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# Solvent-Free Hydrosilylation of Terminal Alkynes by Reaction with a Nonclassical Ruthenium Hydride Pincer Complex

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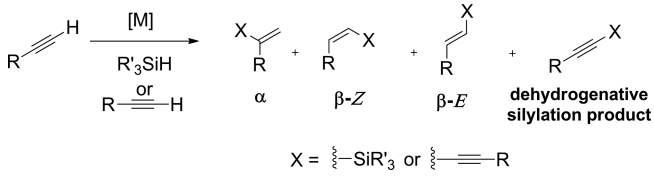
**Keywords:** C–H activation / Hydrosilylation / Dehydrogenative silylation / Nonclassical hydrides / Alkynes / Ruthenium

Upon the simple addition of substrates, the ruthenium pincer complex [Ru($^{t\text{Bu}}$PNP)(H$_2$)(H)$_2$] [**1**; $^{t\text{Bu}}$PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine] is an active and selective catalyst system for the hydrosilylation of terminal alkyl alkynes under mild, solvent-free conditions. The reactivity of this system for other functionalized terminal alkynes was also investigated, and we observed competing catalytic cycles that produce both alkyne dimers and dehydrogenative silylation products. Kinetic measurements for the hydrosilylation of 1-octyne show that the catalyst has an initial turnover frequency of 121 h$^{-1}$ at room temperature. The stoichiometric reaction between **1** and H$_2$SiPh$_2$ yields [Ru($^{t\text{Bu}}$PNP)(H)$_2$(H$_2$SiPh$_2$)], which undergoes Si–H bond activation to yield the catalytically active species [Ru($^{t\text{Bu}}$PNP)(HSiPh$_2$)(H)]. The reaction of **1** with phenylacetylene yielded [Ru($^{t\text{Bu}}$PNP)(H)$_2$(HC≡CPh)] and [Ru($^{t\text{Bu}}$PNP)(H)(C≡CPh)(HC≡CPh)], and we propose that the latter is the active species in the dimerization reaction.

## Introduction

The hydrosilylation of terminal alkynes offers an important route to alkenylsilanes, which have applications in organic synthesis and silicone polymer production. The production of organosilicon compounds, in general, is important for the photoresistor, semiconductor, adhesive and binder industries.[1] Therefore, the hydrosilylation of a range of unsaturated bonds such as carbonyl groups has also been investigated.[2] Catalytic hydrosilylation reactions have been performed with a variety of silanes and metal catalysts for both internal and terminal alkynes,[3] but the reactions generally suffer from low selectivities; therefore, selective synthetic protocols that make use of homogeneous catalysts under mild conditions are desirable.[2d]

The hydrosilylation of terminal alkynes can give different isomeric products, namely, the α isomer, the two β stereoisomers (*Z* and *E*) and also the dehydrogenative silylation product (Scheme 1). Selectivity for the different isomers can be achieved by variation of the catalytic system. A mechanism proposed by Crabtree and Ojima also includes an explanation of how isomerization to reduce steric interactions between the complex and the alkylsilane moiety can lead to the formation of the thermodynamically disfavoured *Z* isomer.[4]




Scheme 1. Reactions of terminal alkynes to yield hydrosilylation, dimerization and dehydrogenative coupling products.

Under hydrosilylation reaction conditions, it is also possible to have competing catalytic cycles that produce dehydrogenative silylation products[2a,4a,5] and oligomers of terminal alkynes (Scheme 1).[6] For example, Field and coworkers observed simultaneous hydrosilylation and dimerization for a variety of terminal alkynes with Co, Ru and Ir catalysts.[6j] Alkyne dimerization reactions to enynes can potentially occur by different mechanisms via vinylidene and alkyne intermediates and, as in the hydrosilylation reaction, it is possible to obtain the *E*, *Z* and α isomers (Scheme 1). For example, the formation of vinylidene complexes by the reactions of terminal alkynes with several different metal centres, including a ruthenium PNP pincer complex,[7] are well known.[6m,7,8] The development of efficient, selective catalytic systems for these competing reactions is also of high interest, particularly the dehydrogenative silylation reaction[2a,4a,5,9] and dehydrogenative coupling reactions in general.[9c]

