL). The reaction mixture was heated at 85°C for 18 hours, diluted with saturated aqueous NH_4Cl (50 mL), extracted with diethylether (3 x 60 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude reaction product was purified by flash column chromatography (250 g SiO_2, 50 mm Ø,

petroleum ether/ethyl acetate 5:1) to give *N*-tosyl-3-butenylamine (1.72 g, 7.6 mmol, 42%) as a yellow oil.

TLC: R_f (SiO_2) = 0.54 (petroleum ether/ethyl acetate 1:1)

^{1}H NMR: (500 MHz, $CDCl_3$)

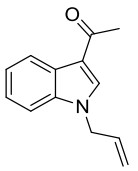
7.77-7.73 (m, 2H), 7.35-7.30 (m, 2H), 5.63 (qt, *J* = 10.3, 6.9 Hz, 1H), 5.10-5.03 (m, 2H), 4.36 (app. t, *J* = 4.7 Hz, 1H), 3.04 (q, *J* = 6.3 Hz, 2H), 2.44 (s, 3H), 2.22 (qt, *J* = 6.7, 1.3 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

143.5, 137.0 134.1, 129.7, 127.1, 118.3, 42.0, 33.6, 21.5.

The spectroscopic data were consistent with those reported.[141]

***N*-Allyl-3-acetylindole**



Allylbromide (350 µL, 4.0 mmol) was added dropwise (over *ca.* 1 minute) to a stirred mixture of 3-acetylindole (620 mg, 3.90 mmol) and sodium hydroxide (400 mg, 10.0 mmol) in dimethylsulfoxide (10 mL). The mixture was stirred for 3 hours at room temperature and water (10 mL) added. The mixture stirred for a further 18 hours, diluted with water (50 mL), extracted with ethyl acetate (4 x 30 mL), washed with brine (30 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (50 g SiO_2, 30 mm Ø, petroleum ether/ethyl acetate/triethylamine 90:9:1) to give *N*-allyl-3-acetylindole (653 mg, 3.30 mmol, 85%) as a colourless amorphous solid.

m.p 50-52°C (pet ether/EtOAc/NEt_3); Lit[15] 54−55°C

IR: *vmax* (*neat*)

1631.8 (C=O)

TLC: R_f (SiO_2) = 0.28 (petroleum ether/ethyl acetate 1:1)

^{1}H NMR: (500 MHz, $CDCl_3$)

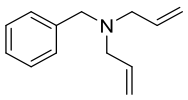
8.42-8.37 (m, 1H), 7.76 (app. s, 1H), 7.37-7.29 (m, 3H), 6.04 (app. qt, *J* = 10.3, 5.5 Hz, 1H), 5.34-5.30 (m, 1H), 5.23-5.17 (m, 1H), 4.79 (dt, *J* = 5.5, 1.5 Hz, 2H), 2.54 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

193.0, 136.9, 134.6, 132.1, 126.4, 123.4, 122.7, 122.6, 118.7, 117.4, 110.0, 49.4, 27.7.

The spectroscopic data were consistent with those reported.[142]

***N,N*-Di-2-propenylbenzylamine**



Allyl bromide (3.8 mL, 44 mmol) was added dropwise (over *ca.* 2 minutes) to a stirred solution of benzylamine (2.2 mL, 20 mmol) and potassium carbonate (12.63 g, 91 mmol) in acetonitrile (120 mL). The mixture was stirred at 50°C for 20 hours, filtered through a Celite pad and the solvent removed *in vacuo* (100 mbar, 40°C). The crude product was purified by flash column chromatography (80 g SiO_2, 40 mm Ø, pentane/diethylether 1:1) to give *N,N*-di-2-propenylbenzylamine (3.66 g, 19.5 mmol, 98%) as a yellow oil.

TLC: R_f (SiO_2) = 0.75 (diethylether) [$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.37-7.29 (m, 4H), 7.27-7.22 (m, 1H), 5.95-5.84 (m, 2H), 5.25-5.13 (m, 4H), 3.59 (s, 2H), 3.16-3.05 (m, 4H).

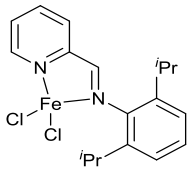
^{13}C NMR: (125 MHz, $CDCl_3$)

139.5, 135.9, 128.9, 128.2, 126.8, 117.4, 57.6, 56.4.

The spectroscopic data were consistent with those reported.[143]

5.4 Complex synthesis

2,6-Di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline iron dichloride



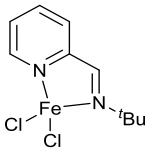
2,6-Di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline (426 mg, 1.60 mmol) in dichloromethane (5 mL) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (201 mg, 1.58 mmol) in dichloromethane (20 mL). The mixture was stirred at room temperature for 48 hours, giving a purple solution. The solution was concentrated *in vacuo* (to ca. 5 mL) and diethylether (60 mL) added. The precipitate was collected and washed with diethylether (20 mL) to give 2,6-di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline iron dichloride (460 mg, 1.17 mmol, 74%) as a purple amorphous solid.

^{1}H NMR: (600 MHz, CD_2Cl_2)

84.7 ($\Delta\nu_{1/2}$ = 474 Hz), 62.2 ($\Delta\nu_{1/2}$ = 861 Hz), 54.2 ($\Delta\nu_{1/2}$ = 277 Hz), 50.6 ($\Delta\nu_{1/2}$ = 274 Hz), 3.82 ($\Delta\nu_{1/2}$ = 235 Hz), 1.83 ($\Delta\nu_{1/2}$ = 196 Hz), −2.98 ($\Delta\nu_{1/2}$ = 282 Hz), −12.55 ($\Delta\nu_{1/2}$ = 179 Hz), −17.4 ($\Delta\nu_{1/2}$ = 196 Hz).

The spectroscopic data were consistent with those reported.[136]

(*E*)-*N*-(Pyridin-2-ylmethylene)*tert*-butylamine iron dichloride[136]



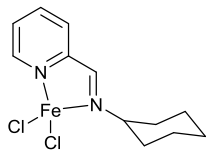
(E)-*N*-(Pyridin-2-ylmethylene)*tert*-butylamine aniline (807 mg, 4.98 mmol) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (596 mg, 4.70 mmol) in dichloromethane (40

mL). The mixture was stirred at room temperature for 26 hours, giving a red solution. The solution was concentrated *in vacuo* (to ca. 10 mL) and diethylether (100 mL) added. The precipitate was collected and washed with diethylether (50 mL) to give *(E)-N*-(pyridin-2-ylmethylene)*tert*-butylamine iron dichloride (1.21 g, 4.19 mmol, 89%) as a red amorphous solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

88.9 ($\Delta\nu_{1/2}$ = 362 Hz), 65.0 ($\Delta\nu_{1/2}$ = 772 Hz), 56.3 ($\Delta\nu_{1/2}$ = 127 Hz), 52.7 ($\Delta\nu_{1/2}$ = 123 Hz), 3.5 ($\Delta\nu_{1/2}$ = 202 Hz), −16.5 ($\Delta\nu_{1/2}$ = 435 Hz).

(*E*)-*N*-(Pyridin-2-ylmethylene)cyclohexylamine iron dichloride[136]

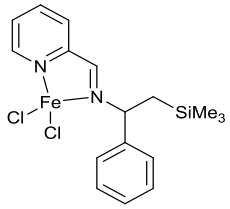


(*E*)-*N*-(Pyridin-2-ylmethylene)cyclohexylamine (850 mg, 4.50 mmol) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (545 mg, 4.30 mmol) in dichloromethane (40 mL). The mixture was stirred at room temperature for 18 hours, giving a purple solution. The solution was concentrated *in vacuo* (to ca. 10 mL) and diethylether (100 mL) added. The precipitate was collected and washed with diethylether (50 mL) to give (*E*)-*N*-(pyridin-2-ylmethylene)cyclohexylamine iron dichloride (1.25 g, 3.97 mmol, 92%) as a purple amorphous solid.

^{1}H NMR: (600 MHz, CD_2Cl_2)

87.3 ($\Delta\nu_{1/2}$ = 743 Hz), 65.1 ($\Delta\nu_{1/2}$ = 980 Hz), 54.5 ($\Delta\nu_{1/2}$ = 344 Hz), 52.3 ($\Delta\nu_{1/2}$ = 310 Hz), 3.4 ($\Delta\nu_{1/2}$ = 386 Hz), −3.4 ($\Delta\nu_{1/2}$ = 294 Hz), −4.9 ($\Delta\nu_{1/2}$ = 291 Hz), −7.7 ($\Delta\nu_{1/2}$ = 297 Hz), −9.2 ($\Delta\nu_{1/2}$ = 282 Hz), −16.2 ($\Delta\nu_{1/2}$ = 282 Hz).

1-Phenyl-*N*-[(*E*)-pyridin-2-ylmethylene]-2-(trimethylsilyl)ethanamine iron dichloride



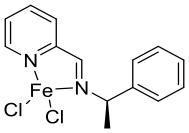
1-Phenyl-*N*-[(*E*)-pyridin-2-ylmethylene]-2-(trimethylsilyl)ethanamine (500 mg, 1.77 mmol) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (215 mg, 1.70 mmol) in dichloromethane (30 mL). The mixture was stirred at room temperature for 24 hours, giving a purple solution. The solution was concentrated *in vacuo* (to ca. 10 mL), diethylether (60 mL) added, the precipitate collected and washed with diethylether (25 mL) to give 1-phenyl-*N*-((*E*)-pyridin-2-ylmethylene)-2-(trimethylsilyl)ethanamine iron dichloride (613 mg, 1.50 mmol, 88%) as a purple amorphous solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

81.9 ($\Delta\nu_{1/2}$ = 826 Hz), 72.9 ($\Delta\nu_{1/2}$ = 620 Hz), 65.3 ($\Delta\nu_{1/2}$ = 934 Hz), 53.6 ($\Delta\nu_{1/2}$ = 170 Hz), 51.7 ($\Delta\nu_{1/2}$ = 144 Hz), 4.7 ($\Delta\nu_{1/2}$ = 115 Hz), 2.0 ($\Delta\nu_{1/2}$ = 7 Hz), 1.7 ($\Delta\nu_{1/2}$ = 5 Hz), −4.5 ($\Delta\nu_{1/2}$ = 130 Hz), −6.0 ($\Delta\nu_{1/2}$ = 295 Hz), −16.6 ($\Delta\nu_{1/2}$ = 185 Hz), −27-(−32) (overlapping resonances).

The spectroscopic data were consistent with those reported.[97]

(*R*)-1-Phenyl-*N*-[(pyridin-2-yl)methylene]ethanamine iron dichloride



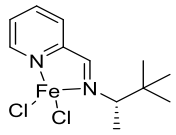
(*R*)-1-Phenyl-*N*-[(pyridin-2-yl)methylene]ethanamine (600 mg, 2.86 mmol) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (363 mg, 2.86 mmol) in dichloromethane (20 mL). The mixture was stirred at room temperature for 28 hours. The mixture was concentrated *in vacuo* and diethylether (100 mL) added. The precipitate was collected and washed with diethylether (50 mL) to give (*R*)-1-phenyl-*N*-[(pyridin-2-yl)methylene]ethanamine iron dichloride (801 mg, 2.37 mmol, 83%) as a purple amorphous solid. The complex was poorly soluble in both tetrahydrofuran and dichloromethane and may be polymeric.[16]

^{1}H NMR: (500 MHz, CD_2Cl_2, 30°C)

85.4 ($\Delta\nu_{1/2}$ = 934 Hz), 67.2 ($\Delta\nu_{1/2}$ = 456 Hz), 52.5 ($\Delta\nu_{1/2}$ = 102 Hz), 50.2 ($\Delta\nu_{1/2}$ = 104 Hz), 4.9 ($\Delta\nu_{1/2}$ = 58 Hz), 4.5 ($\Delta\nu_{1/2}$ = 35 Hz), −4.2 ($\Delta\nu_{1/2}$ = 282 Hz), −17.7 ($\Delta\nu_{1/2}$ = 80 Hz), −26.3 ($\Delta\nu_{1/2}$ = 445 Hz).

The spectroscopic data were consistent with those reported.[97]

(*S*)-3,3-Dimethyl-*N*-(pyridin-2-ylmethylene)butan-2-amine iron dichloride



(S)-3,3-Dimethyl-*N*-(pyridin-2-ylmethylene)butan-2-amine (300 mg, 1.60 mmol) was added dropwise (over ca. 30 seconds) to a stirred suspension of iron dichloride (184 mg, 1.45 mmol) in dichloromethane (20 mL). The mixture was stirred at room temperature for 24 hours. The mixture was concentrated *in vacuo* and diethylether (100 mL) added. The precipitate was collected and washed with diethylether (50 mL) to give (*S*)-3,3-dimethyl-*N*-(pyridin-2-ylmethylene)butan-2-amine iron dichloride (430 mg, 1.36 mmol, 94%) as a red amorphous solid.

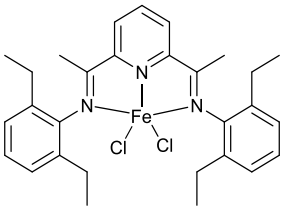
^{1}H NMR: (500 MHz, CD_2Cl_2)

65.5 ($\Delta\nu_{1/2}$ = 834 Hz), 59.4 ($\Delta\nu_{1/2}$ = 564 Hz), 56.7 ($\Delta\nu_{1/2}$ = 224 Hz), 53.3 ($\Delta\nu_{1/2}$ = 225 Hz), 2.5 ($\Delta\nu_{1/2}$ = 116.8 Hz), −15.1−17.1 (overlapping resonance), −19.3 ($\Delta\nu_{1/2}$ = 424 Hz).

MS: **(**HRMS – ESI^+)

Found 339.00630 ($C_{12}H_{18}N_2{}^{35}Cl_2{}^{56}Fe^{23}Na$), requires 339.00886.

(2,6-Bis{1-[(2,6-diethylphenyl)imino]ethyl}pyridine)iron dichloride[144]



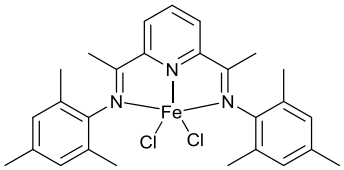
2,6-Bis[(2,6-diethylphenylimino)ethyl]pyridine (700 mg, 1.65 mmol) and anhydrous iron (II) chloride (200 mg, 1.57 mmol) were stirred in anhydrous tetrahydrofuran (40 mL) for 46 hours. Anhydrous diethylether (100 mL) was added and the precipitate collected by filtration, washed with anhydrous diethylether (25 mL) and re-dissolved in anhydrous dichloromethane (200 mL). The resulting solution was filtered and the solvent removed *in vacuo* to give (2,6-bis{1-[(2,6-

diethylphenyl)imino]ethyl}pyridine)iron dichloride (860 mg, 1.55 mmol, 98%) as an amorphous blue solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

81.3 ($\Delta\nu_{1/2}$ = 53 Hz), 52.4 ($\Delta\nu_{1/2}$ = 25Hz), 15.5 ($\Delta\nu_{1/2}$ = 16 Hz), −1.6 ($\Delta\nu_{1/2}$ = 3 Hz), −4.1 ($\Delta\nu_{1/2}$ = 32 Hz), −10.5 ($\Delta\nu_{1/2}$ = 20 Hz), −26.6 ($\Delta\nu_{1/2}$ = 30 Hz).

{[2,6-Bis(2,4,6-trimethylphenylimino)ethyl]pyridine}iron dichloride[144]

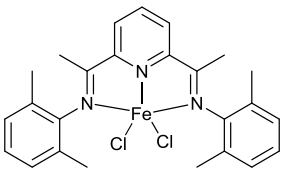


2,6-Bis[(2,4,6-trimethylphenylimino)ethyl]pyridine (507 mg, 1.28 mmol) and anhydrous iron (II) chloride (152 mg, 1.20 mmol) were stirred in anhydrous tetrahydrofuran (30 mL) for 26 hours. Anhydrous diethylether (100 mL) was added and the precipitate collected by filtration, washed with anhydrous diethylether (25 mL) and re-dissolved in anhydrous dichloromethane (200 mL). The resulting solution was filtered and the solvent removed *in vacuo* to give {2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine}iron dichloride (453 mg, 0.86 mmol, 72%) as an amorphous blue solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

81.8 ($\Delta\nu_{1/2}$ = 136 Hz), 36.3 ($\Delta\nu_{1/2}$ = 118 Hz), 21.9 ($\Delta\nu_{1/2}$ = 86 Hz), 15.8 ($\Delta\nu_{1/2}$ = 114 Hz), 12.7 ($\Delta\nu_{1/2}$ = 230 Hz), 1.9 (overlapping resonance), 1.7 (overlapping resonance), 0.5 ($\Delta\nu_{1/2}$ = 84 Hz), −21.7 ($\Delta\nu_{1/2}$ = 130 Hz).

