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Recent Advances in the Synthetic and Mechanistic Aspects of the Ruthenium-catalyzed Carbon-heteroatom Bond Forming Reactions of Alkenes and Alkynes

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Recent Advances in the Synthetic and Mechanistic Aspects of the Ruthenium-Catalyzed Carbon-Heteroatom Bond Forming Reactions of Alkenes and Alkynes

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Abstract: The group's recent advances in catalytic carbon-to-heteroatom bond forming reactions of alkenes and alkynes are described. For the C–O bond formation reaction, a well-defined bifunctional ruthenium-amido catalyst has been successfully employed for the conjugate addition of alcohols to acrylic compounds. The ruthenium-hydride complex $(PCy_3)_2(CO)RuHCl$ was found to be a highly effective catalyst for the regioselective alkyne-to-carboxylic acid coupling reaction in yielding synthetically useful enol ester products. Cationic ruthenium-hydride catalyst generated *in-situ* from $(PCy_3)_2(CO)RuHCl/HBF_4{\cdot}OEt_2$ was successfully utilized for both the hydroamination and related C–N bond forming reactions of alkenes. For the C–Si bond formation reaction, regio- and stereoselective dehydrosilylation of alkenes and hydrosilylation of alkynes have been developed by using a well-

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defined ruthenium-hydride catalyst. Scope and mechanistic aspects of these carbon-to-heteroatom bond-forming reactions are discussed.

Keywords: ruthenium catalyst, alkene, alkyne, carbon-heteroatom bond

1. Introduction

Designing effective catalytic carbon-to-heteroatom (C–X; X = N, O, Si) bond formation reactions constitutes an active area of research that has a wide range of potential applications in both fine and industrial chemical syntheses. For example, transition metal-catalyzed hydroamination of alkenes and alkynes is a highly effective C–N bond forming method to produce elaborated organic amines in an atom-economical way [1]. While remarkable progress has been achieved in developing catalytic methods for both inter- and intramolecular hydroamination of alkenes, dienes and alkynes during the last decades [2], *anti*-Markovnikov-selective hydroamination of simple alkenes still remains an elusive goal [3]. For C–O bond formation reactions via O-H bond activation, late transition metal catalysts have been found to be particularly effective in promoting a number of industrially significant processes, such as Wacker-type oxidation reaction and water-gas shift and hydration reactions, in producing oxygenated organic products [4]. Late transition metal catalysts have also been found to be effective for mediating C–Si bond formation reactions of alkenes and alkynes [5]. Homogeneous catalytic hydrosilylation and related oxidative silylation reactions have been widely utilized in both commercial syntheses of silicone rubbers [6] as well as in the synthesis of organosilicon compounds [7]. Current challenges in these catalytic C–X bond formation reactions are: to develop chemo- and regioselective catalytic systems which can lead to an extension of the reaction scope, and to establish both clear mechanistic pathways and the nature of reactive intermediate species for such processes. For a number of years, we have been investigating the fundamental aspects of catalytic bond activation reactions, and this report presents a summary of the group's synthetic and mechanistic efforts in ruthenium catalyzed C–X bond formation reactions.

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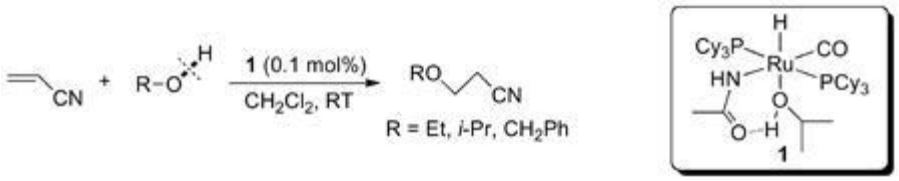
2. Catalytic C–O bond formation reactions via O–H bond activation: conjugate addition of alcohols to acrylic compounds

Conjugate addition of heteroatom nucleophiles to α,β-unsaturated carbonyl compounds has been shown to be an effective C–O bond forming method for producing biologically important β-amino acid derivatives and β-alkoxyketones [8]. Compared to the traditional methods based on stoichiometric reagents, transition metal-catalyzed conjugate addition reaction provides an efficient method for forming new C–O bonds in chemo- and stereoselective manner under environmentally benign conditions.