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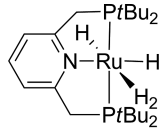
Our group has an ongoing interest in the reactivity of the nonclassical hydride complex [Ru($^{t\text{Bu}}$PNP)($H_2$)($H_2$)] [**1**; $^{t\text{Bu}}$PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine; Figure 1]. Complex **1** is an effective precatalyst in aromatic H–D exchange reactions,[10] the borylation of aromatic substrates such as toluene, anisole and benzene,[11] nitrile hydrogenation[12] and alkyne borylation.[13] In this work, we report the reactivity of **1** from a fundamental point of view in the hydrosilylation of a range of alkynes. We also investigate side reactions that produce both dehydrogenative silylation products and alkyne oligomers. Furthermore, stoichiometric reactions between **1** and substrates are used to elucidate the catalytically active species.



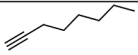
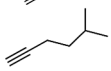
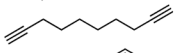
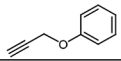

**1**

Figure 1. Nonclassical hydride pincer complex [Ru($^{t\text{Bu}}$PNP)($H_2$)-($H_2$)] (**1**).

## Results and Discussion

The focus of this work is ruthenium-catalyzed hydrosilylation with **1** as the catalyst precursor, and our initial investigations include the hydrosilylation of simple terminal alkyl alkynes. The reactions of 1-octyne or cyclopropylacetylene with $H_2SiPh_2$ in benzene or toluene solutions of **1** at room temperature give the *Z* hydrosilylation products in over 90% yield and selectivity (Table 1). For a variety of simple terminal alkyl alkynes, very similar results could be achieved under solvent-free conditions when the catalyst loading was reduced from 1.3 to 0.2% and the reactions were heated to 50 °C. Cyclopropylacetylene gave the best results of 97% conversion and a selectivity of 95% towards the (*Z*)-vinylsilane.

Table 1. Products from the hydrosilylation of alkyl alkynes.

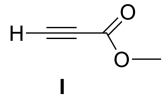
| Substrate | Conversion (%) | Product selectivity (%) | | |
|---|---|---|---|---|
| | | *Z* | *E* | Dehydrogenative silylation |
|  | 92 | 90 | 10 | – |
|  | 97 | 95 | 5 | – |
|  | 91 | 56 | 3 | 41 |
|  | 81 | 10 | 1 | 89 |
|  | 93 | 89 | 11 | – |
|  | 81 | 91 | 9 | – |
|  | 14[b] | 75[b,c] | 25[b,c] | – |

[a] Reaction conditions: 0.2 mol-% [Ru] (**1**), alkyne (1.078 mmol), $H_2SiPh_2$ (1.078 mmol), 16 h, 50 °C. [b] Reaction heated at 90 °C. [c] Characterized by $^1$H NMR spectroscopy and GC–MS.

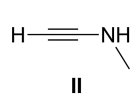
Increasing the steric demand of the substrate through the use of cyclopentyl and cyclohexyl moieties led to an interesting switch in selectivity. The selectivity towards the *Z* hydrosilylation product with cyclopentylacetylene is 56%; however, the conversion to the dehydrogenative silylation product is 41%. With the cyclohexyl substrate, the steric demand appears to have a greater impact on the selectivity, and the dehydrogenative silylation product accounts for 89% of the conversion. Perhaps surprisingly, 3-methylhexyne was completely inactive despite its structural similarity to cyclohexylacetylene.

The reactions of aromatic alkynes were attempted next; however, the reaction between phenylacetylene, $H_2SiPh_2$ and **1** always gave complex mixtures owing to simultaneous hydrosilylation and alkyne dimerization. The reactions were repeated without the silane under the same conditions, and only the dimer product 1,4-diphenyl-1-buten-3-yne was obtained with 34% conversion and selectivity for the *E* product of 76%. The dimerization of octyne showed an even lower reaction rate compared to that of phenylacetylene with 8% conversion and similar selectivity. The low rate of octyne dimerization relative to that of phenylacetylene can help explain why alkyl alkynes cleanly form the hydrosilylation products and phenylacetylene reacts to give both hydrosilylation and enyne products. The hydrosilylation of other aromatic substrates such as 4′-phenoxyphenylacetylene always gave similar mixtures of hydrosilylation and dimer products to those observed with phenylacetylene.