{2,6-Bis[(2,6-dimethylphenylimino)ethyl]pyridine}iron dichloride[144]



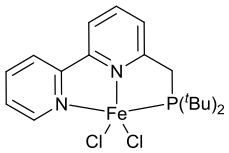
2,6-Bis[(2,4,6-trimethylphenylimino)ethyl]pyridine (512 mg, 1.39 mmol) and anhydrous iron (II) chloride (165 mg, 1.30 mmol) were stirred in anhydrous tetrahydrofuran (35 mL) for 30 hours. Anhydrous diethylether (100 mL) was added and the precipitate collected by filtration, washed with anhydrous diethylether (40 mL) and re-dissolved in anhydrous dichloromethane (200 mL). The resulting solution was filtered and the solvent removed *in vacuo* to give (2,6-bis[(2,6-

dimethylphenylimino)ethyl]pyridine)iron dichloride (384 mg, 0.77 mmol, 59%) as an amorphous purple solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

81.9 ($\Delta\nu_{1/2}$ = 142 Hz), 35.8 ($\Delta\nu_{1/2}$ = 171 Hz), 15.6 ($\Delta\nu_{1/2}$ = 82Hz), 11.6 ($\Delta\nu_{1/2}$ = 210 Hz), 1.4 (overlapping resonance), 1.1 (overlapping resonance), 0.7 (overlapping resonance), −0.1 ($\Delta\nu_{1/2}$ = 71 Hz), −11.1 ($\Delta\nu_{1/2}$ = 120 Hz), −21.5 ($\Delta\nu_{1/2}$ = 152 Hz).

{6-[(Di-*tert*-butylphosphino)methyl]-2,2'-bipyridine}iron dichloride



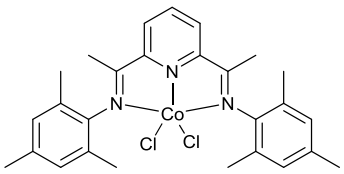
A solution of 6-[(di-*tert*-butylphosphino)methyl]-2,2'-bipyridine (112 mg, 0.36 mmol) in anhydrous tetrahydrofuran (3 mL) was added dropwise (over ca. 30 seconds) to a stirred solution of anhydrous iron (II) chloride (46 mg, 0.36 mmol) in anhydrous tetrahydrofuran (6 mL). The resulting red solution was stirred at room temperature for 18 hours before addition of anhydrous diethylether (60 mL). The precipitate was collected, washed with diethylether (10 mL), re-dissolved in anhydrous dichloromethane (50 mL) and filtered. The solvent was removed *in vacuo* to give {6-[(di-*tert*-butylphosphino)methyl]-2,2'-bipyridine}iron dichloride (70 mg, 0.16 mmol, 40%) as a red amorphous solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

82.3 ($\Delta\nu_{1/2}$ = 793 Hz), 76.9 ($\Delta\nu_{1/2}$ = 336 Hz), 54.6 (overlapping resonance), 53.8 ($\Delta\nu_{1/2}$ = 338 Hz), 22.9 ($\Delta\nu_{1/2}$ = 858 Hz), 15.0 ($\Delta\nu_{1/2}$ = 386 Hz), 9.3 ($\Delta\nu_{1/2}$ = 150 Hz), 6.5 ($\Delta\nu_{1/2}$ = 122 Hz), 5.3 ($\Delta\nu_{1/2}$ = 122 Hz), 4.7 ($\Delta\nu_{1/2}$ = 142 Hz), 3.2 ($\Delta\nu_{1/2}$ = 133 Hz), 2.4 ($\Delta\nu_{1/2}$ = 99 Hz), −12.7 ($\Delta\nu_{1/2}$ = 265 Hz).

The spectroscopic data were consistent with those reported.[83]

{2,6-Bis[(2,4,6-trimethylphenylimino)ethyl]pyridine}cobalt dichloride



2,6-Bis[(2,4,6-trimethylphenylimino)ethyl]pyridine (200 mg, 0.50 mmol) and anhydrous cobalt (II) chloride (65 mg, 0.5 mmol) were stirred in anhydrous tetrahydrofuran (10 mL) for 48 hours. The

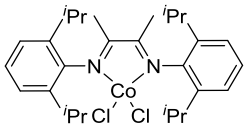
mixture was concentrated *in vacuo* (to *ca.* 3 mL), diethylether (50 mL) was added, the precipitate collected by filtration and washed with diethylether (25 mL) to give {2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine}cobalt dichloride (220 mg, 0.42 mmol, 83%) as a light green amorphous solid.

^{1}H NMR (500 MHz, CD_2Cl_2)

34.9 ($\Delta\nu_{1/2}$ = 40 Hz), 16.4 ($\Delta\nu_{1/2}$ = 12 Hz), 6.3 ($\Delta\nu_{1/2}$ = 11 Hz), 3.7 ($\Delta\nu_{1/2}$ = 14 Hz), 1.8 ($\Delta\nu_{1/2}$ = 14 Hz), 1.6 ($\Delta\nu_{1/2}$ = 8 Hz), 1.3 ($\Delta\nu_{1/2}$ = 9 Hz), −0.7 ($\Delta\nu_{1/2}$ = 21 Hz), −25.6 ($\Delta\nu_{1/2}$ = 61 Hz), −92.2 ($\Delta\nu_{1/2}$ = 60 Hz).

The spectroscopic data were consistent with those reported.[145]

(*2E*)-*N*-((*E*)-(2,6-Di*iso*propylphenylimino)butan-2-ylidene)-2,6-di*iso*propylbenzenamine)cobalt dichloride.[145]

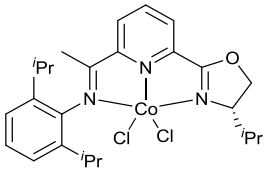


(*2E*)-*N*-[(*E*)-(2,6-Di*iso*propylphenylimino)butan-2-ylidene]-2,6-di*iso*propylbenzenamine (250 mg, 0.62 mmol) and anhydrous cobalt (II) chloride (80 mg, 0.62 mmol) were stirred in anhydrous tetrahydrofuran (10 mL) for 26 hours. The mixture was concentrated *in vacuo* (to ca. 3 mL), diethylether (50 mL) was added, the precipitate collected by filtration and washed with diethylether (25 mL) to give {(*2E*)-*N*-[(*E*)-(2,6-di*iso*propylphenylimino)butan-2-ylidene]-2,6-di*iso*propylbenzenamine}cobalt dichloride (307 mg, 0.57 mmol, 92%) as a green amorphous solid.

^{1}H NMR (500 MHz, CD_2Cl_2)

70.2 ($\Delta\nu_{1/2}$ = 50 Hz), 27.2 ($\Delta\nu_{1/2}$ = 152 Hz), 4.9 ($\Delta\nu_{1/2}$ = 26 Hz), 4.8 ($\Delta\nu_{1/2}$ = 15 Hz), 3.7 ($\Delta\nu_{1/2}$ = 14 Hz), 2.1 ($\Delta\nu_{1/2}$ = 6 Hz), 1.9 ($\Delta\nu_{1/2}$ = 16 Hz), 1.5 ($\Delta\nu_{1/2}$ = 13 Hz), 1.3 ($\Delta\nu_{1/2}$ = 11 Hz), −20.6 ($\Delta\nu_{1/2}$ = 18 Hz).

(*S*)-2,6-Di*iso*propyl-*N*-(1-(6-(4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)aniline cobalt dichloride



(*S*)-2,6-Di*iso*propyl-*N*-(1-(6-(4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)aniline (86 mg, 0.22 mmol) and anhydrous cobalt (II) chloride (29 mg, 0.22 mmol) were stirred in anhydrous tetrahydrofuran (10 mL) for 19 hours. The mixture was concentrated *in vacuo* (to ca. 3 mL), diethylether (50 mL) added, and the precipitate collected by filtration and washed with diethylether (25 mL) to give (*S*)-2,6-di*iso*propyl-*N*-(1-(6-(4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)aniline cobalt dichloride (79 mg, 0.15 mmol, 68%) as an amorphous green solid.

^{1}H NMR (500 MHz, $CDCl_3$)

95.1 ($\Delta\nu_{1/2}$ = 51 Hz), 76.5 ($\Delta\nu_{1/2}$ = 38 Hz), 17.0 ($\Delta\nu_{1/2}$ = 37 Hz), 3.9 ($\Delta\nu_{1/2}$ = 27 Hz), 2.8 ($\Delta\nu_{1/2}$ = 19 Hz), 2.1 ($\Delta\nu_{1/2}$ = 36 Hz), 2.0 ($\Delta\nu_{1/2}$ = 31 Hz), 1.6 ($\Delta\nu_{1/2}$ = 53 Hz), 1.4 ($\Delta\nu_{1/2}$ = 39 Hz), 1.1 ($\Delta\nu_{1/2}$ = 42 Hz), −1.3 ($\Delta\nu_{1/2}$ = 33 Hz), −7.0 ($\Delta\nu_{1/2}$ = 44 Hz), −12.1 ($\Delta\nu_{1/2}$ = 34 Hz), −12.9 ($\Delta\nu_{1/2}$ = 36 Hz), −13.6 ($\Delta\nu_{1/2}$ = 40 Hz), −16.0 ($\Delta\nu_{1/2}$ = 61 Hz), −16.4 ($\Delta\nu_{1/2}$ = 40 Hz), −18.3 ($\Delta\nu_{1/2}$ = 52.4 Hz), −21.7 ($\Delta\nu_{1/2}$ = 58 Hz), −29.7 ($\Delta\nu_{1/2}$ = 70 Hz), −36.2 ($\Delta\nu_{1/2}$ = 115 Hz), −36.4 ($\Delta\nu_{1/2}$ = 115 Hz), −47.4 ($\Delta\nu_{1/2}$ = 177 Hz), −51.7 ($\Delta\nu_{1/2}$ = 232 Hz). The spectroscopic data were consistent with those reported.[89]

5.5 General procedures for hydrofunctionalisation reactions

General Procedure A: 1,4-Hydroboration of myrcene

An (imino)pyridine iron pre-catalyst (0.02 mmol, 5 mol%), sodium *tert*-butoxide (0.04 mmol, 10 mol%), pinacolborane (70 µL, 0.48 mmol), myrcene, and anhydrous tetrahydrofuran (0.5 mL) were sequentially added to a reaction vessel. The resulting mixture was stirred at 25°C for 1 hour, diluted with diethylether (2 mL) and water (2 mL). 1,3,5-Trimethoxybenzene (2 mM solution in diethylether, 2 mL, 8 µmol), as an internal standard, was added and the organic phase of the mixture was sampled. The yield and regioselectivity for the reaction were determined by integration of ^{1}H NMR resonances at 5.36 ppm (q, J = 6.6 Hz, 1H, branched isomer) and 5.63-5.68 (m, 1H, linear isomer) in C_6D_6.

General Procedure B: 1,4-Hydrosilylation of myrcene

An (imino)pyridine iron pre-catalyst (0.02 mmol, 5 mol%), sodium *tert*-butoxide (3.8 mg, 0.04 mmol, 10 mol%), triethoxysilane (110 µL, 0.48 mmol), myrcene (69 µL, 0.4 mmol), and anhydrous tetrahydrofuran (0.5 mL) were sequentially added to a reaction vessel. The resulting mixture was stirred at 25°C for 1 hour, diluted with diethylether (2 mL) and water (2 mL). 1,3,5-Trimethoxybenzene (2 mM solution in diethylether, 2 mL, 8 µmol), as an internal standard, was added

and the organic phase of the mixture was sampled. The yield and regioselectivity for the reaction were determined by integration of ^{1}H NMR resonances at 5.47 ppm (app. tq, J = 8.2, 1.3 Hz, 1H, linear isomer) and 5.34-5.28 (m, 1H, branched isomer) in C_6D_6.

General Procedure C: 1,2-Hydrosilylation of olefins using ^{Ar}BIPFeCl$_2$ or ^{Mes}BIPCoCl$_2$

[^{Ar}BIPFeCl$_2$] or [^{Mes}BIPCoCl$_2$] (5.0 μmol, 1 mol%), activator (2 mol%), silane (0.55 mmol), olefin (0.50 mmol) and anhydrous tetrahydrofuran (0.5 mL) were sequentially added to a reaction vessel. The resulting mixture was stirred at 25°C for 1 hour, diluted with diethylether (2 mL) and sulfate buffer (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

General Procedure D: Hydroboration of olefins using iron or cobalt (pre-)catalysts

[^{Ar}BIPFeCl$_2$] or [^{tBu}PNNFeCl$_2$] or [^{Mes}BIPCoCl$_2$] or [^{iPr}PNNCoCl$_2$] or [*(S)*-^{iPr}IPOCoCl$_2$] or [^{iPr}BICoCl$_2$] (4.0 μmol, 1 mol%), activator (8.0 μmol, 2 mol%), olefin (0.4 mmol), pinacolborane (64 μL, 0.44 mmol, 1.1 equiv) and anhydrous tetrahydrofuran were sequentially added to a reaction vessel. The resulting mixture was stirred at 25°C for 1 hour, diluted with diethylether (2 mL) and water (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

Nickel-catalysed hydrosilylation

2,6-Bis[(2,6-diethylphenylimino)ethyl]pyridine, ^{Et}BIP, (1.8 mg, 5 μmol, 1 mol%) and nickel (II) chloride ethylene glycol dimethyl ether [NiCl$_2$•glyme] (1.1 mg, 5 μmol, 1 mol%) were stirred in anhydrous tetrahydrofuran (5 mL) for 20 hours. The solvent was removed *in vacuo* and sodium *tert*-butoxide (1.0 mg, 10 μmol, 2 mol%), phenylsilane (68 μL, 0.55 mmol), 1-octene (78 μL, 0.5 mmol) and anhydrous tetrahydrofuran (0.5 mL) added. The reaction mixture was stirred at 25°C for 3 hours, diluted with diethylether (2 mL) and sulfate buffer (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

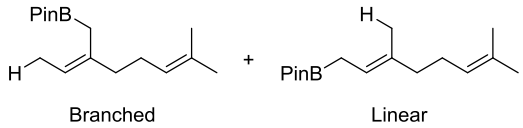
Manganese-catalysed hydrosilylation

2,6-Bis[(2,6-diethylphenylimino)ethyl]pyridine, ^{Et}BIP, (3.6 mg, 10 μmol, 2 mol%) and manganese dibromobis(tetrahydrofuran) (3.6 mg, 10 μmol, 2 mol%) were stirred in anhydrous tetrahydrofuran (5 mL) for 48 hours. The solvent was removed *in vacuo* and sodium *tert*-butoxide (2.0 mg, 20 μmol, 4 mol%), phenylsilane (68 μL, 0.55 mmol) and 1-octene (78 μL, 0.5 mmol) added. The reaction

mixture was stirred at 25°C for 24 hours, diluted with diethylether (2 mL) and sulfate buffer (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

5.6 Product characterisation

(*E*)-2-(2-Ethylidene-6-methylhept-5-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (branched) and (*E*)-2-(3,7-dimethylocta-2,6-dienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (linear)



With modification to general procedure A, myrcene (690 µL, 4.0 mmol), pinacolborane (640 µL, 4.4 mmol), 2,6-di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline iron dichloride (16.0 mg, 40 µmol, 1 mol%) and sodium *tert*-butoxide (8.0 mg, 80 µmol, 2 mol%) were reacted, giving a crude mixture of products which were purified by vacuum distillation (95°C, 0.15 mbar) to give a mixture of two regioisomers [987 mg, 0.37 mmol, 93% overall yield, 20:80 (Linear:Branched)] as a colourless oil.

Mixture:

Asterisks (*) denote resonances from minor (linear) regioisomer.

^{1}H NMR: (500 MHz, C_6D_6)

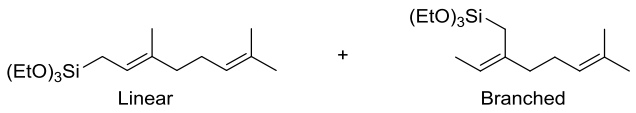
*5.60 (app. tq, *J* = 7.7, 1.3 Hz, 0.2 H), 5.36 (q, *J* = 6.6 Hz, 0.8H), 5.31-5.27 (m, 0.8H), *5.26-5.21 (m, 0.2H), 2.34-2.28 (m, 3.2H), *2.21-2.08 (m, 0.8H), 1.89 (s, 1.6H), *1.85 (d, *J* = 7.7 Hz, 0.6H), 1.70 (d, J = 6.6 Hz, 2.4H), *1.66 (80s, 3.6H, overlapping resonances), *1.54 (s, 0.6H), *1.05 (s, 2.4H), 1.04 (s, 9.6H).

^{13}C NMR: (125 MHz, C_6D_6)

136.7, *134.4, *130.5 (2 resonances), 125.0, *124.9, *119.5, 117.2, 82.6, *82.4, *65.6, 39.8, *27.0 (2 resonances), 25.5, *24.6, 24.5, *24.3, *17.4 (2 resonances), *15.8, 15.2, 13.5.