(1)

We discovered that the ruthenium-acetamido complex **1** is a highly active catalyst for the conjugate addition reactions of alcohols [9]. In a typical setting, the treatment of acrylonitrile with excess amount of an alcohol in the presence of **1** (0.1–0.5 mol %) in CH_2Cl_2 cleanly led to the addition product at room temperature (Eq 1). The amido complex **1** exhibited uniquely high catalytic activity among selected ruthenium complexes under mild conditions without using any additives.

Mechanism of the conjugate addition reaction was examined. First, the reaction rate was found to be virtually independent of [PCy_3] at room temperature. A considerably lower reaction rate in coordinating solvents such as Et_2O and THF (k_{obs} = 1.6 × 10^{-4} s^{-1} and 9.6 × 10^{-5} s^{-1}, respectively) than in non-coordinating ones such as CH_2Cl_2 and benzene (k_{obs} = 2.3 × 10^{-4} s^{-1} and 6.5 × 10^{-4} s^{-1}, respectively) suggests a strong inhibition by coordinating solvent molecules. The Hammett correlation from a series of *para*-substituted benzyl alcohols *p*-X-$C_6H_4CH_2OH$ (X = OMe, CH_3, H, Cl; ρ = +0.18) showed that the reaction is moderately promoted by the alcohol substrate with electron-withdrawing group. Also, the most pronounced

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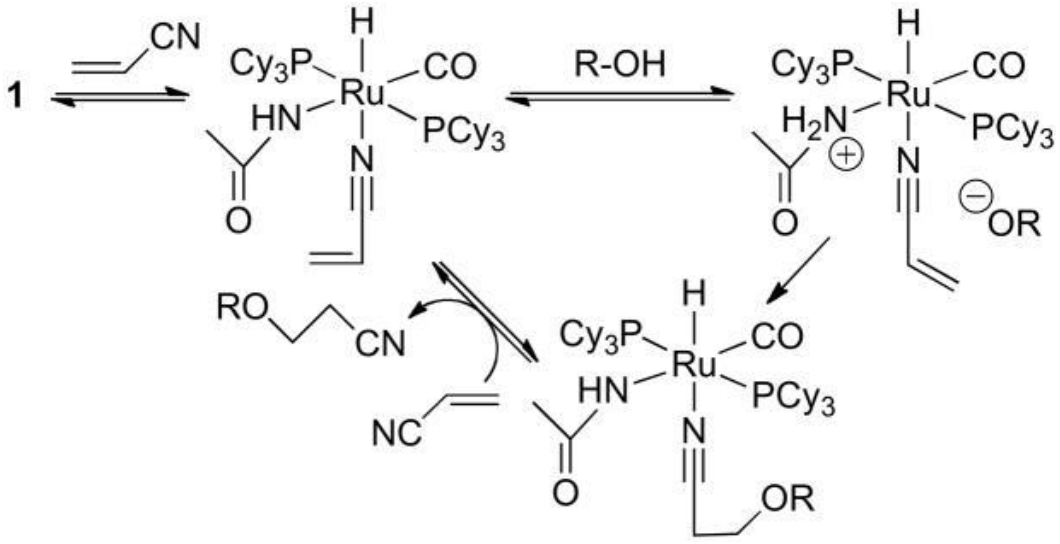
carbon isotope effect was observed on the β-carbon of the carbonyl substrate as analyzed by using Singleton's carbon isotope measurement technique [10]. On the basis of these results, we proposed a mechanism of the conjugate addition reaction involving the bifunctional ruthenium-amido catalyst involving "bifunctional" ruthenium-amido catalyst for mediating heterolytic bond activation reaction (Scheme 1). The key features of the proposed mechanism involve a Lewis acidic ruthenium center for facilitating *N*-coordination of acrylonitrile and the basic amido ligand for promoting heterolytic O–H bond cleavage of the alcohol substrate.