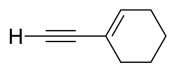
As high conversions and selectivities were achieved with terminal alkyl alkynes, substrates with a methylene linker between a carbon–carbon triple bond and an oxygen- or nitrogen-containing functional group were reacted under hydrosilylation conditions. However, methyl propynoate (**I**) and *N*-methylpropyn-1-amine (**II**) did not react nor did 1-ethynylcyclohexene (**III**) at temperatures up to 120 °C. These substrates probably bind through the oxygen atom, nitrogen atom or double bond and deactivate the catalyst, as preliminary NMR spectroscopy experiments in the absence of silane showed. Therefore, the reaction was attempted with the weakly coordinating ether propynyloxybenzene (**IV**), and a low conversion of 14% was observed at 90 °C; this suggests that substrate chelation or coordination is indeed the problem. The reactions were repeated in tetrahydrofuran (THF) at 80 °C; zero conversion was obtained for methyl propynoate, and a relatively poor conversion of 6% was observed for *N*-methylpropyn-1-amine with 95% selectivity for the *Z* isomer.



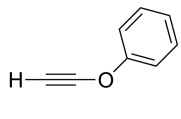

**I**




**II**




**III**




**IV**

The hydrosilylation reactions of terminal alkyl alkynes with **1** result in very good conversions and selectivities, which compare favourably to those of some commercially available hydrosilylation catalysts.[3g,14] Therefore, a kinetic experiment was performed with 1-octyne at room temperature to determine the turnover frequency. Over the first 45 min, there is a clear induction period, which is presumably caused by the formation of the catalytically active species. The average turnover frequency over the first 4 h excluding the induction period was calculated to be 121 $h^{-1}$, which is again competitive with those of the commercially available systems (see Figure S37, Supporting Information).

To investigate the cause of the induction period observed in the kinetic experiment and to better elucidate the catalytically active species, a series of stoichiometric reactions were performed between **1**, $H_2SiPh_2$ and phenylacetylene. Complex **1** and $H_2SiPh_2$ react within a few minutes in [$D_8$]-toluene or [$D_6$]benzene to yield a 1:1 (Ru–Si) complex, which can be identified by $^{31}P$ NMR spectroscopy by a single peak at $\delta$ = 93 ppm. During the course of the reaction between **1** and $H_2SiPh_2$, the solution turns from green to yellow, and the colour change is accompanied by the evolution of a gas, presumably hydrogen. Initial attempts to isolate [Ru($^{t\text{Bu}}$PNP)(H)$_2$($H_2SiPh_2$)] (**2**) by removal of the solvent under vacuum resulted in the decomposition of the complex. The precipitation of the complex from solution with pentane yielded an off-white solid, which was analyzed by mass spectrometry and IR spectroscopy.

The $^1H$ NMR spectrum has two hydride signals at $\delta$ = –3.5 and –7.3 ppm in a 1:2 ratio and a triplet at $\delta$ = 6.7 ppm with an integral of one, which corresponds to a silicon-bound hydrogen atom coupled to two protons. We tentatively assign the spectrum to **2**, in which the two hydride ligands are shared between the ruthenium and silicon centres, and one "free" hydride ligand remains bound to the metal centre (Figure 2). This structure fits well with the $^1H$ NMR spectroscopic data and also a very similar crystallographically determined product from the stoichiometric addition of pinacolborane to **1**.[13] A signal for **2** at *m*/*z* = 682 corresponding to $[M]^+$ (48 %) is observed in the EI-MS spectrum, but it is not the major signal in a cluster of peaks with a characteristic Ru isotope pattern centred at *m*/*z* = 679, which corresponds to the hydride-free ion $[M – 3H]^+$. Analysis of the IR spectrum shows that there is no characteristic signal associated with a $H_2$ ligand and, therefore, provides more evidence for dihydrogen substitution with $H_2SiPh_2$. The Si–H bond absorption is observed at $\tilde{\nu}$ = 2020 $cm^{-1}$, and that of the hydride ligands is observed at $\tilde{\nu}$ = 1717 $cm^{-1}$. The complex is relatively unstable even in the solid state and can only be stored for short periods at –20 °C; therefore, no microanalytical data could be collected. The relative instability of **2** could be attributed to the cleavage of the Si–H bond over time, which is a key step in any hydrosilylation catalytic cycle (Scheme 2) and a likely cause for the 45 min induction period observed in the kinetic experiment.[15] The stoichiometric addition of terminal alkynes to **2** results in the formation of complex product mixtures as observed by $^{31}P$ NMR spectroscopy. The $^{31}P$ NMR spectrum of the reaction mixture during catalysis is similarly complex and no single species can be characterized.