The spectroscopic data were consistent with those reported.[85]

(*E*)-(3,7-dimethylocta-2,6-dien-1-yl)triethoxysilane and (*E*)-(2-Ethylidene-6-methylhept-5-enyl)triethoxysilane



With modification to general procedure **B**, myrcene (690 µL, 4.0 mmol), triethoxysilane (820 µL, 4.4 mmol), 2,6-di*iso*propyl-*N*-(pyridin-2-ylmethylene)aniline iron dichloride (13 mg, 40 µmol, 1 mol%) and sodium *tert*-butoxide (8 mg, 80 µmol, 2 mol%) were reacted, giving a crude mixture of products which was purified by vacuum distillation (50°C, 0.15 mbar) to give a mixture of two regioisomers, (*E*)-(3,7-dimethylocta-2,6-dien-1-yl)triethoxysilane and (*E*)-(2-ethylidene-6-methylhept-5-enyl)triethoxysilane, [1.06 g, 3.53 mmol, 88% overall yield, 92:8 (Linear:Branched)] as a colourless oil. The product was unstable to flash column chromatography conditions.

Linear Regioisomer:

^{1}H NMR: (500 MHz, C_6D_6)

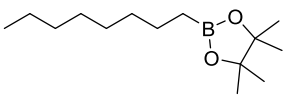
5.47 (app. tq, *J* = 8.2, 1.3 Hz, 1H), 5.26-5.21 (m, 1H), 3.82 (q, *J* = 7.0 Hz, 6H), 2.23-2.08 (m, 4H), 1.73-1.69 (m, 2H), 1.68-1.65 (m, 6H), 1.55 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 9H).

^{13}C NMR: (125 MHz, C_6D_6)

133.6, 130.6, 124.7, 118.0, 58.3, 40.0, 26.9, 25.5, 18.2, 17.3, 15.7, 12.9.

The spectroscopic data were consistent with those reported.[71]

2-(Octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Following general procedure D, 1-octene (63 µL, 0.4 mmol), pinacolborane (70 µL, 0.48 mmol), sodium *tert*-butoxide (1.0 mg, 8.0 µmol, 2 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride iron dichloride [^{Et}BIPFeCl$_2$] (2.1 mg, 4.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (10 g SiO_2, 30 mm Ø, pentane/diethylether 25:1) to give 2-(octyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (84 mg, 0.35 mmol, 88%) as a colourless oil.

TLC: R_f = 0.63 (pentane/diethylether, 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

1.43-1.36 (m, 2H), 1.32-1.20 (m, 22H, overlapping resonance), 0.87 (t, J = 6.8 Hz, 3H), 0.76 (t, J = 7.9 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

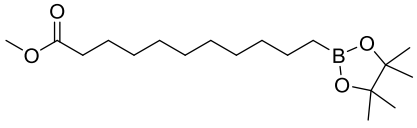
82.8, 32.4, 31.9, 29.4, 29.3, 24.8, 24.0, 22.7, 14.1, 11.2 ($\Delta\nu_{1/2}$ = 105 Hz).

^{11}B NMR: (160 MHz, $CDCl_3$)

34.2.

The spectroscopic data were consistent with those reported.[86]

Methyl 11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecanoate



With slight modification to general procedure D, methyl 10-undecanoate (115 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, pentane/diethylether 10:1)

to give methyl 11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecanoate (125 mg, 0.38 mmol, 77% overall yield) as a colourless oil.

TLC: R_f = 0.70 (pentane/diethylether, 1:1) [$KMnO_4$]

IR: *vmax* (*neat*)

1739.4 cm^{-1} (C=O)

^{1}H NMR: (500 MHz, $CDCl_3$)

3.67 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.62 (app. pent, *J* = 7.3 Hz, 2H), 1.44-1.33 (m, 2H), 1.34-1.25 (m, 12H), 1.25 (s, 12H), 0.77 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

174.4, 82.8, 51.4, 34.1, 32.4, 29.5, 29.4 (2 *x* resonances), 29.3, 29.2, 25.0, 24.8, 24.0.

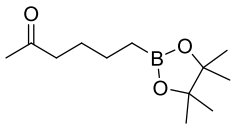
1 carbon resonance not observed.

^{11}B NMR: (160 MHz, $CDCl_3$)

34.2.

The spectroscopic data were consistent with those reported.[88]

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one



With slight modification to general procedure D, 5-hexene-2-one (58 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was quickly purified by flash column chromatography (30 g SiO_2, 30 mm Ø, pentane/diethylether 1:1) to give 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (92 mg, 0.4 mmol, 80% overall yield) as a colourless oil.

TLC: R_f = 0.73 (pentane/diethylether, 1:1) [$KMnO_4$]

IR: *vmax* (*neat*)

1714.7 cm^{-1} (C=O)

MS: (HRMS - ESI^+)

Found 249.16510 ($C_{12}H_{23}O_3{}^{11}B^{23}Na$), requires 249.16325.

^{1}H NMR: (600 MHz, $CDCl_3$)

2.43 (t, *J* = 7.3, 2H), 2.14 (s, 3H), 1.65-1.57 (m, 2H), 1.47-1.38 (m, 2H), 1.26 (s, 12H), 0.80 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

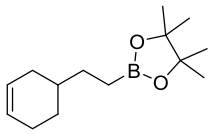
209.2, 83.0, 43.7, 29.8, 26.5, 24.8, 23.6, 11.0 ($\Delta\nu_{1/2}$ = 108 Hz).

^{11}B NMR: (160 MHz, $CDCl_3$)

34.0.

The spectroscopic data were consistent with those reported.[147]

2-[2-(Cyclohex-3-en-1-yl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Following general procedure D, 4-vinylcyclohexene (66 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 8.0 µmol, 2 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl_2] (2.1 mg, 4.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethylether 10:1) to give 2-[2-(cyclohex-3-en-1-yl)ethyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80 mg, 0.34 mmol, 68%) as a colourless oil.

TLC: R_f = 0.73 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

5.68-5.63 (m, 2H), 2.15-2.08 (m, 1H), 2.07-1.97 (m, 2H), 1.79-1.73 (m, 1H), 1.68-1.59 (m, 1H), 1.51-1.43 (m, 1H), 1.42-1.36 (m, 2H), 1.26 (s, 12H), 1.24-1.11 (m, 1H), 0.84-0.78 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

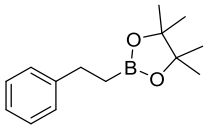
127.0, 126.8, 82.9, 35.8, 31.6, 30.7, 28.5, 25.4, 24.8.

^{11}B NMR: (160 MHz, $CDCl_3$)

34.3.

The spectroscopic data were consistent with those reported.[81]

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane



With slight modification to general procedure D, styrene (58 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was quickly purified by flash column chromatography (20 g SiO_2, 30 mm Ø, pentane/diethylether 9:1) to give 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (102 mg, 0.44 mmol, 88% overall yield) as a colourless oil.

TLC: R_f = 0.52 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.33-7.24 (m, 4H), 7.19 (app. tt, *J* = 7.0, 1.6 Hz, 1H), 2.80 (t, *J* = 8.2 Hz, 2H), 1.26 (s, 12H), 1.19 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

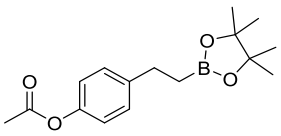
144.4, 128.2, 128.0, 125.5, 83.1, 30.0, 24.8, 13.0 ($\Delta\nu_{1/2}$ = 108 Hz).

^{11}B NMR: (160 MHz, $CDCl_3$)

33.9.

The spectroscopic data were consistent with those reported.[86]

4-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl acetate



With slight modification to general procedure D, 4-acetoxystyrene (65 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and {6-[di-(isobutyl)-phosphinomethyl]-2,2′-bipyridine}cobalt dichloride [^{iPr}PNNCoCl$_2$] (2.1 mg, 5.0 µmol, 1 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, pentane/diethylether 10:1) to give 4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phenyl acetate (132 mg, 0.45 mmol, 90%) as a colourless amorphous solid.

TLC: R_f = 0.54 (pentane/diethylether 1:1) [UV/$KMnO_4$]

m.p 58-60°C (pentane/diethylether)

IR: *vmax* (*neat*)

1747.5 cm^{-1} (C=O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.24-7.20 (m, 2H), 6.99-6.95 (m, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.23 (s, 12H), 1.14 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

169.7, 148.6, 142.0, 128.9, 121.1, 83.2, 29.4, 24.8, 21.1.

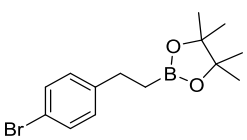
1 carbon resonance not observed.

^{11}B NMR: (160 MHz, $CDCl_3$)

34.1.

The spectroscopic data were consistent with those reported.[88]

2-(4-Bromophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



With slight modification to general procedure D, 4-bromostyrene (65 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and {6-[di-(isobutyl)-phosphinomethyl]-2,2′-bipyridine}cobalt dichloride [^{iPr}PNNCoCl$_2$] (2.1 mg, 5.0 µmol, 1 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, pentane/diethylether 9:1) to give 2-(4-bromophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (105 mg, 0.34 mmol, 68%) as a colourless oil.

TLC: R_f = 0.57 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.38 (app. dt, *J* = 8.4, 2.3 Hz, 2H), 7.12-7.08 (m, 2H), 2.70 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.12 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

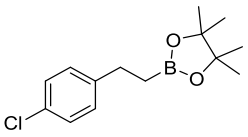
143.4, 131.2, 129.8, 119.2, 83.2, 29.4, 24.8. (1 carbon resonance not observed)

^{11}B NMR: (160 MHz, $CDCl_3$)

33.8.

The spectroscopic data were consistent with those reported.[88]

2-(4-Chlorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



With slight modification to general procedure D, 4-chlorostyrene (60 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 1 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, pentane/diethylether 9:1) to give 2-(4-chlorophenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (106 mg, 0.4 mmol, 80%) as a pale yellow oil.

TLC: R_f = 0.57 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.25-7.20 (m, 2H), 7.17-7.12 (m, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.22 (s, 12H), 1.12 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

142.8, 131.2, 129.4, 128.2, 83.2, 29.3, 24.8.

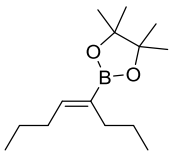
1 carbon resonance not observed.

^{11}B NMR: (160 MHz, $CDCl_3$)

33.8.

The spectroscopic data were consistent with those reported.[88]

(*Z*)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane



Following general procedure D, 4-octyne (74 µL, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (20 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 50:1) to give (*Z*)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (72 mg, 0.30 mmol, 60% overall yield) as a colourless oil.

TLC: R_f = 0.68 (petroleum ether/diethylether, 2:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, CD_2Cl_2)

6.25 (t, *J* = 7.1 Hz, 1H), 2.13-2.05 (m, 4H), 1.45-1.30 (m, 4H), 1.23 (s, 12H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR: (125 MHz, CD_2Cl_2)

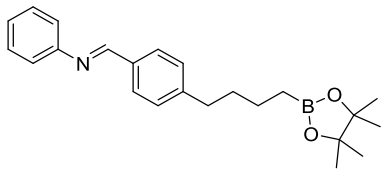
145.8, 82.8, 30.5 (2 *x* resonances), 24.5, 23.3, 22.5, 13.8, 13.7.

^{11}B NMR: (160 MHz, $CDCl_3$)

30.6.

The spectroscopic data were not consistent with those reported for (*E*)-isomer and therefore assigned as shown.[148]

2-[4-(*N*-Phenylbenzaldimine)butyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



With slight modification to general procedure D, *N*-phenyl-4-(3-butenyl)-benzadimine (118 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 8.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture. 1,3,5-Trimethoxybenzene (2 mL, 50 mmolL^{-1} in diethylether) was added, the solvent removed *in vacuo* to give a crude yellow oil containing 2-[4-(*N*-phenylbenzaldimine)butyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 2-[4-(*N*-phenylbenzylamine)butyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 1,3,5-trimethoxybenzene (*ca*. 70:20:10 ratio). Attempts to purify the product resulted in product decomposition.

MS: (HRMS - EI$^+$)

Found 363.23796 ($C_{23}H_{30}O_2N^{11}B$), requires 363.23641.

^{1}H NMR: (500 MHz, $CDCl_3$)

8.45 (s, 1H), 7.86-7.79 (m, 2H), 7.44-7.38 (m, 2H), 7.33-7.29 (m, 2H), 7.27-7.15 (m, 4H), 2.70 (app. t, *J* = 7.8 Hz, 2H), 1.74-1.62 (m, 2H), 1.55-1.47 (m, 2H), 1.27 (s, 12H), 0.85 (app t. *J* = 7.7 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

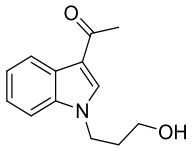
160.4, 152.4, 146.9, 133.9, 129.1, 128.9, 128.8, 127.5, 125.7, 120.9, 83.0, 35.8, 33.9, 23.7.

^{11}B NMR: (160 MHz, $CDCl_3$)

34.1.

The spectroscopic data were consistent with those reported.[81]

1-(3-Hydroxypropyl)-3-acetylindole



Following general procedure D, *N*-allyl-3-acetylindole (100 mg, 0.5 mmol), pinacolborane (80 µL, 0.55 mmol), sodium *tert*-butoxide (1.0 mg, 8.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture. Aqueous hydrogen peroxide (1.5 mL, 15 mmol, 30% in water) was added dropwise (over ca. 5 minutes) to a stirred biphasic mixture of aqueous sodium hydroxide (6.0 mL, 2M) and the crude reaction mixture dissolved in diethylether (10 mL) at 0°C. The mixture was stirred at 0°C for 20 minutes, warmed to room temperature and stirred for a further 2 hours, diluted with sat. aqueous sodium thiosulfate (10 mL), extracted with diethylether (3 x 40 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The product was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/ethyl acetate 1:1 to 0:1) to give an off-white amorphous solid which was recrystallised from petroleum ether/ethyl acetate (ca. 2:1, 10 mL) giving *1-(3-hydroxypropyl)-3-acetylindole* (2 crops, 0°C, 54 mg, 0.25 mmol, 50%) as a colourless microcrystalline solid.

Attempts to purify the hydroboration product {1-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)propyl]-3-acetylindole} resulted in decomposition.

TLC: R_f = 0.80 (ethyl acetate).

m.p 92-94°C (ethyl acetate)

MS: (HRMS - EI^+)

Found 217.10978 ($C_{13}H_{15}O_2N$), requires 217.10973.

IR: *vmax* (*neat*)

3441.0 (br, OH), 1616.4 (C=O)

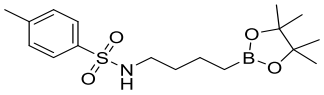
^{1}H NMR: (500 MHz, $CDCl_3$)

8.40-8.32 (m, 1H), 7.80 (s, 1H), 7.43-7.36 (m, 1H), 7.33-7.27 (m, 2H), 4.35 (t, J = 6.8 Hz, 2H), 3.65 (app. q, J = 4.4 Hz, 2H), 2.51 (s, 3H), 2.18-2.14 (br. m, 1H, OH), 2.11 (q, J = 6.2 Hz, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

193.3, 136.8, 135.4, 126.4, 123.3, 122.6, 117.0, 109.9, 58.9, 43.4, 32.2, 27.6.

***N*-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)butyl]-4-methylbenzenesulfonamide**



Following general procedure D, *N*-tosyl-3-butenylamine (113 mg, 0.5 mmol), pinacolborane (80 µL, 0.550 mmol), sodium *tert*-butoxide (1.0 mg, 8.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL), diluted with diethylether (5 mL) and water (5 mL), extracted with diethylether (3 *x* 5 mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The resulting solid was recrystallised from petroleum ether/ethyl acetate (ca. 7 mL, 20:1) to give *N-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)butyl]-4-methylbenzenesulfonamide* (3 crops, −20ºC, 124 mg, 0.35 mmol, 70%) as a colourless microcrystalline solid.

Attempts to purify the product using SiO_2 resulted in product decomposition.

m.p 84-86ºC (ethyl acetate)

MS: (HRMS - EI^+)

Found 353.18422 ($C_{17}H_{28}O_4N^{11}B^{32}S$), requires 353.18266.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.77-7.73 (m, 2H), 7.33-7.28 (m, 2H), 4.40 (app. t, *J* = 5.8 Hz, 1H), 2.93 (q, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.50-1.42 (m, 2H), 1.42-1.33 (m, 2H), 1.23 (s, 12H), 0.72 (t, *J* = 7.6 Hz, 2H).

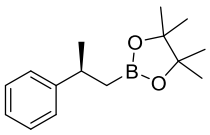
^{13}C NMR: (125 MHz, $CDCl_3$)

143.2, 137.1, 129.7, 127.1, 83.1, 42.9, 31.9, 24.8, 21.5, 20.8.

^{11}B NMR: (160 MHz, $CDCl_3$)

34.0.

(*S*)-(+)-4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane



With slight modification to general procedure D, α-methylstyrene (52 µL, 0.4 mmol), pinacolborane (64 µL, 0.44 mmol), sodium *tert*-butoxide (0.9 mg, 8.0 µmol, 2 mol%) and *(S)*-2,6-di*iso*propyl-*N*-[1-(6-(4-*iso*propyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl]ethylidene)aniline cobalt dichloride [*(S)*-^{iPr}IPOCoCl$_2$] (2.1 mg, 4.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/diethylether 25:1) to give *(S)*-(+)-4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (93 mg, 0.38 mmol, 95% overall yield) as a colourless oil.

TLC: R_f = 0.53 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$].