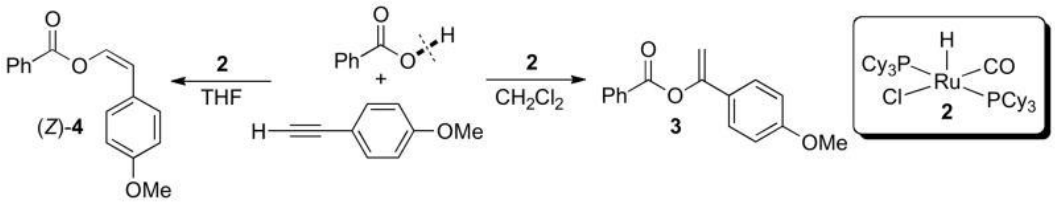
Scheme 1

2.2. Formation of enol esters from the coupling reaction of alkynes and carboxylic acids

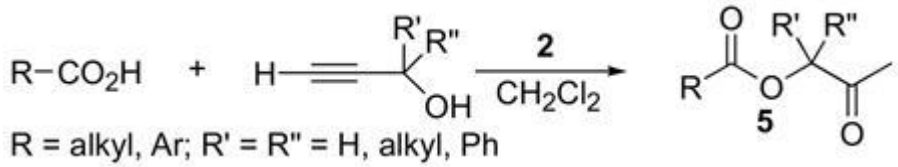
Enol esters are a versatile class of precursors for a variety of synthetically important organic transformations such as asymmetric hydrogenation and Aldol- and Mannich-type of condensation reactions [11]. Compared to the classical methods that utilize stoichiometric amounts of strong base or toxic Hg salts, transition metal-catalyzed alkyne-to-carboxylic acid coupling reaction offers considerable advantages in terms of increasing synthetic efficiency as well as for reducing waste byproducts. However, despite such salient features, its synthetic potential has not been fully exploited in part because the

catalytic method typically produces a mixture of *gem*- and (*E*)/(*Z*)-enol ester products [12]. In general, transition metal-catalyzed alkyne-to-carboxylic acid coupling reaction has been found to favor *anti*-Markovnikov addition of carboxylic acids to produce a mixture of (*E*)- and (*Z*)-enol esters over *gem*-enol ester products, but recent efforts have led to the development of regioselective formation of *gem*-enol esters by using Ru and Rh catalysts [13]. For example, Goossen and co-workers reported that the regioselectivity of the coupling reaction could be controlled by using different base in forming both Markovnikov (Na_2CO_3) and the *anti*-Markovnikov addition products (DMAP) [13c]. Dixneuf achieved a regioselective 2:1 alkyne-to-carboxylic acid coupling reaction to form the dienyl esters by using Cp*Ru(COD)Cl catalyst, in which a ruthenacyclopentadiene complex has been proposed as the key intermediate species for the coupling reaction [14]. Both intra- and intermolecular versions of the catalytic alkyne-to-carboxylic acid coupling methods have been successfully applied to the synthesis of complex organic molecules [15].

We recently discovered that a coordinatively usaturated ruthenium-hydride complex $(PCy_3)_2(CO)RuHCl$ (**2**) exhibits uniquely high catalytic activity and selectivity patterns for the alkyne-to-carboxylic acid coupling reaction in giving the enol ester products (Scheme 2) [16]. A particularly remarkable feature for the catalyst **2** is that excellent degree of solvent-control effect was observed in facilitating regio- and stereoselective formation of the enol ester products. Thus, the coupling reaction in CH_2Cl_2 led to the exclusive formation of the *gem*-enol ester product **3** for both aliphatic and aryl-substituted terminal alkynes. In contrast, the coupling reaction for aryl-substituted alkynes in THF predominantly gave the (*Z*)-enol ester products (*Z*)-**4**. A relatively low catalyst loading (1–2 mol %) was used for the coupling reaction, and the enol ester products were isolated in high yields after a simple column chromatography on silica gel.