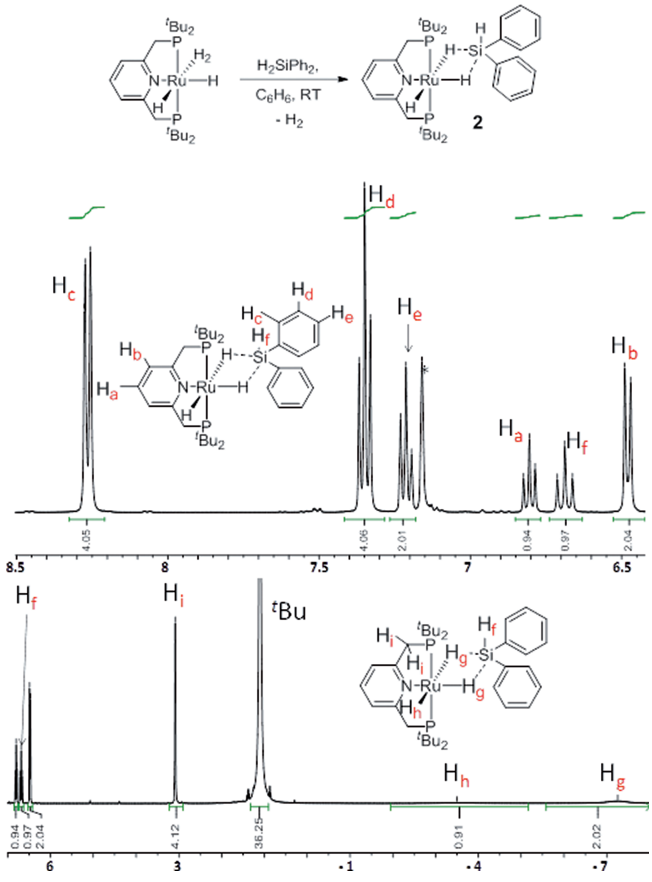
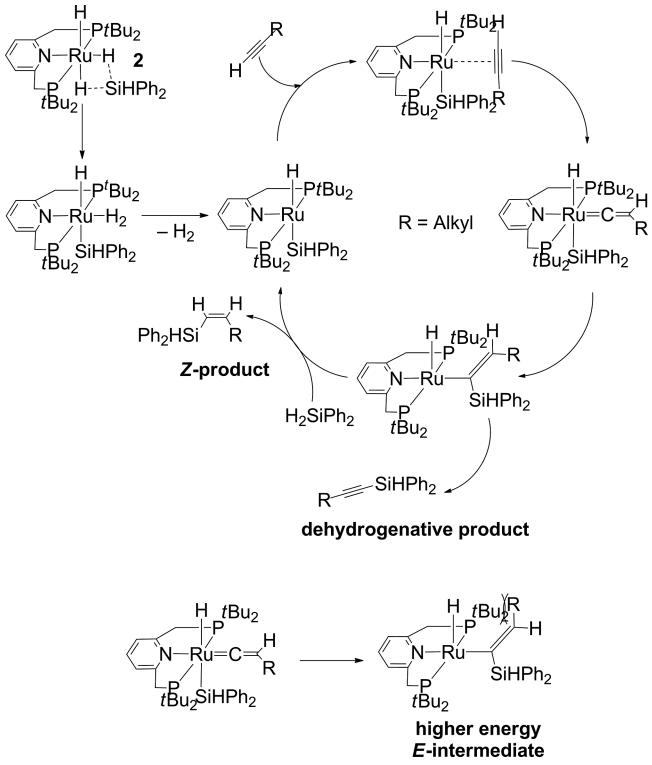



Figure 2. $^1H$ NMR spectrum of **2** in [$D_6$]benzene.