HPLC: 98% ee [Daicel Chiralpak IB (0.46 *x* 25 cm), particle size = 5 µm hexane/^{i}PrOH = 99.75:0.25, ν = 0.4 mL min^{-1}, λ = 254 nm, t (minor) = 11.20 min, t (major) = 12.04 min.]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.30-7.22 (m, 4H), 7.18-7.13 (m, 1H), 3.04 (sext. *J* = 7.8 Hz, 1H), 1.28 (d, J = 6.9 Hz, 3H), 1.18-1.16 (m, 2H, overlapping resonances), 1.17 (s, 12H, overlapping resonances).

^{13}C NMR: (125 MHz, $CDCl_3$)

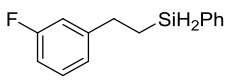
149.3, 128.2, 126.6, 125.7, 83.0, 35.8, 24.9, 24.8, 24.7.

^{11}B NMR: (160 MHz, $CDCl_3$)

33.4.

The spectroscopic data were consistent with those reported.[89]

1-(3-Fluorophenyl)-2-(phenylsilyl)ethane



With modification to general procedure C, 3-fluorostyrene (60 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%), and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/diethylether 25:1) to give *1-(3-fluorophenyl)-2-(phenylsilyl)ethane* (102 mg, 0.44 mmol, 89%) as a colourless oil.

TLC: R_f = 0.69 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

IR: *vmax* (*neat*)

2131.3

MS: (HRMS - EI^+)

Found 230.09198 ($C_{14}H_{15}F^{28}Si$), requires 230.09216.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60-7.55 (m, 2H), 7.44-7.36 (m, 3H), 7.26-7.20 (m, 1H), 6.99-6.95 (m, 1H), 6.92-6.85 (m, 2H), 4.33 (t, *J* = 3.6 Hz, 2H), 2.80-2.75 (m, 2H), 1.34-1.27 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

163.0 (d, *J* = 245 Hz), 146.5 (d, *J* = 7.0 Hz), 135.2, 131.9, 129.8, 129.7 (d, *J* = 8.5 Hz), 128.1, 123.5 (d, *J* = 2.5 Hz), 114.7 (d, *J* = 21 Hz), 112.7 (d, *J* = 21 Hz), 30.9 (d, *J* = 1.5 Hz), 11.9.

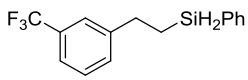
^{19}F NMR: (470 MHz, $CDCl_3$)

−113.6.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−31.2.

1-[3-(Trifluoromethyl)phenyl]-2-(phenylsilyl)ethane



With modification to general procedure C, 3-trifluoromethylstyrene (74 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%), and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/diethylether 25:1) to give 1-[3-(trifluoromethyl)phenyl]-2-(phenylsilyl)ethane (119 mg, 0.43 mmol, 85%) as a colourless oil.

TLC: R_f = 0.60 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.55 (m, 2H), 7.47-7.35 (m, 7H), 4.34 (t, *J* = 3.6 Hz, 2H), 2.86-2.80 (m, 2H), 1.36-1.30 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

144.8, 135.2, 131.7, 131.3, 130.6 (d, *J* = 32 Hz), 129.8, 128.8, 128.1, 124.6 (q, *J* = 4.0 Hz), 124.3 (d, *J* = 272.3 Hz), 122.7 (q, *J* = 4.0 Hz), 31.0, 12.0.

^{19}F NMR: (470 MHz, $CDCl_3$)

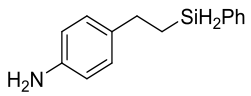
−62.6.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−31.2.

The spectroscopic data were consistent with those reported.[69]

1-(4-Aminophenyl)-2-(phenylsilyl)ethane



With modification to general procedure C, 4-aminostyrene (59 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%), and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (25 g SiO_2, 30 mm Ø, hexane/ethyl acetate 9:1) to give 1-(4-aminophenyl)-2-(phenylsilyl)ethane (79 mg, 0.35 mmol, 70%) as a yellow oil.

TLC: R_f = 0.48 (hexane/ethyl acetate, 1:1) [UV/$KMnO_4$]

IR: *vmax* (*neat*)

2125.6 (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.55 (m, 2H), 7.43-7.35 (m, 3H), 7.01-6.97 (m, 2H), 6.65-6.60 (m, 2H), 4.31 (t, *J* = 3.7 Hz, 2H), 3.56 (bs, 2H), 2.71-2.65 (m, 2H), 1.31-1.24 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

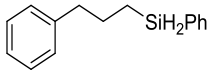
144.3, 135.3, 134.2, 132.4, 129.6, 128.7, 128.0, 115.3, 30.9, 12.4.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−31.2.

The spectroscopic data were consistent with those reported.[69]

1-Phenyl-3-(phenylsilyl)propane



With modification to general procedure C, allylbenzene (61 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%), and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/ethyl acetate 25:1) to give 1-phenyl-3-(phenylsilyl)propane (99 mg, 0.44 mmol, 88%) as a colourless oil.

TLC: R_f = 0.80 (petroleum ether/ethyl acetate, 1:1) [UV/$KMnO_4$]

IR: *vmax* (*neat*)

2127.5 (Si-H).

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.54 (m, 2H), 7.43-7.34 (m, 3H), 7.30-7.25 (m, 2H), 7.21-7.15 (m, 3H), 4.31 (t, *J* = 3.6 Hz, 2H), 2.68 (app. t, *J* = 7.6 Hz, 2H), 1.83-1.76 (m, 2H), 1.02-0.96 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

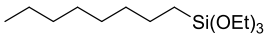
142.1, 135.2, 132.5, 129.6, 128.5, 128.3, 128.0, 125.8, 39.0, 27.0, 9.8.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−30.8.

The spectroscopic data were consistent with those reported.[66]

Octyltriethoxysilane



With modification to general procedure C, 1-octene (1.24 mL, 8 mmol), triethoxysilane (1.64 mL, 8.8 mmol), sodium *tert*-butoxide (1 mg, 8.0 µmol, 0.10 mol%, 430 ppm) and 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine iron dichloride [^{Et}BIPFeCl$_2$] (2.2 mg, 4.0 µmol, 0.05 mol%, 940 ppm) were reacted, giving a crude product which was purified by vacuum distillation (88°C, 0.15 mbar) to give octyltriethoxysilane (2.08 g, 7.52 mmol, 94%) as a colourless oil.

^{1}H NMR: (500 MHz, C_6D_6)

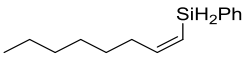
3.83 (q, *J* = 7.0 Hz, 6H), 1.66-1.59 (m, 2H), 1.42-1.36 (m, 2H), 1.33-1.21 (m, 8H), 1.19 (t, *J* = 7.0 Hz, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.80-0.76 (m, 2H).

^{13}C NMR: (125 MHz, C_6D_6)

58.3, 33.2, 31.9, 29.2 (2 resonances), 22.8, 22.7, 18.3, 14.1, 10.4.

The spectroscopic data were consistent with those reported.[60]

(*Z*)-1-(Phenylsilyl)oct-1-ene



With modification to general procedure C, 1-octyne (74 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,6-diethylphenylimino)ethyl]pyridine)iron dichloride [^{Et}BIPFeCl$_2$] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/diethylether 50:1) to give (*Z*)-*1-(phenylsilyl)oct-1-ene* (104 mg, 0.48 mmol, 95%) as a colourless oil.

TLC: R_f = 0.77 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

IR: *vmax* (*neat*)

2133.3 (Si-H)

MS: (HRMS - EI$^+$)

Found 218.14790 ($C_{14}H_{22}{}^{28}Si$), requires 218.14853.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.61-7.57 (m, 2H), 7.42-7.34 (m, 3H), 6.62 (dt, *J* = 13.6, 7.5 Hz, 1H), 5.68 (dtt, *J* = 13.7, 4.1, 1.3 Hz, 1H), 4.61 (d, *J* = 4.1 Hz, 2H), 2.24 (qd, *J* = 7.4, 1.2 Hz, 2H), 1.45-1.36 (m, 2H), 1.34-1.23 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 3H).

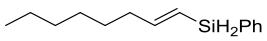
^{13}C NMR: (125 MHz, $CDCl_3$)

153.8, 135.3, 132.4, 129.5, 128.0, 118.8, 33.4, 31.7, 29.2, 28.8, 22.6, 14.1.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−50.3.

(*E*)-1-(Phenylsilyl)oct-1-ene



With modification to general procedure C, 1-octyne (74 µL, 0.5 mmol), phenylsilane (68 µL, 0.55 mmol), sodium *tert*-butoxide (1 mg, 10.0 µmol, 2 mol%) and (2,6-bis[(2,4,6-trimethylphenylimino)ethyl]pyridine)cobalt dichloride [^{Mes}BIPCoCl_2] (2.8 mg, 5.0 µmol, 1.0 mol%) were reacted in anhydrous tetrahydrofuran (0.5 mL) to give the crude product mixture which was purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/diethylether 50:1) to give *(E)-1-(phenylsilyl)oct-1-ene* (83 mg, 0.38 mmol, 75%) as a colourless oil.

TLC: R_f = 0.79 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60-7.57 (m, 2H), 7.43-7.35 (m, 3H), 6.37 (dt, *J* = 18.4, 6.3 Hz, 1H), 5.73 (dsept., *J* = 18.4, 1.6 Hz, 1H), 4.54 (d, *J* = 3.2 Hz, 2H), 2.22-2.16 (m, 2H), 1.47-1.40 (m, 2H), 1.36-1.25 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

154.2, 135.4, 132.4, 129.6, 128.0, 119.8, 37.0, 31.7, 28.9, 28.4, 22.6, 14.1.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−38.0

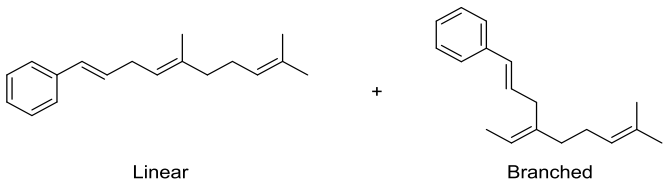
IR: *vmax* (*neat*)

2131.3 (Si-H)

MS: (HRMS - EI^+)

Found 218.14907 ($C_{14}H_{22}{}^{28}Si$), requires 218.14853.

[(1*E*,4*E*)-5,9-Dimethyldeca-1,4,8-trienyl]benzene



Myrcene (95 µL, 0.55 mmol) was added to a mixture of 1-phenyl-*N*-[(*E*)-pyridin-2-ylmethylene]-2-(trimethylsilyl)ethanamine iron dichloride (8.0 mg, 20 µmol, 4 mol%) and sodium *tert*-butoxide (2.0 mg, 40 µmol, 8 mol%). Phenylsilane (5 µL, 40 µmol, 8 mol%), styrene (57 µL, 0.5 mmol) and anhydrous tetrahydrofuran (0.2 mL) were sequentially added to the reaction vessel. The resulting mixture was stirred at 25°C for 5 hours, diluted with diethylether (2 mL) and sulfate buffer (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

The crude reaction product was purified by flash column chromatography (25 g SiO_2, 30 mm Ø, pentane) to give a mixture of linear and branched hydrovinylation product (85 mg, 0.35 mmol, 70%, 90:10 linear/branched).

TLC: R_f = 0.41 (pentane) [UV]

Linear Regioisomer:

^{1}H NMR: (500 MHz, $CDCl_3$)

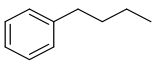
7.39-7.33 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.17 (m, 1H), 6.43-6.36 (m, 1H), 6.21 (dt, *J* = 15.8, 6.46 Hz, 1H), 5.26 (tq, *J* = 7.3, 1.3 Hz, 1H), 5.17-5.10 (m, 1H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.18-2.03 (m, 4H), 1.71 (s, 3H), 1.68 (s, 3H), 1.63 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

137.9, 136.7, 131.5, 129.5 (2 x resonances), 128.5, 126.8, 126.0, 124.2, 121.4, 39.7, 31.5, 26.7, 25.7, 17.7, 16.1.

The spectroscopic data were consistent with those reported.[97]

1-Butylbenzene



In an autoclave, 4-phenyl-1-butene (156 µL, 1.0 mmol) was added to a mixture of 6-[(diisopropylphosphino)methyl]-2,2′-bipyridine cobalt dichloride (4.2 mg, 10 µmol, 1 mol%) and sodium *tert*-butoxide (2.0 mg, 20 µmol, 2 mol%). Phenylsilane (5 µL, 40 µmol, 4 mol%) and anhydrous tetrahydrofuran (0.2 mL) were sequentially added, and the autoclave pressurised with H_2 (10 bar). The resulting mixture was stirred at 25°C for 5 hours, diluted with diethylether (2 mL) and sulfate buffer (2 mL). 1,3,5-Trimethoxybenzene, as an internal standard, was added and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

The crude reaction product was purified by flash column chromatography (25 g SiO_2, 30 mm Ø, pentane) and the pentane removed *in vacuo* (400 mbar, 35°C) to give the volatile product 1-butylbenzene (89 mg, 0.66 mmol, 66%) as a colourless oil.

TLC: R_f = 0.52 (pentane) [UV]

^{1}H NMR: (600 MHz, $CDCl_3$)

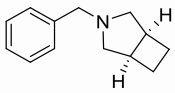
7.35-7.28 (m, 2H), 7.26-7.17 (m, 3H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.68-1.61 (m, 2H), 1.44-1.36 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR: (150 MHz, $CDCl_3$)

142.9, 128.4, 128.2, 125.6, 35.7, 33.7, 22.4, 14.0.

The spectroscopic data were consistent with those reported.[108]

_N_-Benzyl-3-azabicyclo[0.2.3]heptane



A 1:1 pre-mixed solution of NaO^{t}Bu and phenylsilane (300 µL, 0.15M in anhydrous THF, 10 mol%) was added to a mixture of *N*,*N*-di-2-propenylbenzylamine (94 mg, 0.5 mmol) and ^{iPr}BIPCoCl$_2$ (15 mg, 25 µmol, 5 mol%). The mixture was stirred at room temperature for 16 hours, diluted with diethylether (2 mL) and water (2 mL) and the organic phase dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (300 mbar, 40°C). The crude product was purified by flash column chromatography (50 g SiO_2, 30 mm Ø, pentane/diethylether 10:1) to give *N*-benzyl-3-azabicyclo[0.2.3]heptane – contaminated with *ca.* 2% *N*,*N*-di-2-propenylbenzylamine – (63 mg, 0.36 mmol, 72%) as a yellow oil.
n.b The pre-mixed NaO^{t}Bu/phenylsilane should be quenched immediately after use with aqueous NaOH (2M) to avoid formation of silane gas. This reaction is particularly sensitive to air/moisture, and we recommend the use of strictly anhydrous and inert conditions.

TLC: R_f = 0.35 (pentane/diethylether 1:1) [$KMnO_4$]

^{1}H NMR: (400 MHz, C_6D_6)

7.46-7.41 (m, 2H), 7.25-7.18 (m, 2H), 7.14-7.09 (m, 1H), 3.56 (s, 2H), 2.73 (d, *J* = 9.5 Hz, 2H), 2.60-2.50 (m, 2H), 2.07-1.98 (m, 2H), 1.95-1.89 (m, 2H), 1.88-1.81 (m, 2H).

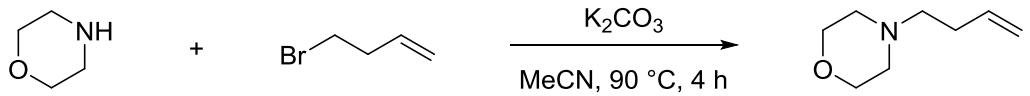
^{13}C NMR: (100 MHz, C_6D_6)

140.3, 128.5, 128.2, 126.7, 60.7, 59.9, 37.5, 24.4.

The spectroscopic data were consistent with those reported.[101]

5.7 Substrate Synthesis

4-But-3-enyl-morpholine



4-Bromo-1-butene (3.0 mL, 29.6 mmol) was added dropwise to a stirred mixture of morpholine (2.60 mL, 29.6 mmol) and potassium carbonate (9.94 g, 71.9 mmol, 2.43 equiv.) in acetonitrile (100 mL). The mixture was heated at reflux (*ca.* 90°C) for 4 hours, cooled to room temperature, potassium carbonate removed by filtration and the solvent removed *in vacuo* (40°C, 500 mbar to 500 mbar). The crude product was purified *via* flash column chromatography (200 g SiO_2, 50 mm Ø, 3:7 to 0:1 petroleum ether/ethyl acetate) to give 4-but-3-enyl-morpholine (1.87 g, 13.2 mmol, 45%) as a yellow oil. Alternatively the crude product (*repeat reaction*) could be purified by vacuum distillation (40−43°C, 0.15 mbar) to give 4-but-3-enyl-morpholine (2.34 g, 16.6 mmol, 56%) as a colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

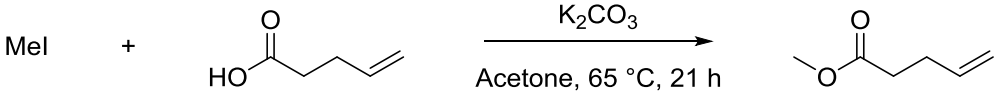
5.87-5.78 (m, 1H), 5.11-5.00 (m, 2H), 3.73 (t, *J* = 4.7 Hz, 4H), 2.51-2.39 (m, 6H), 2.30-2.23 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

136.4, 115.8, 67.0, 58.4, 53.8, 31.0.