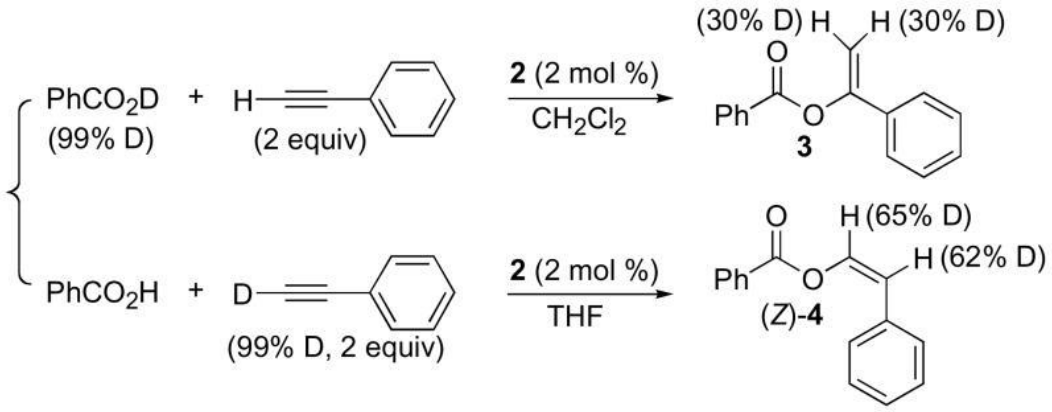
Scheme 2



(2)

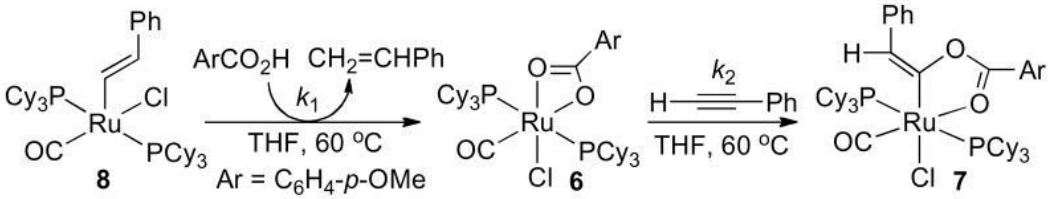
The synthetic efficacy of the ruthenium catalyst **2** was further extended to the coupling reaction of carboxylic acids with propargylic alcohols (Eq 2). The catalyst **2** was found to catalyze the coupling reaction of carboxylic acids with propargylic alcohols to give the ester products **5** in high yields, in which the exclusive formation of the acetomethyl ester product **5** was resulted from the Markovnikov-selective hydration of the alkynes. Previously, the formation of ketoesters has been explained via a Markovnikov-selective addition followed by an intramolecular transesterification steps [17].

We performed detailed kinetic and mechanistic studies on the coupling reaction. First, inverse rate dependence on added [PCy_3] indicates that active Ru catalyst is formed by a reversible dissociation of the phosphine ligand. The treatment of $PhCO_2D$ with PhC≡CH (2.0 equiv) and **2** (2 mol %) in CH_2Cl_2 at 95 °C yielded the *gem*-enol ester product **3** with ca. 30% D on both vinyl positions as determined by ^1H and ^2H NMR (Scheme 3). Conversely, the reaction of $PhCO_2H$ with PhC≡CD (2 equiv) in THF formed the products (*Z*)-**4** with nearly equal amounts of the deuterium (62–65%) on both vinyl positions. In a control experiment, the treatment of $PhCO_2D$ with PhC≡CH (2.0 equiv) in the presence of **2** (2 mol %) led to almost complete H/D exchange within 10 min at 95 °C prior to the product formation. These results indicate that the H/D exchange between the acid and alkynyl hydrogens is rapid and reversible, and that neither the alkynyl C–H bond nor the carboxylic acid O–H bond activation step is rate-limiting for the coupling reaction.



Scheme 3

The catalytically relevant ruthenium-carboxylate and -vinylcarboxylate complexes have been successfully isolated from the reaction of **2** with a carboxylic acid and a terminal alkyne (Scheme 4). For example, the treatment of **2** with *p*-OMe-$C_6H_4CO_2H$ in CH_2Cl_2 led to the clean formation of the ruthenium-carboxylate complex **6**. The further reaction of the ruthenium-carboxylate complex **6** with a terminal alkyne led to the coupling product **7**, which clearly implicates the formation of the (*Z*)-enol ester product (*Z*)-**4**.