On the basis of the data for **2**, we can propose an entry point into the hydrosilylation catalytic cycle. In the first step, $H_2SiPh_2$ reacts with **1** to eliminate dihydrogen and yield **2** (Scheme 2). The cleavage of a Si–H bond and the subsequent elimination of a second equivalent of $H_2$ yields a ruthenium–silane complex with a vacant coordination site for alkyne coordination. The catalytic cycle is anticipated to proceed via ruthenium vinylidene intermediates as observed in the analogous borylation system, and the Z-selectivity observed in both systems stems from the interaction of the R group of the terminal vinyl intermediate with the sterically demanding phosphine *t*Bu groups (Scheme 2, bottom).[13,17] The conversion of [Ru($^{t\text{Bu}}$PNP)(H)(HSi-$Ph_2$)(HC≡CR)] to a vinylidene is followed by the migration of the silyl ligand. The dehydrogenative silylation products can be obtained when β-hydride elimination is faster than elimination of the vinylsilane, and this appears to be related to the steric demands of the substrate. Crabtree and coworkers proposed that an interaction between the R group and the silyl moiety in the vinyl intermediate orientates the β-hydride towards the metal centre and, thus, facilitates the elimination reaction.[4a] Another possibility is that the steric




Scheme 2. Top: proposed catalytic cycle for the hydrosilylation of terminal alkynes starting from complex **2**. Bottom: higher energy *E* vinyl intermediate.

demands of vinyl intermediates with relatively large R group slow coordination of $H_2SiPh_2$ to the metal centre and allow the β-hydride elimination reaction to dominate over vinylsilane formation (Scheme 2).

Stoichiometric reactions were also conducted with phenylacetylene and **1** to determine if the active species in the dimerization reaction could be observed and isolated. To separate solutions of **1** in [$D_8$]toluene, phenylacetylene (1, 2 and 10 equiv.) was added, and the reactions were monitored by $^{31}$P NMR spectroscopy (Figure 3). The addition of 1 equiv. of phenylacetylene results in the formation of a new peak in the $^{31}$P NMR spectrum at $\delta$ = 82 ppm in addition to a signal at $\delta$ = 109 ppm, which corresponds to **1**, in an approximate 5:1 ratio.

When phenylacetylene (1.5 equiv.) is added to **1**, there are initially signals at $\delta$ = 82, 70 and 64 ppm in a 96:2:2 ratio in the $^{31}$P NMR spectrum. After 2 h, the only signal observed is at $\delta$ = 82 ppm, and the complex can be isolated from solution by precipitation for further spectroscopic analysis. In the $^1$H NMR spectrum, the aromatic peaks integrate to eight protons, which suggests that a reaction occurs with 1 equiv. of phenylacetylene to displace the dihydrogen ligand and yield [Ru($^{t\mathrm{Bu}}$PNP)(H)$_2$(HC≡CPh)] (**3**). Mass spectrometry and $^{13}$C NMR and IR spectroscopic analysis provide further evidence for the identity of **3**. As no dihydrogen bands are observed in the IR spectrum, the reaction of one of the ruthenium hydride bonds with phenylacetylene to yield [Ru($^{t\mathrm{Bu}}$PNP)(H$_2$)(H)(C≡CPh)] can be ruled out.