The spectroscopic data were consistent with those reported.

Methyl 4-pentenoate



Methyl iodide (2.50 mL, 40 mmol) was added dropwise (over *ca.* 2 minutes) to a stirred mixture of 4-pentenoic acid (4.10 mL, 40 mmol) and potassium carbonate (9.33 g, 67.6 mmol, 1.7 equiv.) in acetone (120 mL). The reaction mixture was heated at reflux (*ca.* 65 °C) for 21 hours, cooled to room temperature, diluted with diethylether (50 mL) and aqueous sodium hydroxide (100 mL, 1 M), extracted with diethylether (50 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 500 to 320 mbar). The crude product was purified by vacuum distillation (20-22 °C, 0.13 mbar) to give methyl 4-pentenoate (1.43 g, 12.5 mmol, 31%) as a volatile colourless oil.

^{1}H NMR: (500 MHz, $CDCl_3$)

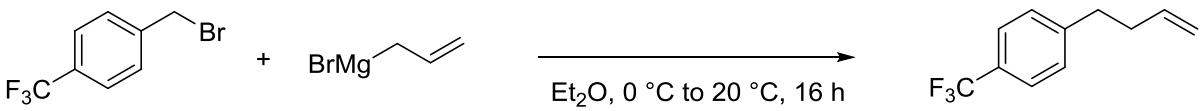
5.88-5.78 (m, 1H), 5.11-4.98 (m, 2H), 3.68 (s, 3H), 2.45-2.35 (m, 4H).

^{13}C NMR: (125 MHz, $CDCl_3$)

173.6, 136.7, 115.5, 51.4, 33.4, 28.9.

The spectroscopic data were consistent with those reported.[69]

1-(But-3-en-1-yl)-4-(trifluoromethyl)benzene



Allyl bromide (29.0 mL, 25 mmol, 0.87 M in diethylether) was added dropwise (over *ca.* 5 minutes) to a stirred mixture of 4-trifluoromethylbenzylbromide (3.0 g, 12.5 mmol) in anhydrous diethylether (25 mL) at 0°C. The reaction mixture was warmed to room temperature and stirred for 16 hours, diluted with water (50 mL, *carefully*! over *ca.* 2 minutes), extracted with diethylether (40 mL x 3),

dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 455 to 150 mbar). The crude oil was purified by flash column chromatography (110 g SiO_2, 40 mm Ø, 50:1 petroleum ether/diethyl ether) to give 1-(but-3-en-1-yl)-4-(trifluoromethyl)benzene (1.89 g, 9.4 mmol, 76%) as a colourless oil.

TLC: R_f = 0.63 (petroleum ether/diethylether, 9:1) [$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.56 (app. d, *J* = 8.1 Hz, 2H), 7.32 (app. d, *J* = 8.0 Hz, 2H), 5.90-5.81 (m, 1H), 5.10-5.00 (m, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.45-2.38 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

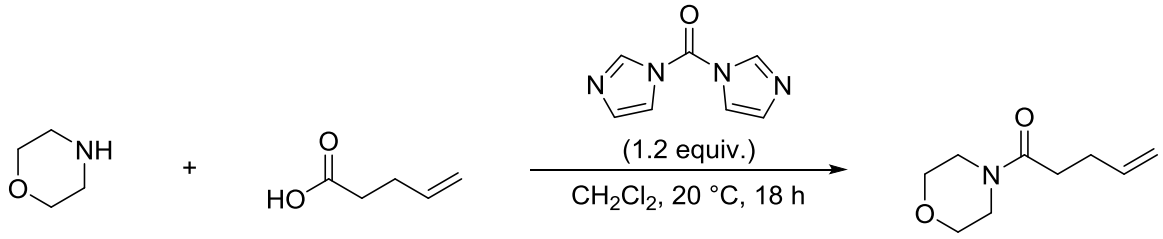
145.9, 137.4, 128.8, 128.2 (q, *J* = 31.9 Hz), 125.2 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 271.8 Hz), 115.5, 35.2, 35.1.

^{19}F NMR: (470 MHz, $CDCl_3$)

−62.3.

The spectroscopic data were consistent with those reported.[149]

***N*-(4-Pentenoyl)morpholine**



4-Pentenoic acid (3.57 mL, 35 mmol) was added dropwise (over *ca.* 30 seconds) to a stirred mixture of carbonyldiimidazole (6.80 g, 42 mmol, 1.2 equiv.) in dichloromethane (150 mL) at room temperature for 3 hours. Morpholine (6.00 mL, 70 mmol, 2.0 equiv.) was added dropwise (over *ca.* 60 seconds) and the mixture stirred for 18 hours. The solvent was removed *in vacuo* (40 °C, 500 mbar to 50 mbar) and the crude product purified by flash column chromatography (100 g SiO_2, 40 mm Ø, 10:1 to 1:1 petroleum ether/ethyl acetate) to give *N*-(4-pentenoyl)morpholine (5.16 g, 34.6 mmol, 98%) as a colourless oil.

TLC: R_f = 0.18 (petroleum ether/diethylether, 2:1) [$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

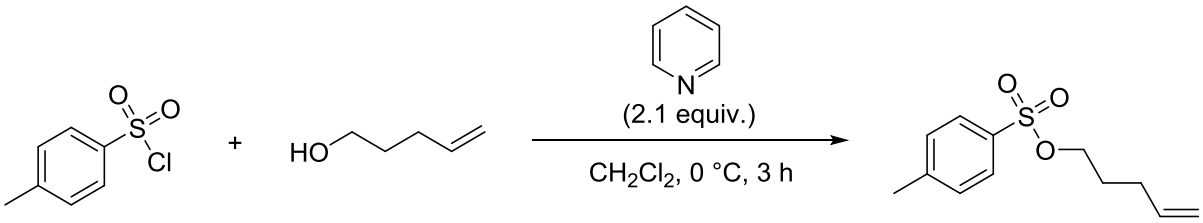
5.93-5.83 (m, 1H), 5.12-4.98 (m, 2H), 3.71-3.65 (m, 4H), 3.65-3.60 (m, 2H), 3.48 (t, *J* = 4.90 Hz, 2H), 2.43-2.39 (m, 4H).

^{13}C NMR: (125 MHz, $CDCl_3$)

171.0, 137.4, 115.3, 68.0, 67.0, 66.7, 46.0, 41.0, 32.3, 29.2, 25.6.

The spectroscopic data were consistent with those reported.[150]

Pent-4-enyl 4-toluenesulfonate



Tosyl chloride (16.6 g, 87 mmol) was added portion-wise (4 portions, over *ca*. 25 minutes) to a stirred mixture of 4-penten-1-ol (6.0 mL, 58 mmol) and pyridine (9.7 mL, 120 mmol, 2.1 equiv.) in dichloromethane (60 mL) at 0 °C. The reaction was stirred for 3 hours, diluted with water (30 mL) and aqueous hydrogen chloride (50 mL, 2 M), extracted with dichloromethane (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (30 °C, 550 mbar to 30 mbar). The crude oil was purified by flash column chromatography (350 g SiO_2, 50 mm Ø, 1:0 to 4:1 heptane/ethyl acetate) to give pent-4-enyl 4-toluenesulfonate (8.52 g, 35 mmol, 60 %) as a colourless oil.

TLC: R_f = 0.44 (heptane/ethyl acetate, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.83-7.78 (m, 2H), 7.38-7.33 (m, 2H), 5.76-5.66 (m, 1H), 5.00-4.94 (m, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 2.46 (s, 3H), 2.13-2.06 (m, 2H), 1.79-1.72 (m, 2H).

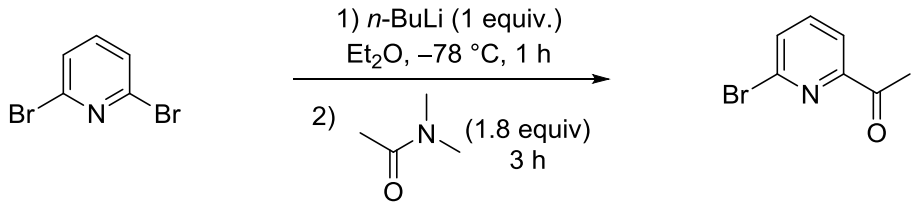
^{13}C NMR: (125 MHz, $CDCl_3$)

144.7, 136.6, 133.2, 129.8, 128.0, 115.8, 69.8, 29.3, 28.0, 21.7.

The spectroscopic data were consistent with those reported.[151]

5.8 Ligand and Complex Synthesis

1-(6-Bromopyridin-2-yl)-ethanone



n-Butyllithium solution (53 mL, 84 mmol, 1.6 M in hexane) was added dropwise (over *ca.* 10 minutes) to a stirred mixture of 2,6-dibromopyridine (20.0 g, 84 mmol) in anhydrous diethylether (240 mL) at −78 °C. The reaction mixture was stirred for 1 hour before the dropwise addition (over *ca.* 10 minutes) of dimethylacetamide (14 mL, 151 mmol, 1.8 equiv.). The reaction mixture was stirred at −78 °C for 3 hours, warmed to room temperature (20 °C), aqueous ammonium chloride solution (100 mL, saturated) added and the mixture stirred for 1 h. The mixture was extracted with diethylether (60 mL x 5), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 550 mbar

to 30 mbar). The crude solid was purified by recrystallization using hexane (200 mL, 75 °C) to give 1-(6-bromopyridin-2-yl)-ethanone (14.7 g, 73.5 mmol, 88%) as a yellow microcrystalline solid.

m.p: 56-58 °C (hexane)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.00 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.73-7.65 (m, 2H), 2.72 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

198.6, 154.3, 141.3, 139.2, 131.8, 120.5, 27.4.

The spectroscopic data were consistent with those reported.[152]

2-Acetyl-6-cyanopyridine

2-Acetyl-6-cyanopyridine (500 mg, 2.5 mmol), copper cyanide (270 mg, 3 mmol, 1.2 equiv.) and dimethylformamide (10 mL) were heated to 180 °C in a sealed tube for 18 hours. The reaction mixture was cooled to room temperature (20 °C), aqueous ethylene diamine (40 mL, 10% v/v in H_2O) added, extracted with diethylether (20 mL x 6), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 550 mbar to 30 mbar). The crude yellow/brown oil was purified by flash column chromatography (50 g SiO_2, 50 mm Ø, 2:1 petroleum ether/diethylether) to give 2-acetyl-6-cyanopyridine (130 mg, 0.89 mmol, 36%) as an off-white amorphous solid. The reaction was repeated to give 2-acetyl-6-cyanopyridine (530 mg, 3.6 mmol, 15%, *25 mmol scale reaction*).

TLC: R_f = 0.1 (petroleum ether/diethylether, 3:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

1697.4 cm^{-1} (C=O)

^{1}H NMR: (500 MHz, $CDCl_3$)

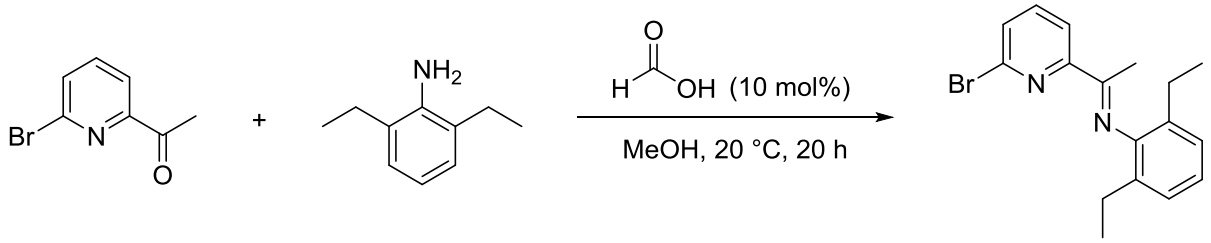
8.25 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.02 (t, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.1 Hz, 1H), 2.75 (s, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

198.2, 154.4, 138.2, 133.2, 131.2, 124.4, 116.7, 25.6.

The spectroscopic data were consistent with those reported.[153]

(*E*)-N-(1-(6-Bromopyridin-2-yl)ethylidene)-2,6-diethylaniline



Formic acid (26 µL, 0.68 mmol, 10 mol%) and 2,6-diethylaniline (1.10 mL, 6.8 mmol) were sequentially added to a stirred mixture of 2-acetyl-6-bromopyridine (1.0 g, 6.8 mmol) in methanol (20 mL). The reaction was stirred for 20 hours at 20 °C, the solvent removed *in vacuo* (40 °C, 200 mbar to 15 mbar) and the crude oil purified by flash column chromatography (200 g SiO_2, 50 mm Ø, 10:1 petroleum ether/diethylether) to give **(***E***)**-N-(1-(6-bromopyridin-2-yl)ethylidene)-2,6-diethylaniline (1.52 g, 4.6 mmol, 68%) as a yellow oil.

TLC: R_f = 0.70 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

8.33 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.04 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.42-2.27 (m, 4H), 2.18 (s, 3H), 1.13 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$)

165.9, 157.5, 147.5, 141.0, 138.8, 131.1, 129.2, 126.0, 123.5, 120.0, 24.6, 16.9, 13.7.

The spectroscopic data were consistent with those reported.[154]

(*E*)-N-(1-(6-Cyanopyridin-2-yl)ethylidene)-2,6-diethylaniline

(*E***)**-N-(1-(6-Bromopyridin-2-yl)ethylidene)-2,6-diethylaniline (1.40 g, 4.2 mmol), copper cyanide (450 mg, 5.0 mmol, 1.2 equiv.) and dimethylformamide (15 mL) were heated to 180 °C in a sealed

tube for 18 hours. The reaction mixture was cooled to room temperature (20 °C), aqueous ethylene diamine (80 mL, 10% v/v in H_2O) added, extracted with diethylether (30 mL x 6), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 550 mbar to 30 mbar). The crude yellow oil was purified by flash column chromatography (150 g SiO_2, 50 mm Ø, 5:1 petroleum ether/diethylether) to give (*E*)-N-(1-(6-cyanopyridin-2-yl)ethylidene)-2,6-diethylaniline (870 mg, 3.1 mmol, 74%) as a yellow oil.

TLC: R_f = 0.45 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

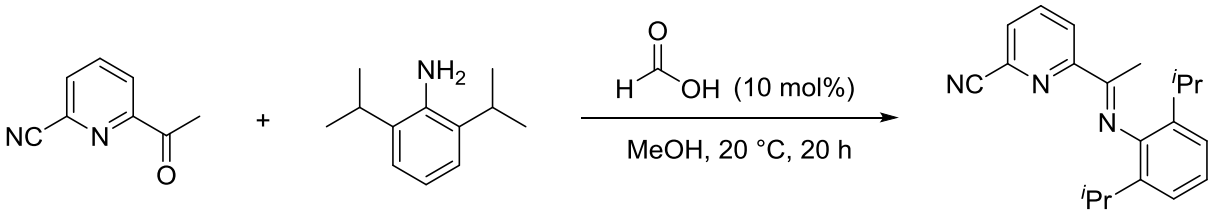
^{1}H NMR: (500 MHz, $CDCl_3$)

8.61 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.95 (t, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.15-7.11 (m, 2H), 7.08-7.04 (m, 1H), 2.41-2.28 (m, 4H), 2.20 (s, 3H), 1.13 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR: (125 MHz, $CDCl_3$)

165.7, 157.8, 147.2, 137.3, 132.8, 130.9, 129.4, 126.0, 124.4, 123.8, 117.2, 24.6, 16.8, 13.7.

(*E*)-N-(1-(6-Cyanopyridin-2-yl)ethylidene)-2,6-diisopropylaniline



Formic acid (10 µL, 0.27 mmol, 10 mol%) and 2,6-diisopropylaniline (0.53 mL, 2.8 mmol) were sequentially added to a stirred mixture of 2-acetyl-6-cyanopyridine (400 mg, 2.7 mmol) in methanol (10 mL). The reaction was stirred for 20 hours at 20 °C, the solvent removed *in vacuo* (40 °C, 200 mbar to 15 mbar) and the crude oil purified by flash column chromatography (180 g SiO_2, 50 mm Ø, 5:1 petroleum ether/diethylether) to give **(***E***)**-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (428 mg, 1.4 mmol, 53%) as a yellow amorphous solid. *n.b the product obtained was contaminated with ca. 50% 2,6-diisopropylaniline and used without further purification (actual yield ~25%).*

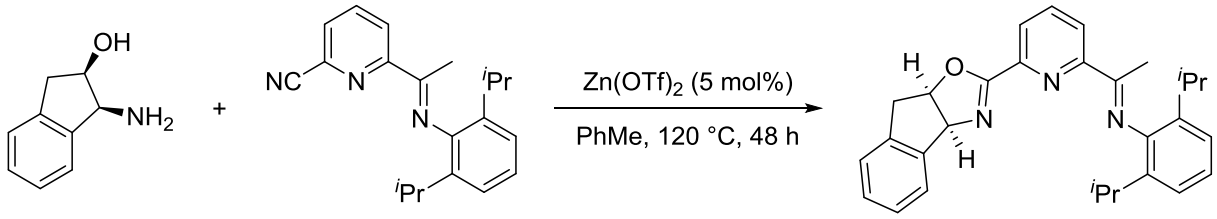
TLC: R_f = 0.10 (petroleum ether/diethylether, 3:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

8.65 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.53 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.0 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.14-7.09 (m, 1H), 2.76 (hept., *J* = 6.91 Hz, 2H), 2.27 (s, 3H), 1.18 (d, *J* = 2.0 Hz, 6H), 1.17 (d, *J* = 2.1 Hz, 6H).