Scheme 4

The successful isolation of the catalytically relevant complexes **6** and **7** enabled us to further examine kinetics for the formation of these complexes. The treatment of **2** with excess *p*-OMe-$C_6H_4CO_2H$ (10 equiv) and HC≡CPh (15 equiv) in THF initially formed the previously known ruthenium-vinyl complex **8** after 15 min at room temperature. The vinyl complex **8** was slowly converted to the carboxylate complex **6**, which in turn was converted to the vinyl-carboxylate complex **7** upon warming to 60 °C. The kinetics of the conversion of the vinyl complex **8** to the vinylcarboxylate complex **7** was successfully fitted to

the two-consecutive reaction kinetics (k_1 = 0.039 min^{-1} and k_2 = 0.013 min^{-1}).

We proposed a mechanism of the coupling reaction involving a coordinatively unsaturated ruthenium-carboxylate complex **9** as one of the key intermediate species (Scheme 5). The phosphine inhibition study suggests that the catalytically active 16 e- complex **9** is formed from the Ru-carboxylate complex **6** by a reversible phosphine dissociation. For the coupling reaction in a non-coordinating solvent CH_2Cl_2, the direct migratory insertion of the internal carbon of the alkyne substrate to Ru-O bond would be sterically preferred over to the terminal carbon in giving the *gem*-enol ester product **3**. The dative coordination of carboxylic oxygen atom should also promote the insertion by stabilizing intermediate species. On the other hand, the formation of (*Z*)-enol ester product (*Z*)-**4** is rationalized by invoking the formation of Ru-vinylidene species **10**. The ability of the ruthenium catalyst to promote the acetylene-to-vinylidene rearrangement seems to be a determining factor for the stereoselective formation of (*Z*)-enol ester products, and in this regard, the coordinating solvent THF should facilitate such rearrangement by stabilizing a coordinatively unsaturated Ru-vinylidene species.