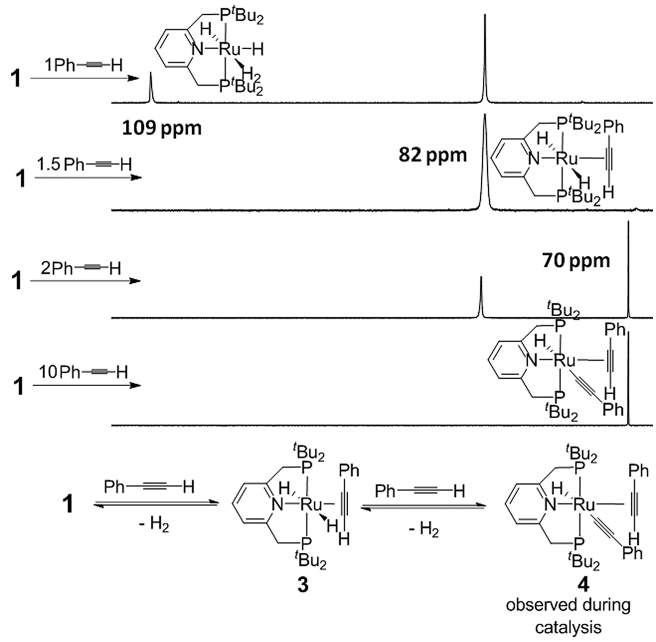



Figure 3. Stacked $^{31}$P NMR spectra showing stoichiometric reactions between **1** and phenylacetylene in [$D_8$]toluene to yield alkyne complexes **3** and **4**.

The addition of 10 equiv. of phenylacetylene to **1** yields a single product with a peak at $\delta$ = 70 ppm (Figure 3), which can also be isolated by precipitation from solution with pentane. The product was analyzed by mass spectrometry as well as IR and multinuclear NMR spectroscopy. The mass spectrometry data shows the parent ion peak at *m*/*z* = 700, which corresponds to the dialkyne complex [Ru($^{t\mathrm{Bu}}$PNP)(H)(C≡CPh)(HC≡CPh)] (**4**). The IR spectrum shows signals at $\tilde{\nu}$ = 2075 and 2047 cm$^{-1}$ for the carbon–carbon triple bonds and a hydride signal at $\tilde{\nu}$ = 1586 cm$^{-1}$; these values are very similar to those reported by Gusev

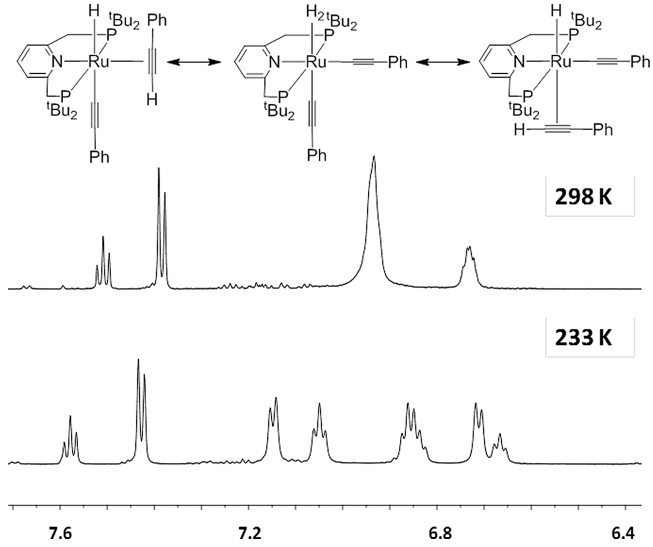
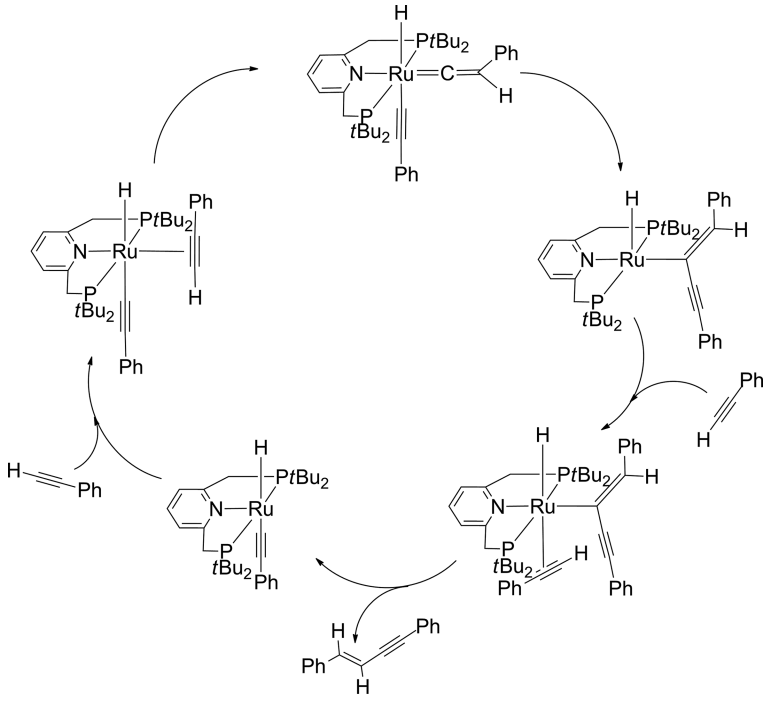