The spectroscopic data were consistent with those reported.[89]

(*E*)-N-(1-(6-((3*α*S,8*α*R)-8,8*α*-Dihydro-3*α*H-indeno[1,2-d]oxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline



(1R, 2S)-(+)-*cis*-1-Amino-2-indanol (75 mg, 0.5 mmol, 1.5 equiv.), **(***E***)**-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (202 mg, 0.66 mmol, 1.0 equiv – *ca.* 50% purity) and zinc triflate (10 mg, 16.5 µmol, 5 mol%) were heated in refluxing toluene (10 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 15 mbar). The crude oil was purified by flash column chromatography (80 g SiO_2, 30 mm Ø, 10:1 to 2:1 petroleum ether/ethyl acetate) to give (*E*)-N-(1-(6-((3αS,8αR)-8,8α-dihydro-3αH-indeno[1,2-d]oxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline (20 mg, 46 µmol, 14%) as a yellow amorphous solid.

m.p: 170-173 °C (ethyl acetate)

TLC: R_f = 0.62 (petroleum ether/ethyl acetate, 1:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

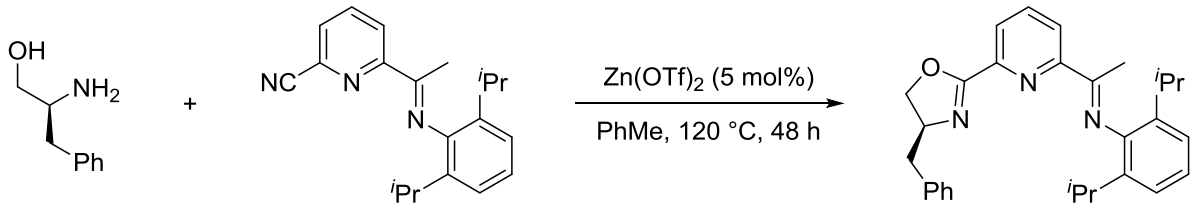
8.48 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.30 (s, 3H), 7.20-7.15 (m, 2H), 7.14-7.08 (m, 1H), 5.87 (d, *J* = 7.9 Hz, 1H), 5.64 (t, *J* = 6.8 Hz, 1H), 3.62-3.45 (m, 2H), 2.73 (hept. *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 1.15 (d, *J* = 5.9 Hz, 12H).

^{13}C NMR: (125 MHz, $CDCl_3$)

166.8, 163.1, 156.2, 146.3, 146.1, 141.6, 139.8, 136.9, 135.7, 128.6, 127.5, 125.8, 125.4, 125.3, 123.6, 123.1, 123.0, 84.0, 39.9, 28.2, 23.2, 22.9, 17.3.

The spectroscopic data were consistent with those reported.[155]

(*S*)-(-)-N-(1-(6-(4-Benzyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline



(S)-(-)-2-Amino-3-phenyl-1-propanol (47 mg, 0.3 mmol, 1.5 equiv.), **(***E***)**-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (122 mg, 0.4 mmol, 1.0 equiv – *ca.* 50% purity) and zinc triflate (6 mg, 15.0 µmol, 5 mol%) were heated in refluxing toluene (10 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 15 mbar). The crude oil was purified by flash column chromatography (100 g SiO_2, 30 mm Ø, 15:1 petroleum ether/ethyl acetate) to (*S*)-(-)-N-(1-(6-(4-benzyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline (50 mg, 0.11 mmol, 57%) as a yellow amorphous solid.

m.p: 125-128 °C (ethyl acetate)

TLC: R_f = 0.48 (petroleum ether/ethyl acetate, 5:1) [UV/$KMnO_4$]

^{1}H NMR: (400 MHz, $CDCl_3$)

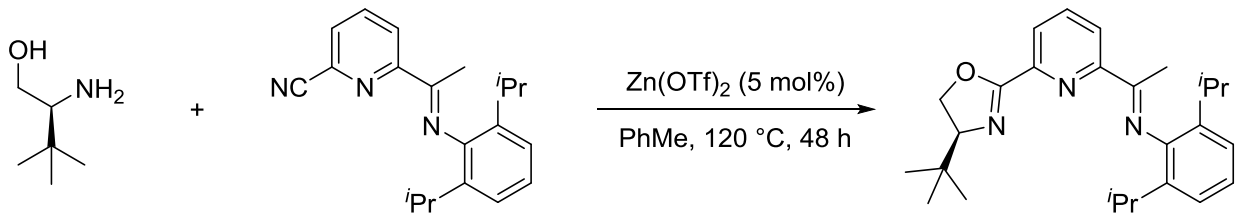
8.51 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.35-7.28 (m, 2H), 7.28-7.20 (m, 3H), 7.18-7.13 (m, 2H), 7.12-7.05 (m, 1H), 4.73-4.63 (m, 1H), 4.47 (t, *J* = 8.8 Hz, 1H), 4.27 (t, *J* = 7.8 Hz, 1H), 3.32 (dd, *J* = 13.7, 5.0 Hz, 1H), 2.83-2.66 (m, 3H), 2.29 (s, 3H), 1.13 (d, q*J* = 6.9 Hz, 12H).

^{13}C NMR: (100 MHz, $CDCl_3$)

166.6, 163.2, 156.2, 146.4, 146.0, 137.8, 137.0, 135.7, 129.3, 128.7, 126.6, 125.4, 123.7, 123.3, 123.0, 72.5, 68.3, 41.7, 28.2, 23.2, 22.9, 17.3.

The spectroscopic data were consistent with those reported.[155]

(*S*)-(-)-*N*-(1-(6-(4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline



(*S*)-2-Amino-3,3-dimethyl-1-butanol (55 mg, 0.47 mmol, 1.2 equiv.), **(***E*)-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (240 mg, 0.8 mmol, 1.0 equiv – *ca.* 50% purity) and zinc triflate (8 mg, 20 µmol, 5 mol%) were heated in refluxing toluene (15 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 15 mbar). The crude oil was purified by flash column chromatography (220 g SiO_2, 40 mm Ø, 15:1 to 5:1 petroleum ether/diethylether) to (*S*)-(-)-N-(1-(6-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline (71 mg, 0.18 mmol, 45%) as a yellow amorphous solid.

TLC: R_f = 0.47 (petroleum ether/diethylether, 5:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

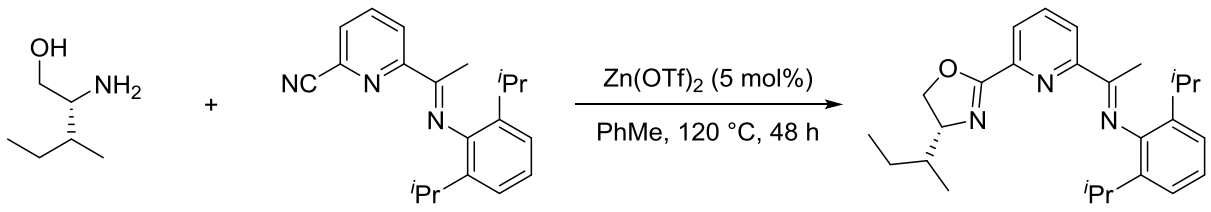
8.53 (d, *J* = 7.9, 1.0 Hz, 1H), 8.25 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.21- 7.17 (m, 2H), 7.15-7.10 (m, 1H), 4.52 (dd, *J* = 10.3, 8.8 Hz, 1H), 4.38 (t, *J* = 8.5 Hz, 1H), 4.18 (dd, *J* = 10.3, 8.4 Hz, 1H), 2.76 (hept. d, *J* = 6.9, 2.9 Hz, 2H), 2.32 (s, 3H), 1.20-1.13 (m, 12H), 1.03 (s, 9H).

^{13}C NMR: (125 MHz, $CDCl_3$)

166.8, 162.6, 156.1, 146.4, 146.2, 136.9, 135.7 (2 x resonances), 125.4, 123.6, 123.1, 123.0, 76.4, 69.5, 34.0, 28.3 (2 x resonances), 26.0, 23.3, 22.9 (2 x resonances), 17.2.

The spectroscopic data were consistent with those reported.[155]

(*S*)-(-)-*N*-(1-(6-(4-(*sec*-Butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline



(*S*)-Isoleucinol (55 mg, 0.47 mmol, 1.2 equiv.), **(***E*)-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (240 mg, 0.80 mmol, 1.0 equiv – *ca.* 50% purity) and zinc triflate (8 mg, 20 µmol, 5 mol%) were heated in refluxing toluene (15 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 15 mbar). The crude oil was purified by flash column chromatography (120 g SiO_2, 40 mm Ø, 10:1 to 5:1 petroleum ether/diethylether) to (*S*)-(-)-N-(1-(6-(4-(*sec*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diisopropylaniline (104 mg, 0.26 mmol, 65%) as a yellow amorphous solid.

TLC: R_f = 0.2 (petroleum ether/diethylether, 4:1) [UV/$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

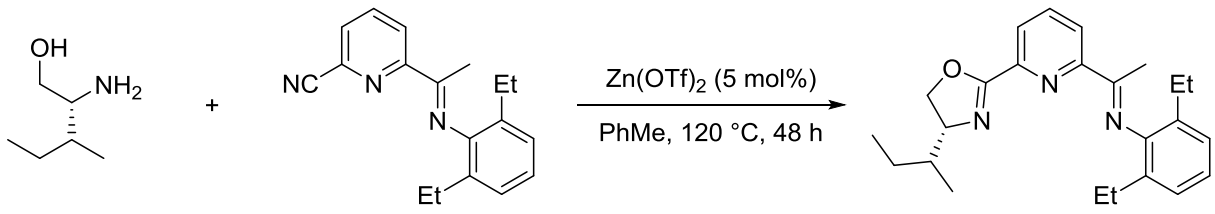
8.51 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.20 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 1H), 7.19-7.15 (m, 2H), 7.10 (dd, *J* = 8.4, 6.8 Hz, 1H), 4.54 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.33 (td, *J* = 8.4, 6.2 Hz, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 2.73 (sept. d, *J* = 6.9, 1.8 Hz, 2H), 2.30 (s, 3H), 1.84-1.75 (m, 1H), 1.74-1.64 (m, 1H), 1.37-1.24 (m, 2H), 1.17-1.11 (m, 12H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR: (150 MHz, $CDCl_3$)

166.7, 162.6, 156.2, 146.4, 146.1, 137.0, 135.7, 125.3, 123.6, 123.0, 123.0, 71.6, 70.4, 39.2, 28.2, 26.3, 23.3, 22.8, 17.3, 14.5, 11.6.

The spectroscopic data were consistent with those reported.[89]

(*S*)-(-)-*N*-(1-(6-(4-(*sec*-Butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diethylaniline



(*S*)-Isoleucinol (59 mg, 0.5 mmol, 1.2 equiv.), **(***E*)-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diethylaniline (110 mg, 0.4 mmol, 1.0 equiv) and zinc triflate (8 mg, 20 µmol, 5 mol%) were heated in refluxing toluene (10 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 15 mbar). The crude oil was purified by flash column chromatography (120 g SiO_2, 40 mm Ø, 10:1 petroleum ether/diethylether) to (*S*)-(-)-N-(1-(6-(4-(*sec*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diethylaniline (81 mg, 0.21 mmol, 54%) as a yellow amorphous solid.

TLC: R_f = 0.57 (petroleum ether/diethylether, 1:1) [UV]

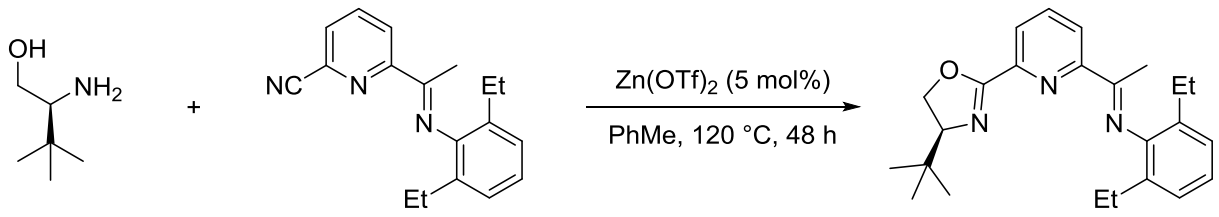
^{1}H NMR: (500 MHz, $CDCl_3$)

8.51 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.20 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.90 (t, *J* = 7.9 Hz, 1H), 7.15-7.11 (m, 2H), 7.05 (dd, *J* = 8.2, 6.9 Hz, 1H), 4.55 (dd, *J* = 9.4, 8.0, 1H), 4.38-4.31 (m, 1H), 4.29 (q, *J* = 8.1 Hz, 1H), 2.46-2.30 (m, 4H), 2.29 (s, 3H), 1.86-1.75 (m, 1H), 1.75-1.65 (m, 1H), 1.36-1.26 (m, 1H), 1.15 (td, *J* = 7.5, 2.0 Hz, 6H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.94 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

166.8, 162.5, 156.3, 147.6, 146.2, 136.9, 131.1, 125.9, 125.3, 123.4, 123.0, 71.5, 70.4, 39.1, 26.2, 24.6, 16.9, 14.5, 13.7, 11.6.

(*S*)-(-)-*N*-(1-(6-(4-(*tert*-Butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diethylaniline



(*S*)-2-Amino-3,3-dimethyl-1-butanol (82 mg, 0.7 mmol, 1.2 equiv.), **(***E*)-N-(1-(6-cyanoopyridin-2-yl)ethylidene)-2,6-diisopropylaniline (166 mg, 0.6 mmol, 1.0 equiv) and zinc triflate (11 mg, 30 µmol, 5 mol%) were heated in refluxing toluene (15 mL) at 120 °C for 48 hours. The reaction mixture was cooled to room temperature (20 °C), diluted with saturated aqueous sodium bicarbonate solution (30 mL), brine (30 mL), extracted with ethyl acetate (30 mL x 3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* (40 °C, 400 mbar to 20 mbar). The crude oil was purified by flash column chromatography (105 g SiO_2, 40 mm Ø, 10:1 to 5:1 petroleum ether/diethylether) to (*S*)-(-)-N-(1-(6-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-2-yl)ethylidene)-2,6-diethylaniline (87 mg, 0.23 mmol, 38%) as a yellow amorphous solid.

TLC: R_f = 0.50 (petroleum ether/diethylether, 1:1) [UV]

^{1}H NMR: (500 MHz, $CDCl_3$)

8.51 (dd, *J* = 8.0, 1.0, 1H), 8.25 (dd, J = 8.5, 0.9, 1H), 7.90 (t, J = 7.8 Hz, 1H), 7.15-7.11 (m, 2H), 7.05 (dd, J = 8.2, 6.9 Hz, 1H), 4.55-4.49 (m, 1H), 4.38 (t, J = 8.4 Hz, 1H), 4.20 (dd, J = 10.1, 8.4 Hz, 1H), 2.46-2.30 (m, 4H), 2.28 (s, 3H), 1.15 (td, J = 7.5, 3.3 Hz, 6H), 1.02 (s, 9H).

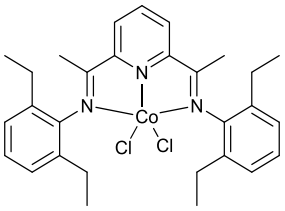
^{13}C NMR: (125 MHz, $CDCl_3$)

166.8, 162.5, 156.1, 147.6, 146.2, 136.9, 131.1 (2 x resonances), 125.9, 125.4, 123.4, 123.0, 76.4, 69.5, 34.0, 26.0, 24.5 (2 x resonances), 16.9, 13.7 (2 x resonances).

General procedure for the preparation of cobalt complexes:

Ligand (1.05 equiv.) and anhydrous cobalt (II) chloride (1 equiv.) were stirred in anhydrous tetrahydrofuran for 24 hours at room temperature. Anhydrous diethylether was added and the precipitate collected by filtration, washed with anhydrous diethylether and the solid dried *in vacuo* to give the cobalt complex.