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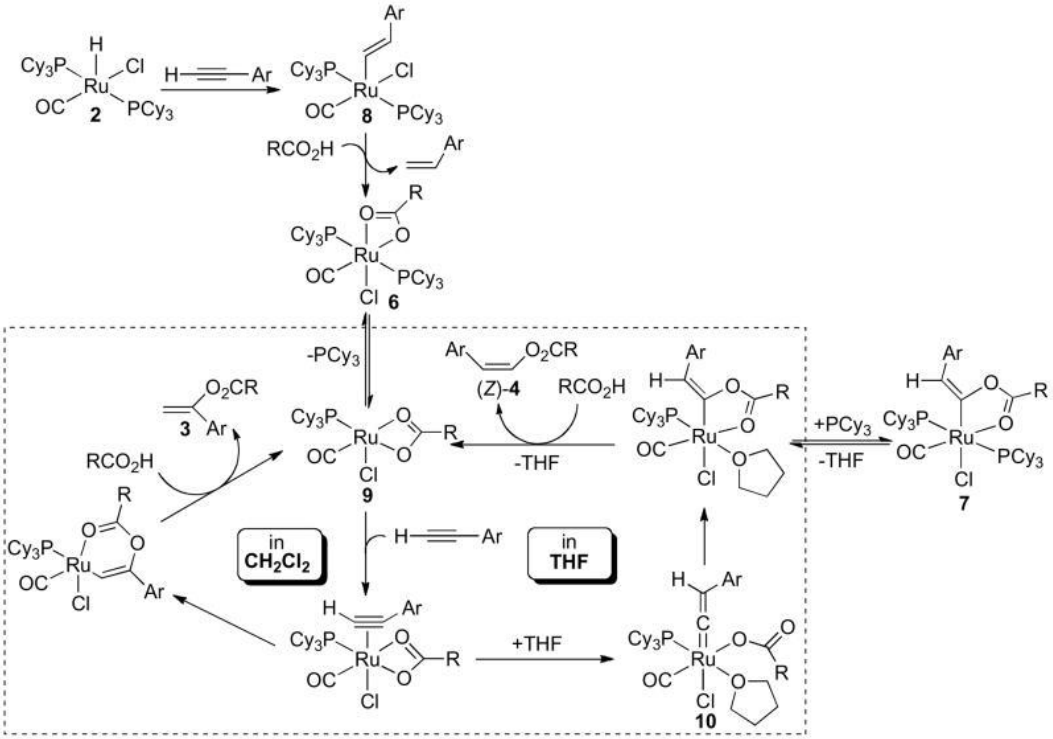
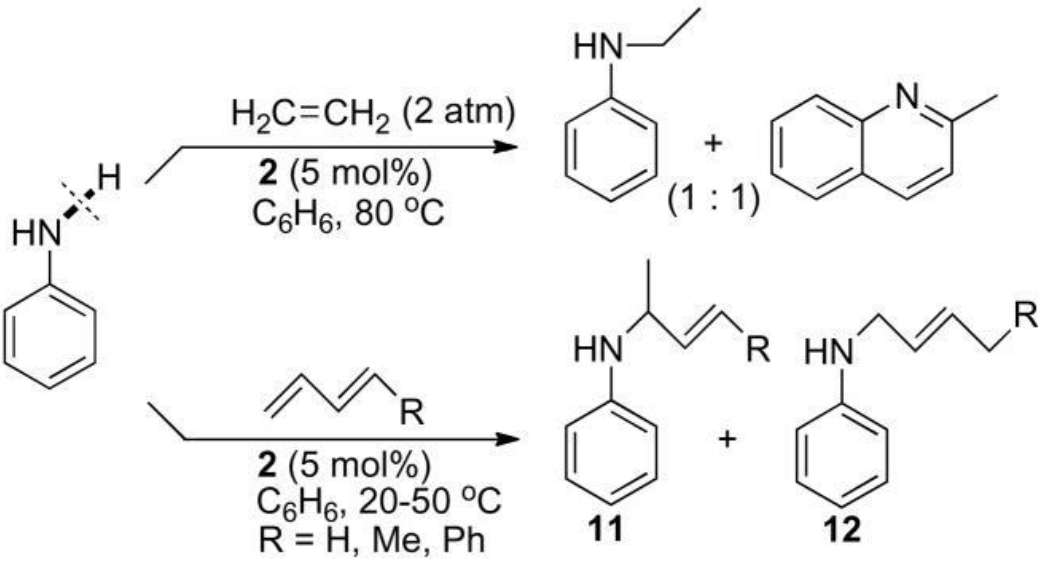


Scheme 5 Proposed mechanism of the coupling reaction of carboxylic acids and terminal alkynes.

3. Catalytic C–C and C–N bond formation reactions via N–H bond activation: hydroamination of ethylene and dienes

Since Milstein's pioneering report on Ir-catalyzed hydroamination reaction of norbornene [18], a number of highly effective late transition metal catalysts have developed for the hydroamination of alkenes and dienes as well as for asymmetric version of the reaction [2]. Recently, several groups have also achieved *anti*-Markovnikov-selective hydroamination of α-olefins and intramolecular hydroamination of unactivated alkenes by using Pd and Ru catalysts [3]. One of the current challenges for the hydroamination reaction centers on the development of practical catalytic systems, which leads to an extension of reaction scope, and are applicable to asymmetric synthesis of chiral amines.

We found that the cationic ruthenium-hydride complex, formed *in-situ* from **2**/$HBF_4 \cdot OEt_2$, is an effective catalyst for the hydroamination of ethylene and dienes (Scheme 6) [19]. For example, the treatment of aniline with ethylene in the presence of **2**/$HBF_4 \cdot OEt_2$ (5 mol %) in benzene at 80 °C gave a ~1:1 mixture of *N*-ethylaniline and 2-methylquinoline in 71% combined yield. Only ethylene was found to give the coupling products among selected alkenes; no activity was observed with α-olefins. In contrast, both primary arylamines and secondary benzocyclic amines reacted smoothly with 1,3-dienes at a considerably lower temperature (20–50 °C) to form the Markovnikov addition product **11** predominantly over the *anti*-Markovnikov addition product **12**. No *ortho*-C–H bond insertion product was observed for these dienes. The observation of the normal isotope effect of k_{NH}/k_{ND} = 2.2 (aniline and aniline-d_7 at 80 °C) and the Hammett ρ = −0.43 (correlation of *para*-substituted *p*-X-$C_6H_4NH_2$) suggest of an N-H bond activation rate-limiting step for the hydroamination reaction.

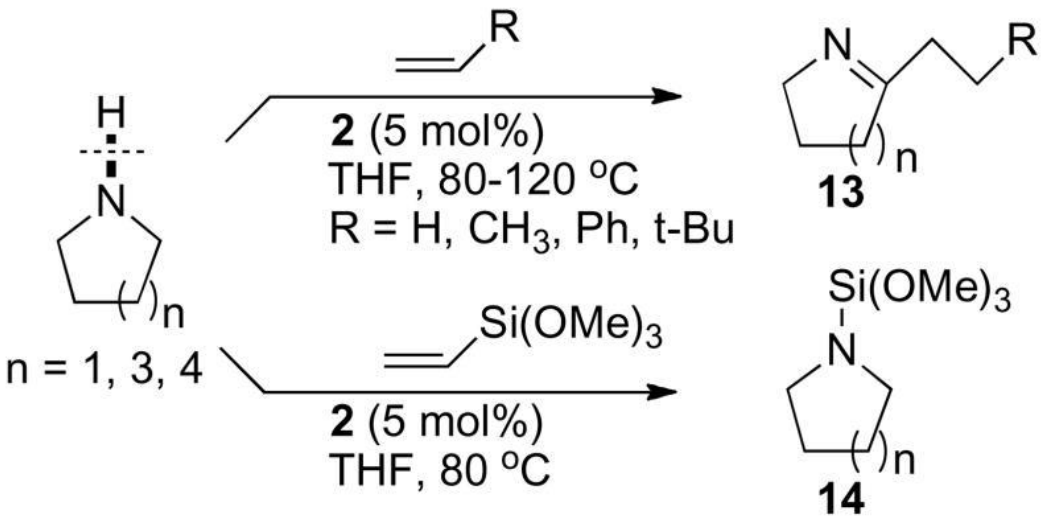


Scheme 6

3.1. Cyclic imine vs N*-silylamine formation*

An unusually selective dehydrogenative coupling reaction of cyclic amines and alkenes has been discovered by using the ruthenium-hydride catalyst **2** (Scheme 7) [20]. The coupling reaction

of secondary cyclic amines with unactivated alkenes preferentially gave the cyclic imine products **13**, in which both α-C–H and N–H bonds of amines have been selectively activated. In contrast, the reaction with a vinylsilane selectively yielded the *N*-silylation products **14**. The catalytically active anionic ruthenium-amido complex was isolated from the reaction mixture, and its structure was established by X-ray crystallography. The preliminary mechanistic studies suggested that both C–H and N–H bond activation steps are mediated by a highly unsaturated ruthenium-amido species.

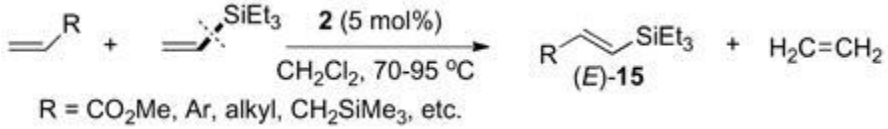


Scheme 7

4. Catalytic C–Si bond formation reactions: regio- and stereoselective hydrosilylation and oxidative silylation of alkenes and alkynes

Considerable efforts to develop new catalytic methods for vinylsilanes have been in part motivated by their versatility as reagents for both fine chemical and polymer synthesis [21]. Late transition metal catalysts such as H_2PtCl_6 and $(PPh_3)_3RhCl$ have been commonly used for the hydrosilylation of alkynes [5], but the catalytic method has been known to produce a mixture of vinylsilanes and other byproducts. Catalytic oxidative silylation reaction has been emerged as a viable alternative method for forming vinylsilanes, as exemplified by Wakatsuki's ruthenium-catalyzed dehydrosilylation of alkenes [22]. On