Figure 4. $^1$H NMR spectra of **4** in [$D_8$]THF at 298 and 233 K; the rapid exchange of the inequivalent phenyl groups at room temperature is demonstrated.



Scheme 3. Proposed catalytic cycle for the dimerization of phenylacetylene.

and co-workers for the complex [Ru($^{t\text{Bu}}$PCP)(H)(CO)(C≡CPh)], which gives peaks at $\tilde{\nu}$ = 2065 cm$^{-1}$ for the C≡C bond and 1583 cm$^{-1}$ for the Ru–H bond.[16]

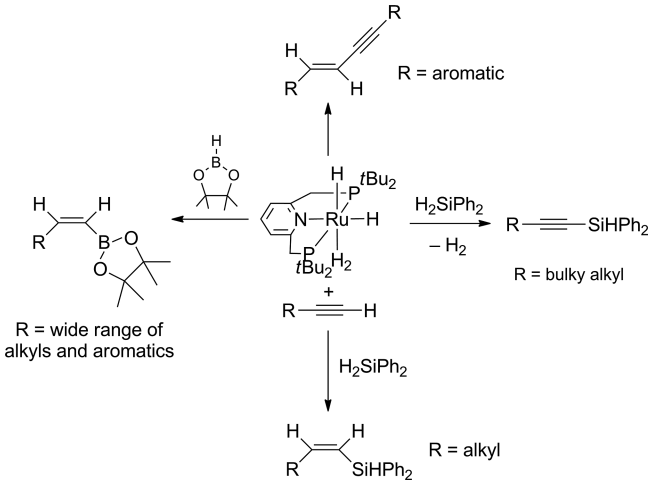
The hydride and alkyne proton signals in **3** and **4** are not observed in the $^1$H NMR spectrum. Presumably, the signals are very broad owing to rapid exchange. The spectrum of **4** in particular has very broad signals, including those of the phenyl groups, which are equivalent on the NMR timescale at room temperature. The cooling of **4** to 233 K results in the clear resolution of the two phenyl signals; however, the alkyne proton and hydride signals are still not observed (Figure 4). The vinylidene tautomers of **3** and **4** cannot be completely ruled out as possible products; however, the characteristic $^{13}$C NMR, $^1$H NMR and IR vinylidene spectroscopic signals are not observed.[6m,7,8]

$^{31}$P NMR spectroscopic measurements during the catalytic dimerization of phenylacetylene show that **4** is the only observable species during the reaction. Similar alkyne complexes and their vinylidene tautomers have been described as intermediates in the oligomerization of terminal alkynes by the mechanism shown in Scheme 3, and this mechanism fits very well with the catalytic cycle proposed for the hydrosilylation and borylation systems.[6m,8g,13]