(2,6-Bis{1-[(2,6-diethylphenyl)imino]ethyl}pyridine)cobalt dichloride

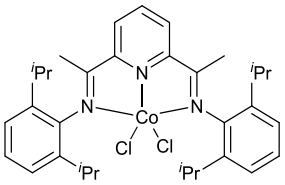


2,6-Bis[(2,6-diethylphenylimino)ethyl]pyridine (1.00 g, 2.30 mmol, 1.05 equiv.) and anhydrous cobalt (II) chloride (284 mg, 2.19 mmol, 1.0 equiv.) were stirred in anhydrous tetrahydrofuran (40 mL) for 24 hours. Anhydrous diethylether (100 mL) was added and the precipitate collected by filtration, washed with anhydrous diethylether (25 mL). The solid was dried *in vacuo* (*ca*. 20 °C, 0.1 mbar) to give (2,6-bis{1-[(2,6-diethylphenyl)imino]ethyl}pyridine)cobalt dichloride (1.17 g, 2.11 mmol, 96%) as an amorphous brown solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

40.4 ($\Delta\nu_{1/2}$ = 38 Hz), 8.2 ($\Delta\nu_{1/2}$ = 19 Hz), 2.1 ($\Delta\nu_{1/2}$ = 25 Hz), −10.0 ($\Delta\nu_{1/2}$ = 19 Hz), −19.0 ($\Delta\nu_{1/2}$ = 29 Hz), −36.0 ($\Delta\nu_{1/2}$ = 101 Hz), −41.4 ($\Delta\nu_{1/2}$ = 121 Hz).

(2,6-Bis{1-[(2,6-diisopropylphenyl)imino]ethyl}pyridine)cobalt dichloride

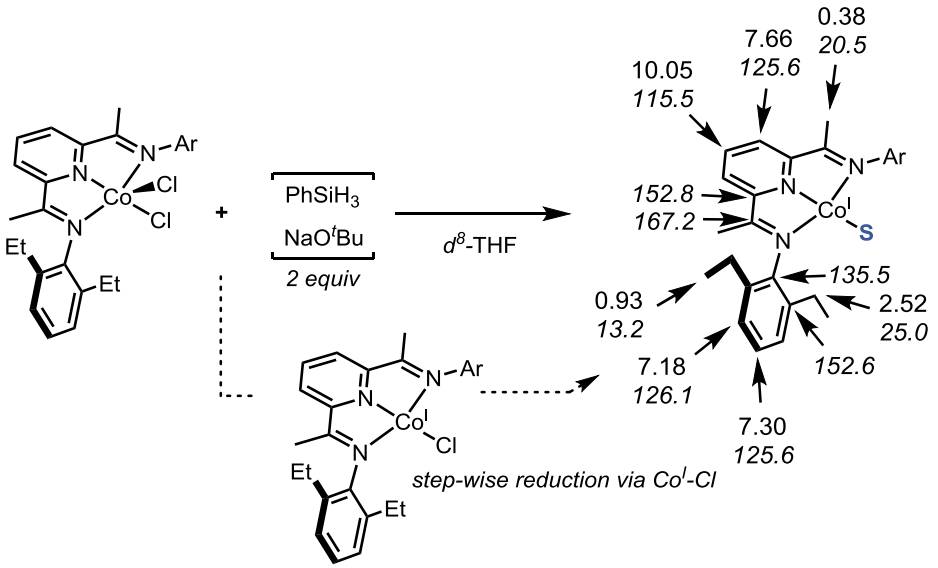


2,6-Bis[(2,6-diisopropylphenylimino)ethyl]pyridine (1.44 g, 2.99 mmol, 1.05 equiv.) and anhydrous cobalt (II) chloride (368 mg, 2.85 mmol, 1.0 equiv.) were stirred in anhydrous tetrahydrofuran (40 mL) for 24 hours. Anhydrous diethylether (100 mL) was added and the precipitate collected by filtration, washed with anhydrous diethylether (25 mL). The solid was dried *in vacuo* (*ca*. 20 °C, 0.1 mbar) to give (2,6-bis{1-[(2,6-diethylphenyl)imino]ethyl}pyridine)cobalt dichloride (1.17 g, 2.11 mmol, 74%) as an amorphous brown solid.

^{1}H NMR: (500 MHz, CD_2Cl_2)

47.7 ($\Delta\nu_{1/2}$ = 48 Hz), 9.8 ($\Delta\nu_{1/2}$ = 24 Hz), 4.0 ($\Delta\nu_{1/2}$ = 41 Hz), −8.6 ($\Delta\nu_{1/2}$ = 26 Hz), −17.2 ($\Delta\nu_{1/2}$ = 41 Hz), −18.5 ($\Delta\nu_{1/2}$ = 41 Hz), −82.5 ($\Delta\nu_{1/2}$ = 41 Hz).

Identification of low oxidation-state active species



In a J-Young's NMR tube, phenylsilane (ca. 3.3 µL, 27 µmol, 2 equiv.) was added to a mixture of ^{Et}BIPCoCl$_2$ (7.5 mg, 13.5 µmol, 1 equiv.) and sodium *tert*-butoxide (2.6 mg, 27 µmol, 2 equiv.) in anhydrous d_8-tetrahydrofuran (1.5 mL). The mixture changed colour from brown (*pre-catalyst*) to deep red/burgundy, and this resulting solution was analysed by ^{1}H, ^{13}C, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC ^{1}H-^{1}H COSY and APPI-MS.

^{1}H NMR: (500 MHz, d_8-THF)

10.05 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.32-7.29 (m, 2H), 7.18 (d, *J* = 7.7 Hz, 4H), 2.52 (app. non., *J* = 7.4 Hz, 8H), 0.93 (t, *J* = 7.6 Hz, 12H), 0.39 (s, 6H).

^{13}C NMR: (125 MHz, d_8-THF)

167.2, 152.8, 152.6, 135.5, 126.1, 125.6 (2 x resonances), 115.5, 25.0, 20.5, 13.2.

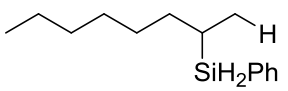
MS (APPI): Expected m/z: ^{Et}BIPCoCl = 519.18515, found m/z: 519.18219
Expected m/z: ^{Et}BIPCo(THF) = 556.27381, found m/z: 556.27115
Expected m/z: ^{Et}BIPCo = 484.21630, found m/z: 484.21309
Expected m/z: ^{Et}BIP = 425.28310, found m/z: 426.28593

General procedure A: Cobalt-catalysed hydrosilylation of alkenes

[^{Et}BIPCoCl$_2$] or [^{iPr}BIPCoCl$_2$] (5.0 µmol, 0.5 mol%), sodium *tert*-butoxide (1 mg, 1 mol%), anhydrous tetrahydrofuran (1.0 mL), phenylsilane (135 µL, 1.1 mmol) and olefin (1.0 mmol) were sequentially added to a reaction vessel. The resulting mixture was stirred at room temperature for 1 hour, diluted with diethylether (2 mL) and sulfate buffer (1 mL) or water (1 mL). Trimethoxybenzene

was added as an internal standard and the organic phase of the mixture was sampled. The yield for the reaction was determined by integration of product ^{1}H NMR resonances.

2-(Phenylsilyl)octane



Following general procedure A, 1-octene (157 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (35 g SiO_2, 30 mm Ø, petroleum ether/diethylether 25:1) to give a mixture of 2-(phenylsilyl)octane and 1-(phenylsilyl)octane (195 mg, 0.88 mmol, 88%, 95:5) as a colourless oil.

TLC: R_f = 0.42 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.63-7.54 (m, 2H), 7.45-7.33 (m, 3H), 4.23 (ABdd, $\Delta\nu_{AB}$ = 21.6 Hz, J_{AB} = 6.0, 2.4 Hz, 2H), 1.55-1.23 (m, 10H), 1.20-1.11 (m, 1H), 1.09-1.05 (m, 3H), 0.89 (t, J = 6.9 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

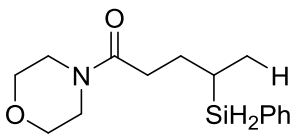
135.6, 132.3, 129.4, 127.9, 33.5, 31.8, 29.4, 28.5, 22.7, 16.3, 16.1, 14.0.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−23.7.

The spectroscopic data were consistent with those reported.[89]

2-(Phenylsilyl)-*N*-(4-pentanoyl)morpholine



Following general procedure A, *N*-(4-pentenoyl)morpholine (169 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/ethyl acetate 9:1) to give a mixture of 2-(phenylsilyl)-*N*-(4-pentanoyl)morpholine and 1-(phenylsilyl)-*N*-(4-pentanoyl)morpholine (238 mg, 0.86 mmol, 86%, 96:4) as a colourless oil.

TLC: R_f = 0.20 (petroleum ether/ethyl acetate, 3:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2125.6 cm^{-1} (Si-H), 1643.4 cm^{-1} (C=O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60-7.56 (m, 2H), 7.44-7.33 (m, 3H), 4.25 (ABdd, $\Delta\nu_{AB}$ = 11.2 Hz, J_{AB} = 6.0, 2.9 Hz, 2H), 3.68-3.55 (m, 6H), 3.33 (app. t, *J* = 4.7 Hz, 2H), 2.44-2.27 (m, 2H), 1.92-1.83 (m, 1H), 1.74-1.66 (m, 1H), 1.26-1.18 (m, 1H), 1.12 (d, *J* = 7.2 Hz, 3H).

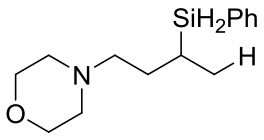
^{13}C NMR: (150 MHz, $CDCl_3$)

171.5, 135.6, 131.7, 129.7, 128.0, 66.9, 66.6, 45.9, 41.9, 32.1, 29.0, 16.2, 16.1.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−23.3.

2-(Phenylsilyl)-4-butylmorpholine



Following general procedure A, 4-(3-buten-1-yl)morpholine (141 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/ethyl acetate/triethylamine 90:9.5:0.5) to give a mixture of 2-(phenylsilyl)-4-butylmorpholine and 1-(phenylsilyl)-4-butylmorpholine (185 mg, 0.74 mmol, 74%, 96:4) as a colourless oil.

TLC: R_f = 0.17 (petroleum ether/ethyl acetate, 1:1) [$KMnO_4$]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60-7.55 (m, 2H), 7.42-7.34 (m, 3H), 4.25 (ABdd, $\Delta\nu_{AB}$ = 23.3 Hz, J_{AB} = 6.0, 2.9 Hz, 2H), 3.70 (t, J = 4.7 Hz, 4H), 2.47-2.31 (m, 6H), 1.75-1.67 (m, 1H), 1.60-1.50 (m, 1H), 1.25-1.18 (m, 1H), 1.09 (d, J = 7.3 Hz, 3H).

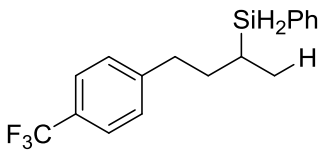
^{13}C NMR: (125 MHz, $CDCl_3$)

135.5, 132.4, 129.5, 127.9, 67.0, 57.9, 53.8, 30.2, 16.3, 14.5.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−23.3.

2-(Phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane]



Following general procedure A, 4-[4-(trifluoromethyl)phenylbut-1-ene] (200 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (30 g SiO_2, 30 mm Ø, petroleum ether/diethylether 50:1) to give a mixture of *2-(phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane]* and 1-(phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane] (267 mg, 0.87 mmol, 87%, 97:3) as a colourless oil.

TLC: R_f = 0.55 (petroleum ether/diethylether, 9:1) [UV]

MS: (HRMS – EI$^+$)

Found 308.11881 ($C_{17}H_{19}F_3{}^{28}Si$), requires 308.12027.

IR: *vmax (neat)*

2127.5 cm^{-1}

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.54 (m, 2H), 7.52 (app. d, J = 8.0 Hz, 2H), 7.44-7.40 (m, 1H), 7.39-7.35 (m, 2H), 7.25 (app. d, J = 8.0 Hz, 2H), 4.27 (ABdd, $\Delta\nu_{AB}$ = 16.3 Hz, J_{AB} = 6.0, 2.5 Hz,

2H), 2.84-2.64 (m, 2H), 1.91-1.62 (m, 2H), 1.24-1.16 (m, 1H), 1.15 (app. d, *J* = 6.3 Hz, 3H).

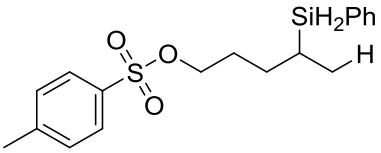
^{13}C NMR: ($CDCl_3$, 125 MHz)

146.6, 135.6, 131.6, 129.7, 128.7, 128.1 (q, *J* = 32.4 Hz), 128.0, 125.2 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 271.8), 35.1, 34.6, 16.0, 15.9.

^{29}Si NMR: ($CDCl_3$, 99 MHz)

−22.9.

2-(Phenylsilyl)-5-(4-methylsulfonyloxy)pentane



Following general procedure A, 5-(4-methylsulfonyloxy)pentene (240 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl_2] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (60 g SiO_2, 20 mm Ø, pentane/diethylether 20:1 to 10:1) to give a mixture of *2-(phenylsilyl)-5-(4-methylsulfonyloxy)pentane* and 1-(phenylsilyl)-5-(4-methylsulfonyloxy)pentane (305 mg, 0.88 mmol, 88%, 92:8) as a colourless oil.

TLC: R_f = 0.63 (pentane/diethylether, 1:1) [UV]

MS: (HRMS – EI^+)

Found 348.11991 ($C_{18}H_{24}O_3{}^{32}S^{28}Si$), requires 348.12100.

IR: *vmax (neat)*

2125.6 cm^{-1} (Si-H)

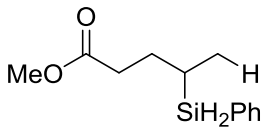
^{1}H NMR: ($CDCl_3$, 600 MHz)

7.80-7.76 (m, 2H), 7.54-7.51 (m, 2H), 7.43-7.39 (tt, *J* = 7.4, 2.3 Hz, 1H), 7.39-7.32 (m, 4H), 4.18 (ABdd, $\Delta\nu_{AB}$ = 21.1 Hz, J_{AB} = 6.1, 2.5 Hz, 2H), 4.05-3.98 (m, 2H), 2.46 (s, 3H), 1.83-1.76 (m, 1H), 1.70-1.62 (m, 1H), 1.55-1.49 (m, 1H), 1.36-1.29 (m, 1H), 1.10-1.04 (m, 1H), 1.02 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR: ($CDCl_3$, 150 MHz)

144.7, 135.5, 133.2, 131.5, 129.8, 129.7, 128.0, 127.9, 70.5, 29.0, 27.8, 21.7, 15.8, 15.7.

2-Phenylsilyl-4-methylpenataneoate



Following general procedure A, methyl 4-pentenoate (114 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (80 g SiO_2, 30 mm Ø, petroleum ether/diethylether 20:1) to give a mixture of 2-phenylsilyl-4-methylpenataneoate and 1-phenylsilyl-4-methylpenataneoate (190 mg, 0.86 mmol, 86%, 96:4) as a colourless oil.

TLC: R_f = 0.78 (petroleum ether/diethylether, 1:1) [$KMnO_4$]

MS: (HRMS – EI^+)

Found 222.10594 ($C_{12}H_{18}O_2{}^{28}Si$), requires 222.10706.

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H), 1753.9 cm^{-1} (C=O)

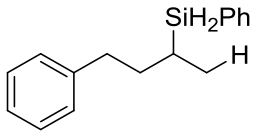
^{1}H NMR: (600 MHz, $CDCl_3$)

7.61-7.57 (m, 2H), 7.45-7.36 (m, 3H), 4.25 (ABdd, $\Delta\nu_{AB}$ = 24.8 Hz, J_{AB} = 6.1, 2.7 Hz, 2H), 3.68 (s, 3H), 2.49-2.35 (m, 2H), 1.96-1.89 (m, 1H), 1.70-1.64 (m, 1H), 1.22-1.16 (m, 1H), 1.10 (d, J = 7.2 Hz, 3H).

^{13}C NMR: (150 MHz, $CDCl_3$)

174.1, 135.7, 131.4, 129.7, 128.1, 51.6, 33.2, 28.4, 16.0, 15.6.

1-Phenyl-3-(phenylsilyl)butane



Following general procedure A, 4-phenyl-1-butene (150 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (50 g SiO_2, 20 mm Ø, petroleum ether/diethylether 20:1) to give a mixture of 1-phenyl-3-(phenylsilyl)butane and 1-phenyl-4-(phenylsilyl)butane (220 mg, 0.92 mmol, 92%, 95:5) as a colourless oil.

TLC: R_f = 0.65 (petroleum ether/diethylether, 1:1) [UV]

MS: (HRMS – EI^+)

Found 240.13153 ($C_{16}H_{20}{}^{28}Si$), requires 240.13288.

IR: *vmax (neat)*

2125.6 cm^{-1} (Si-H)

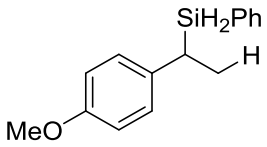
^{1}H NMR: (600 MHz, $CDCl_3$)

7.61-7.56 (m, 2H), 7.45-7.36 (m, 3H), 7.30-7.27 (m, 2H), 7.22-7.15 (m, 3H), 4.32-4.25 (m, 2H), 2.82-2.74 (m, 1H), 2.69-2.71 (m, 1H), 1.92-1.84 (m, 1H), 1.70-1.63 (m, 1H), 1.26-1.19 (m, 1H), 1.16 (d, *J* = 7.10 Hz, 3H).

^{13}C NMR: (150 MHz, $CDCl_3$)

142.5, 135.7, 131.9, 129.6, 128.4, 128.3, 128.0, 125.7, 35.4, 34.8, 16.0, 15.9.

[1-(4-Methoxyphenyl)-1-ethyl](phenyl)silane



Following general procedure A, 4-methoxystyrene (134 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (80 g SiO_2, 20 mm Ø, petroleum ether/diethylether 10:1) to give a mixture of [1-(4-

methoxyphenyl)-1-ethyl](phenyl)silane and [2-(4-methoxyphenyl)ethyl](phenyl)silane (210 mg, 0.87 mmol, 87%, 57:43) as a colourless oil.

TLC: R_f = 0.49 (petroleum ether/diethylether, 9:1) [UV]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (600 MHz, $CDCl_3$)

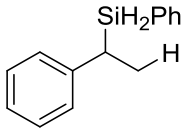
7.46-7.41 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.13-7.10 (m, 2H), 7.05-7.01 (m, 2H), 7.34-7.30 (m, 2H), 3.80 (s, 3H), 2.60-2.55 (m, 1H), 1.44 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

157.3, 136.6, 135.7, 131.6, 129.7, 128.0, 127.9, 113.9, 52.3, 24.3, 16.8.

The spectroscopic data were consistent with those reported.[156]

1-Phenyl-ethyl(phenylsilane)



Following general procedure A, styrene (115 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl_2] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/diethylether 50:1) to give a mixture of 1-phenyl-ethyl(phenylsilane) and 1-phenyl-2-(phenylsilyl)ethane (180 mg, 0.85 mmol, 85%, 5:95) as a colourless oil.

TLC: R_f = 0.58 (petroleum ether/diethylether, 9:1) [UV]

IR: *vmax (neat)*

2129.4 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

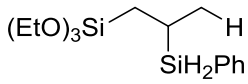
7.44-7.38 (m, 3H), 7.35-7.30 (m, 2H), 7.30-7.24 (m, 2H), 7.17-7.09 (m, 3H), 4.37-4.31 (m, 2H), 2.68-2.60 (m, 1H), 1.48 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

144.6, 135.7, 131.4, 129.7, 128.0, 127.9, 127.1, 125.0, 25.4, 16.4.

The spectroscopic data were consistent with those reported.[157]

[2-(Phenylsilyl)propyl]triethoxysilane



Following general procedure A, allyltriethoxysilane (225 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{Et}BIPCoCl$_2$] (2.8 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (45 g SiO_2, 30 mm Ø, petroleum ether/diethylether 50:1) to give [2-(phenylsilyl)propyl]triethoxysilane (266 mg, 0.85 mmol, 85%) as a colourless oil.

TLC: R_f = 0.45 (petroleum ether/diethylether, 9:1) [UV]

^{1}H NMR: (600 MHz, $CDCl_3$)

7.60-7.57 (m, 2H), 7.42-7.34 (m, 3H), 4.23 (ABdd, $\Delta\nu_{AB}$ = 20.3 Hz, J_{AB} = 6.4, 2.6 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 1.40-1.32 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 9H), 1.16 (d, *J* = 7.4 Hz, 3H), 0.90 (dd, *J* = 15.4, 4.5 Hz, 1H), 0.59 (dd, *J* = 15.4, 10.3 Hz, 1H).

^{13}C NMR: (150 MHz, $CDCl_3$)

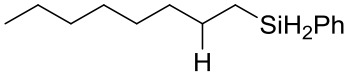
135.7, 132.3, 129.5, 127.9, 58.3, 18.6, 18.3, 13.8, 10.3.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−19.7, −46.2.

The spectroscopic data were consistent with those reported.[70]

1-(Phenylsilyl)octane



Following general procedure A, 1-octene (157 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography

(80 g SiO_2, 20 mm Ø, petroleum ether/diethylether 20:1) to give a mixture of 2-(phenylsilyl)octane and 1-(phenylsilyl)octane (211 mg, 0.96 mmol, 96%, 6:94) as a colourless oil.

TLC: R_f = 0.76 (pentane/diethylether, 1:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

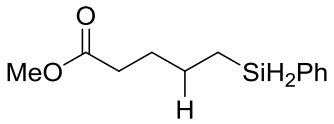
7.61-7.57 (m, 2H), 7.44-7.35 (m, 3H), 4.31 (t, *J* = 3.7 Hz, 2H), 1.51-1.44 (m, 2H), 1.41-1.34 (m, 2H), 1.33-1.24 (m, 8H), 0.99-0.93 (m, 2H), 0.90 (t, *J* = 7.25 Hz, 3H).

^{13}C NMR: (125 MHz, $CDCl_3$)

135.2, 132.9, 129.5, 128.0, 32.8, 31.9, 29.2 (2 x resonances), 25.1, 22.7, 14.1, 10.0.

The spectroscopic data were consistent with those reported.[70]

1-Phenylsilyl-4-methylpenataneoate



Following general procedure A, methyl 4-pentenoate (114 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl_2] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (80 g SiO_2, 20 mm Ø, petroleum ether/diethylether 9:1) to give a mixture of 2-phenylsilyl-4-methylpenataneoate and 1-phenylsilyl-4-methylpenataneoate (190 mg, 0.86 mmol, 86%, 4:96) as a colourless oil.

TLC: R_f = 0.75 (petroleum ether/diethylether, 1:1) [$KMnO_4$]

MS: (HRMS – EI^+)

Found 222.10499 ($C_{12}H_{18}O_2{}^{28}Si$), requires 222.10706.

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H), 1753.9 cm^{-1} (C=O)

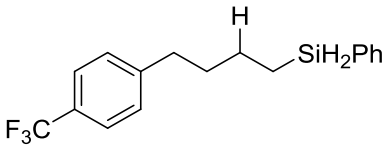
^{1}H NMR: (600 MHz, $CDCl_3$)

7.60-7.56 (m, 2H), 7.44-7.36 (m, 3H), 4.31 (t, *J* = 3.7 Hz, 2H), 3.68 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.73 (app. quin, *J* = 7.6 Hz, 2H), 1.54-1.48 (m, 2H), 1.01-0.95 (m, 2H).

^{13}C NMR: (150 MHz, $CDCl_3$)

174.1, 135.2, 132.4, 129.6, 128.0, 51.5, 33.7, 28.0, 24.7, 9.8.

1-(Phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane]



Following general procedure A, 4-(4-trifluoromethyphenyl)-1-butene (200 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (70 g SiO_2, 20 mm Ø, petroleum ether/diethylether 20:1) to give a mixture of 2-(phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane] and *1-(phenylsilyl)-4-[4-(trifluoromethyl)phenylbutane]* (298 mg, 0.97 mmol, 97%, 4:96) as a colourless oil.

TLC: R_f = 0.80 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

MS: (HRMS – EI$^+$)

Found 308.11845 ($C_{17}H_{19}F_3{}^{28}Si$), requires 308.12027.

IR: *vmax (neat)*

2129.4 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.51 (m, 4H), 7.43-7.36 (m, 3H), 7.29-7.24 (m, 2H), 4.31 (t, *J* = 3.6 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.76-1.68 (m, 2H), 1.57-1.50 (m, 2H), 1.03-0.97 (m, 2H).

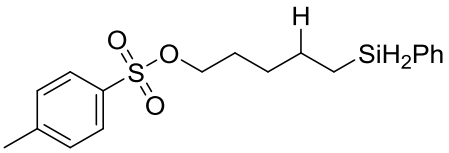
^{13}C NMR: (125 MHz, $CDCl_3$)

146.6, 135.2, 132.4, 129.6, 128.7, 128.3 (q, *J* = 31.9 Hz), 128.0, 125.2 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 271.0 Hz), 35.4, 34.2, 24.6, 9.9.

^{19}F NMR: (471 MHz, $CDCl_3$)

–62.3.

1-Phenylsilyl-5-(4-methylsulfonyloxy)pentane



Following general procedure A, 5-(4-methylsulfonyloxy)pentene (240 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (60 g SiO_2, 20 mm Ø, pentane/diethylether 20:1 to 10:1) to give a mixture of 2-(phenylsilyl)-5-(4-methylsulfonyloxy)pentane and *1-(phenylsilyl)-5-(4-methylsulfonyloxy)pentane* (313 mg, 0.90 mmol, 90%, 7:93) as a yellow oil.

TLC: R_f = 0.63 (pentane/diethylether, 1:1) [UV]

MS: (HRMS – EI^+)

Found 371.11040 ($C_{18}H_{24}O_3{}^{23}Na^{32}S^{28}Si$), requires 371.11077.

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

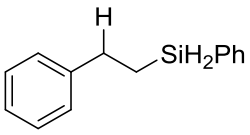
^{1}H NMR: (500 MHz, $CDCl_3$)

7.82-7.77 (m, 2H), 7.56-7.53 (m, 2H), 7.42-7.32 (m, 5H), 4.26 (t, *J* = 3.8 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 1.64 (app. quin., *J* = 7.3 Hz, 2H), 1.44-1.34 (m, 4H), 0.92-0.86 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

144.6, 135.2, 133.3, 132.3, 129.8, 129.6, 128.0, 127.9, 70.5, 28.5, 24.5, 21.7, 9.9.

1-Pheny-2-(phenylsilyl)ethane



Following general procedure A, styrene (115 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (50 g SiO_2, 20 mm Ø, petroleum ether/diethylether 10:1) to give a mixture of 1-phenyl-ethyl(phenylsilane) and 1-phenyl-2-(phenylsilyl)ethane (191 mg, 0.90 mmol, 90%, 5:95) as a colourless oil.

TLC: R_f = 0.63 (pentane/diethylether, 1:1) [UV]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (600 MHz, $CDCl_3$)

7.60-7.56 (m, 2H), 7.44-7.36 (m, 3H), 7.31-7.27 (m, 2H), 7.23-7.17 (m, 3H), 4.33 (t, *J* = 3.6 Hz, 2H), 2.79 (t, *J* = 8.6 Hz, 2H), 1.35-1.30 (m, 2H).

^{13}C NMR: (150 MHz, $CDCl_3$)

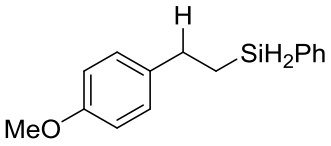
144.1, 135.4, 132.3, 129.8, 128.5, 128.2, 128.1, 126.0, 31.3, 12.3.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−30.9.

The spectroscopic data were consistent with those reported.[81]

[2-(4-Methoxyphenyl)ethyl]phenylsilane



Following general procedure A, 4-methoxystyrene (134 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (50 g SiO_2, 20 mm Ø, petroleum ether/diethylether 10:1) to give a mixture of [1-(4-methoxyphenyl)ethyl]phenylsilane and [2-(4-methoxyphenyl)ethyl]phenylsilane (227 mg, 0.94 mmol, 94%, 5:95) as a colourless oil.

TLC: R_f = 0.64 (petroleum ether/diethylether, 1:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

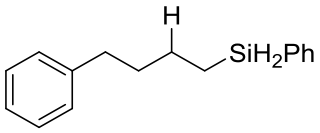
7.61-7.57 (m, 2H), 7.43-7.34 (m, 3H), 7.21-7.14 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.12 Hz, 1H), 4.32 (t, *J* = 3.7 Hz, 2H), 3.81 (s, 3H), 2.82-2.77 (m, 2H), 1.33-1.27 (m, 2H).

^{13}C NMR: (150 MHz, $CDCl_3$)

157.7, 136.1, 135.3, 132.2, 129.6, 128.8, 128.0, 113.8, 55.3, 30.3, 12.3.

The spectroscopic data were consistent with those reported.[66]

1-Phenyl-4-(phenylsilyl)butane



Following general procedure A, 4-phenyl-1-butene (150 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl_2] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (60 g SiO_2, 20 mm Ø, petroleum ether/diethylether 20:1 to 10:1) to give a mixture of 2-phenyl-4-(phenylsilyl)butane and 1-phenyl-4-(phenylsilyl)butane (218 mg, 0.91 mmol, 91%, 6:94) as a colourless oil.

TLC: R_f = 0.76 (pentane /diethylether, 1:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

^{1}H NMR: (500 MHz, $CDCl_3$)

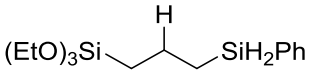
7.59-7.55 (m, 2H), 7.34-7.35 (m, 3H), 7.30-7.26 (m, 2H), 7.20-7.14 (m, 3H), 4.30 (t, *J* = 3.6 Hz, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 1.74 (m, 2H), 1.57-1.49 (m, 2H), 1.02-0.96 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

142.6, 135.2, 132.7, 129.5, 128.4, 128.3, 128.0, 125.6, 35.6, 34.5, 24.8, 9.9.

The spectroscopic data were consistent with those reported.[81]

(3-Triethoxysilyl)propylsilylbenzene



Following general procedure A, allyltriethoxysilane (226 µL, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (35 g SiO_2, 20 mm Ø, petroleum ether/diethylether 50:1) to give a mixture of [2-phenylsilyl)propyl]triethoxysilane and (3-triethoxysilyl)propylsilylbenzene (280 mg, 0.94 mmol, 94%, 5:95) as a colourless oil.

TLC: R_f = 0.45 (petroleum ether/diethylether, 9:1) [UV/$KMnO_4$]

IR: *vmax (neat)*

2127.5 cm^{-1} (Si-H)

MS: (HRMS – EI^+)

Found 311.14846 ($C_{15}H_{27}O_3{}^{28}Si$), requires 311.14933.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.55 (m, 2H), 7.42-7.33 (m, 3H), 4.30 (t, *J* = 3.7 Hz, 2H), 3.81 (q, *J* = 6.9 Hz, 6H), 1.67-1.58 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 1.08-1.02 (m, 2H), 0.81-0.73 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

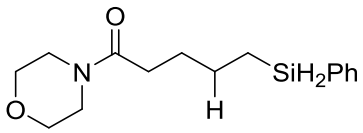
135.2, 132.6, 129.5, 127.9, 58.3, 18.7, 18.3, 14.1, 13.9.

^{29}Si NMR: (99 MHz, $CDCl_3$)

−32.1, −45.9.

The spectroscopic data were consistent with those reported.[70]

1-(Phenylsilyl)-*N*-(4-pentanoyl)morpholine



Following general procedure A, *N*-(4-pentenoyl)morpholine (169 mg, 1.0 mmol), phenylsilane (135 µL, 1.1 mmol), sodium *tert*-butoxide (1 mg, 1 mol%) and [^{iPr}BIPCoCl$_2$] (3.1 mg, 5.0 µmol, 0.5 mol%) were reacted in anhydrous tetrahydrofuran (2.5 mL) and the crude mixture purified by flash column chromatography (40 g SiO_2, 30 mm Ø, petroleum ether/diethyl ether 1:1 to 0:1) to give a mixture of 2-(phenylsilyl)-*N*-(4-pentanoyl)morpholine and 1-(phenylsilyl)-*N*-(4-pentanoyl)morpholine (235 mg, 0.85 mmol, 85%, 15:85) as a colourless oil.

TLC: R_f = 0.14 (petroleum ether/diethylether, 1:1) [$KMnO_4$]

IR: *vmax (neat)*

2125.6 cm^{-1} (Si-H)

MS: (HRMS – EI^+)

Found 276.14020 ($C_{15}H_{22}O_2N^{28}Si$), requires 276.14143.

^{1}H NMR: (500 MHz, $CDCl_3$)

7.59-7.54 (m, 2H), 7.43-7.34 (m, 3H), 4.30 (t, *J* = 3.8 Hz, 2H), 3.70-3.56 (m, 6H), 3.43 (t, *J* = 4.6 Hz, 2H), 1.72 (app. quin, *J* = 7.7 Hz, 2H), 1.55-1.48 (m, 2H), 1.01-0.95 (m, 2H).

^{13}C NMR: (125 MHz, $CDCl_3$)

171.6, 135.2, 132.4, 129.6, 128.0, 67.0, 66.7, 46.0, 41.9, 32.8, 28.3, 25.0, 10.0.

6.0 References

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7.0 Appendix: Publications

Journal Publications (chronological order):

1. **Docherty, J. H**.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and Discovery of Earth-Abundant Metal Catalysts Using Sodium *tert*-Butoxide. *Nature Chemistry* **2017**, *9* (6), 595–600.
2. Peng, J.; **Docherty, J. H**.; Dominey, A. P.; Thomas, S. P. Cobalt-Catalysed Markovnikov Selective Hydroboration of Vinylarenes. *Chemical Communications* **2017**, *53* (34), 4726–4729.
3. Ang, N.; Buettner, C.; Docherty, S.; Bismuto, A.; Carney, J.; **Docherty, J. H**.; Cowley, M.; Thomas, S. Borane-Catalysed Hydroboration of Alkynes and Alkenes. *Synthesis* **2018**, *50* (04), 803–808.

Book Chapters:

1. Iron Oxides and Simple Iron Salt-based Catalysis. **Docherty, J. H.** and Thomas, S. P., in *Sustainable Catalysis: With Non-endangered Metals, Part 1*.; North, M Ed.; The Royal Society of Chemistry, **2015**, pp. 344-372.