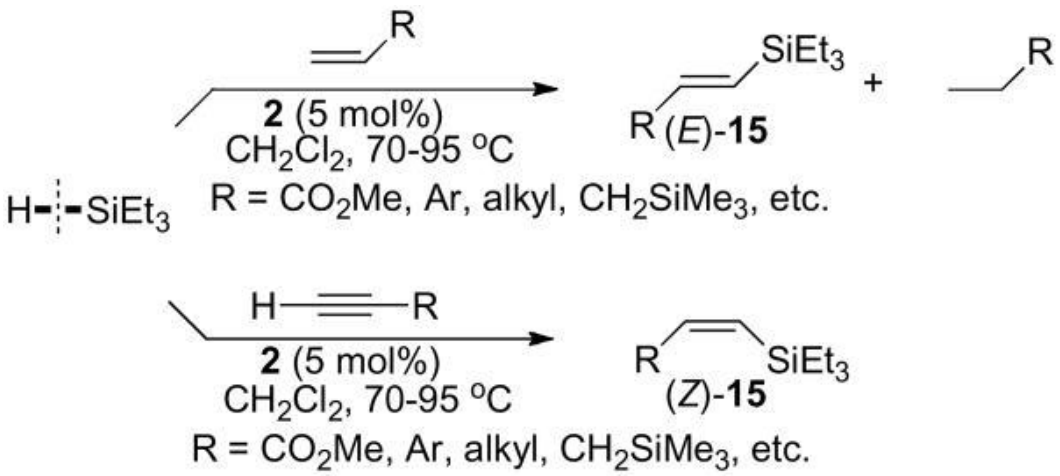
the basis of detailed kinetic and mechanistic study by using well-defined cationic Co and Pd complexes, Brookhart proposed a mechanism of the dehydrogenative silylation reactions of alkenes, as the vinylsilane formation could not be readily explained by a classical Chalk-Harrod mechanism [23].



(3)

We initially found that the ruthenium-hydride complex **2** is an active catalyst for the dehydrogenative silylation of alkenes (Eq 3) [24]. For example, the treatment of styrene and 1.5 equiv of CH_2=$CHSiEt_3$ in the presence of **2** (1.0 mol %) in CH_2Cl_2 solution at 95 °C led to the dehydrosilylation product (*E*)-**15** (>95% yield after 4 h). The formation of a trace amount of the hydrosilylation product and the homocoupling product Et_3SiCH=$CHSiEt_3$ was also detected by the GC.

Regio- and stereoselective formation of vinylsilanes has also been achieved from the silylation reactions of alkenes and alkynes (Scheme 8) [24, 25]. Regioselective dehydrosilylation of α-olefins with $HSiEt_3$ was achieved in forming *trans*-vinylsilane (*E*)-**15**, while the analogous treatment of terminal alkynes and $HSiEt_3$ led to the exclusive formation of the *cis*-vinylsilane product (*E*)-**15**. In the latter case, a mixture of cis and trans products (*Z*)/(*E*)-**15** was resulted from the alkynes with sterically demanding group (R = Cy, *t*-Bu). The preliminary mechanistic investigations suggest the involvement of a Ru-vinyl species, but much research still awaits for establishing the detailed reaction mechanism and for elucidating the factors governing the product formation. Transition metal-catalyzed alkyne hydrosilation reaction has been successfully employed in the synthesis of complex organic molecules as well as polymeric and surface materials [26].



Scheme 8

5. Conclusions

The group's recent advances in catalytic C–X bond formation reactions (X = O, N, Si) have been highlighted. The bifunctional ruthenium-amido catalyst **1** was found to be effective for the conjugate addition of alcohols to acrylic compounds. Regioselective alkyne-to-carboxylic acid coupling reaction as well as the oxidative silylation of alkenes and alkynes have been realized by using a well-defined 16-electron ruthenium-hydride catalyst **2**. The cationic ruthenium-hydride catalyst generated *in-situ* from **2**/$HBF_4 \cdot OEt_2$ was successfully employed for the hydroamination and related C–N bond forming reactions. Mechanistic knowledge gained from these study would be invaluable in designing the next generation of metal catalysts.

Footnotes

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