## Conclusions

We report a new catalyst for the hydrosilylation of terminal alkynes. We have shown **1** to be a *Z*-selective precatalyst for the hydrosilylation of terminal alkyl alkynes under mild conditions with low catalyst loading. The reaction between 1-octyne and $H_2SiPh_2$ proceeds with an initial turnover frequency of 121 h$^{-1}$ at room temperature. When coordinating functionalities are introduced at or close to the C–C triple bond, a significant decrease in activity is observed for weakly coordinating groups, and no conversion is observed for strongly coordinating groups; this suggests that the active site is poisoned. Phenylacetylene undergoes simultaneous hydrosilylation and dimerization to yield enynes with selectivity for the *E* product. Stoichiometric reactions between precatalyst **1**, $H_2SiPh_2$ and phenylacetylene were performed, and the products were characterized. The reaction of **1** with $H_2SiPh_2$ results in the substitution of the dihydrogen ligand to yield the new ruthenium silane complex **2** (Figure 2). Presumably, this complex is involved in the catalytic cycle and undergoes Si–H bond activation to yield a ruthenium–silane bond. The reactions of **1** with varying equivalents of phenylacetylene ultimately yield the dialkyne complex **4** (Figure 3), which is also observed by $^{31}$P NMR spectroscopy during the catalytic dimerization reaction. The dimerization of terminal aryl alkynes is much faster than that of terminal alkyl alkynes. This explains why a mixture of dimer and hydrosilylation products is observed from the hydrosilylation of terminal aryl alkynes but only hydrosilylation products are observed with terminal alkyl alkynes. An interesting observation was the relatively unusual conversion to dehydrogenative silylation products when sterically demanding alkynes were used. This selectivity could be of interest for the production of alkyne synthons for coupling reactions. These results in combination with work previously reported by our group show that **1** is a versatile precatalyst for the conversion of terminal alkynes to a range of useful products (Scheme 4).[13] Further investigations with sterically demanding silanes to obtain only dehydrogenative silylation products and also the catalytic synthesis of enynes are currently under investigation.




Scheme 4. Reaction of nonclassical hydride complex **1** with terminal alkynes to yield borylation,[13] hydrosilylation, dimerization and dehydrogenative coupling products.

## Experimental Section

**General Remarks:** All moisture- and oxygen-sensitive compounds were prepared by using standard high vacuum line, Schlenk and cannula techniques. A standard argon-filled glovebox was used for any subsequent manipulation and storage of these compounds. Complex **1** was prepared as described previously (see Supporting Information). All other reagents were commercially sourced, dried and deoxygenated before use.

**General Reaction Protocol for Acetylene Hydrosilylation Reactions:** Complex **1** (1 mg, 2 μmol) was dissolved in $H_2SiPh_2$ (200 mg, 1.1 mmol) to give a yellow solution. Once hydrogen evolution had ceased, the acetylene (1.1 mmol) was added. The reaction mixture was then heated for 16 h. The product distribution was analyzed by $^1H$ NMR spectroscopy against an internal standard of dioxane and by GC–MS. The major products were isolated by column chromatography and characterized by multinuclear NMR spectroscopy. Further details are given in the Supporting Information.

## Acknowledgments

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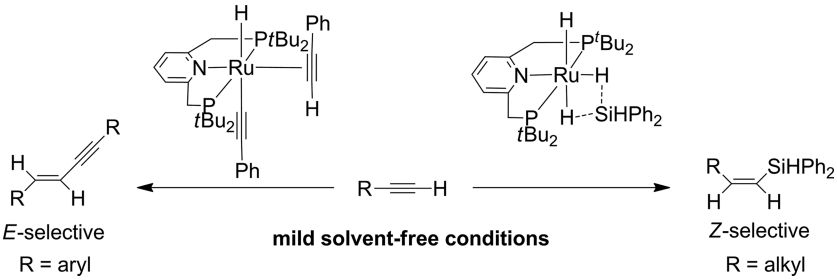
## Hydrosilylation

**C. Conifer, C. Gunanathan, T. Rinesch, M. Hölscher,* W. Leitner* ..... 1–8**

Solvent-Free Hydrosilylation of Terminal Alkynes by Reaction with a Nonclassical Ruthenium Hydride Pincer Complex

**Keywords:** C–H activation / Hydrosilylation / Dehydrogenative silylation / Nonclassical hydrides / Alkynes / Ruthenium




A selective catalyst system for the hydrosilylation of alkyl alkynes under mild, solvent-free conditions has been developed with the ruthenium pincer complex [Ru($^{t\text{Bu}}$PNP)($H_2$)($H_2$)] [$^{t\text{Bu}}$PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine].