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Syntheses and Reactivity Studies of Transition Metal Complexes featuring Metal – Main Group Multiple Bonds

by

Meg Elaine Fasulo

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor T. Don Tilley, Chair

Professor John Arnold

Professor Alexis Bell

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Abstract

Syntheses and Reactivity Studies of Transition Metal Complexes featuring Metal – Main Group Multiple Bonds

Meg Elaine Fasulo

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor T. Don Tilley, Chair

The ruthenium triflate complex $Cp^*(PiPr_3)RuOTf$ (**1**) was generated from the reaction of $Cp^*(PiPr_3)RuCl$ with Me_3SiOTf in dibutyl ether. Complex **1** reacted with primary and secondary silanes to produce a family of Ru(IV) silyl dihydride complexes of the type $Cp^*(PiPr_3)Ru(H)_2(SiRR'OTf)$ (**3** – **12**). Structural analyses of complexes **8** (R = R' = Ph) and **12** (R = R' = fluorenyl) revealed the presence of a tetrahedral silicon center and a four-legged piano stool geometry about ruthenium. Anion abstraction from $Cp^*(PiPr_3)Ru(H)_2(SiHROTf)$ by $[Et_3Si\bullet toluene][B(C_6F_5)_4]$ afforded hydrogen-substituted cationic ruthenium silylene complexes $[Cp^*(PiPr_3)Ru(H)_2(=SiHR)][B(C_6F_5)_4]$ (R = Mes (**13**), R = Si(SiMe$_3$) (**14**)) that display a significant Ru – H ··· Si interaction, as indicated by relatively large $^2J_{SiH}$ coupling constants ($^2J_{SiH}$ = 58.2 Hz (**13**), $^2J_{SiH}$ = 37.1 Hz (**14**)). The syntheses of secondary silylene complexes $[Cp^*(PiPr_3)Ru(H)_2(=SiRR')][B(C_6F_5)_4]$ (R = R' = Ph (**15**); R = Ph, R' = Me (**16**), R = R' = fluorenyl (**17**)) were also achieved by anion abstraction with $[Et_3Si\bullet toluene][B(C_6F_5)_4]$. Complexes **15** – **17** do not display strong Ru – H ··· Si secondary interactions, as indicated by very small $^2J_{SiH}$ coupling constant values.

The cationic ruthenium silylene complex $[Cp^*(PiPr_3)Ru(H)_2(SiHMes)]$ $[CB_{11}H_6Br_6]$, a catalyst for olefin hydrosilations with primary silanes, was isolated and characterized by X-ray crystallography. Relatively strong interactions between the silylene Si atom and Ru–H hydride ligands appear to reflect a highly electrophilic silicon center. Kinetic and mechanistic studies on hydrosilations with this catalyst reveal a fast, initial addition of the Si–H bond of the silylene complex to the olefin. Subsequent migration of a hydride ligand to silicon produces a 16-electron intermediate, which can be trapped by olefin, resulting in inhibition of catalysis, or intercepted by the silane substrate. The latter reaction pathway, involving oxidative addition of the Si–H bond and a somewhat concomitant loss of product, is the rate-determining step in the catalytic cycle.

Reactions of the cationic ruthenium silylene complexes $[Cp^*(PiPr_3)Ru(H)_2(=SiRR')][B(C_6F_5)_4]$ (R = Mes, R' = H, **1**; R = R' =Ph, **2**) with alkenes, alkynes, ketones, and Lewis bases were explored. Addition of 1-hexene, 3,3-dimethylbut-1-ene, styrene, and cyclopentene to **1** afforded the disubstituted silylene products $[Cp^*(PiPr_3)Ru(H)_2(=SiMesR)][B(C_6F_5)_4]$ (R = Hex, **3**; R = CH_2CH_2tBu, **4**; R = CH_2CH_2Ph, **5**; R = C_5H_9, **6**). Analogous reactions with 2-butyne and 3,3-dimethylbut-1-yne yielded the vinyl-substituted silylene complexes $[Cp^*(PiPr_3)Ru(H)_2(=Si(CR=CHR')Mes)][B(C_6F)_4]$ (R = R' =

Me, **7**; R = H, R' = tBu, **8**). Complex **1** undergoes reactions with ketones to give the heteroatom-substituted silylene complexes [Cp*($PiPr_3$)Ru($H)_2$(=Si(OCHPhR)Mes)][$B(C_6F)_4$] (R = Ph, **9**; R = Me, **10**). Interestingly, complexes **3** – **8** display a weak interaction between the hydride ligands and the silicon center, while **9** and **10** exhibit a relatively large interaction (as determined by $^2J_{SiH}$ values). The reaction of isocyanates with **1** resulted in the silyl complexes [Cp*($PiPr_3$)Ru($H)_2$(Si(Mes)[κ^2-O(CH)(NC_6H_4R)][$B(C_6F_5)_4$] (R = H, **11**; R = CF_3, **12**), and an intermediate in this transformation is observed. Complex **2** was subjected to various Lewis bases to yield the base-stabilized silylene complexes [Cp*($PiPr_3$)Ru($H)_2$($SiPh_2$•L)][$B(C_6F)_4$] (L = DMAP, **13**; L = Ph_2CO, **14**; L = $PhCONH_2$, **15**; L = NHMePh, **16**, L = $tBuSONH_2$, **18**) and the reaction of **1** with NHMePh gave [Cp*($PiPr_3$)Ru($H)_2$(SiHMes•NHMePh)][$B(C_6F)_4$].

The cationic germylene complex [Cp*($PiPr_3$)Ru($H)_2$(=$GeMes_2$)][OTf] (**1**) was synthesized from the reaction of Cp*($PiPr_3$)RuOTf with H_2GeMes_2, and addition of DMAP to **1** yielded the neutral germylene complex [Cp*($PiPr_3$)Ru(H)(=$GeMes_2$) (**2**). The reaction of H_3GeTrip and Cp*($PiPr_3$)RuCl gave the germyl complex Cp*($PiPr_3$)Ru($H)_2$(GeHTripCl) (**3**), which undergoes a reaction with Li($Et_2O)_2$[$B(C_6F_5)_4$] to afford the cationic H-substituted germylene complex [Cp*($PiPr_3$)Ru($H)_2$(=GeHTrip)][$B(C_6F_5)_4$] (**4**). Addition of 1-hexene, 3,3-dimethylbut-1-ene, styrene, and allyl chloride to **4** afforded the disubstituted germylene products [Cp*($PiPr_3$)Ru($H)_2$(=GeTripR)][$B(C_6F_5)_4$] (R = Hex, **5**; R = CH_2CH_2Ph, **6**; R = CH_2CH_2tBu, **7**; R = $CH_2CH_2CH_2$Cl, **8**). Analogous reactions with 2-butyne and 3,3-dimethylbut-1-yne yielded the vinyl-substituted germylene complexes [Cp*($PiPr_3$)Ru($H)_2$(=Ge(CR=CHR')Trip)][$B(C_6F)_4$] (R = H, R' = tBu, **9**; R = R' = Me, **10**).

New di(phosphine)-supported rhodium and iridium silyl complexes were synthesized. Reactions of the di(t-butylphosphino)ethane complex (dtbpe)Rh(CH_2Ph) with Ph_2SiH_2 and Et_2SiH_2 resulted in isolation of (dtbpe)Rh($H)_2$($SiBnPh_2$) (**1**, Bn = CH_2Ph) and (dtbpe)Rh(H)-$_2$($SiBnEt_2$) (**2**), respectively. Both **1** and **2** display strong interactions between the rhodium hydride ligands and the silyl ligand, as indicated by large $^2J_{SiH}$ values (44.4 and 52.1 Hz). The reaction of (dtbpm)Rh(CH_2Ph) (dtbpm = di(t-butylphosphino)methane) with Mes_2SiH_2 gave the pseudo-three-coordinate Rh complex (dtbpm)Rh($SiHMes_2$) (**3**), which is stabilized in the solid state by agostic interactions between the rhodium center and two C – H bonds of a methyl substituent of a mesityl group. The analogous germanium compound (dtbpm)Rh($GeHMes_2$) (**4**) is also accessible. Complex **3** readily undergoes reactions with diphenylacetylene, phenylacetylene, and 2-butyne to give the silaallyl complexes (dtbpm)Rh[Si(CPh=CHPh)Mes_2] (**5**), (dtbpm)Rh[Si(CH=CHPh)Mes_2] (**7**), and (dtbpm)Rh(Si(CMe=CHMe)Mes_2) (**8**) via net insertions into the Si – H bond. The germaallyl complexes (dtbpm)Rh[Ge(CPh=CHPh)Mes_2] (**6**) and (dtbpm)Rh[Ge(CMe=CHMe)Mes_2] (**9**) were synthesized under identical conditions starting from **4**. The reaction of (dtbpm)Rh(CH_2Ph) with 1 equiv of $TripPhSiH_2$ yielded (dtbpm)Rh($H)_2$[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindenyl-κSi] (**11**), and catalytic investigations indicate that both (dtbpm)Rh(CH_2Ph) and **11** are competent catalysts for the conversion of $TripPhSiH_2$ to 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. A dtbpm-supported Ir complex, [(dtbpm)IrCl]$_2$, was used to access the dinuclear bridging silylene complexes [(dtbpm)IrH](μ-$SiPh_2$)(μ-Cl)$_2$[(dtbpm)IrH] (**12**) and [(dtbpm)IrH](μ-SiMesCl)(μ-Cl)(μ-H)[(dtbpm)IrH] (**13**). The reaction of [(dtbpm)IrCl]$_2$ with a sterically bulky primary silane, (dmp)SiH_3 (dmp = 2,6-dimesitylphenyl), allowed isolation of the mononuclear complex (dtbpm)Ir($H)_4$(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydrosilaphenanthrene-κSi) (**14**), in which the dmp substituent has undergone C–H activation.

The dichloride complex Cp*(Am)WCl_2 (**1,** Am = $[(iPrN)_2CMe]^-$) reacted with the primary silanes $PhSiH_3$, (*p*-tolyl)SiH_3, (3,5-xylyl)SiH_3, and $(C_6F_5)SiH_3$ to produce the W(VI) (silyl)trihydrides Cp*(Am)$W(H)_3$(SiHPhCl) (**2**), Cp*(Am)$W(H)_3$(SiHTolylCl) (**3**), Cp*(Am)$W(H)_3$(SiHXylylCl) (**4**), and Cp*(Am)$W(H)_3$[$SiH(C_6F_5)Cl$] (**5**). In an analogous manner, **1** reacted with $PhSiH_2Cl$ to give Cp*(Am)$W(H)_3(SiPhCl_2)$ (**6**). Complex **6** can alternatively be quantitatively produced from the reaction of **2** with Ph_3CCl. NMR spectroscopic studies and X-ray crystallography reveal an interligand H···Si interaction between one W – H and the chlorosilyl group, which is further supported by DFT calculations.

Complexes of Ru(II) containing the pincer ligand [$^-N(2\text{-}PPh_2\text{-}4\text{-}Me\text{-}C_6H_3)_2$] ($PNP^{Ph}$) were prepared. The complex ($PNP^{Ph}H$)$RuCl_2$ (**1**) was treated with 2 equiv AgOTf to produce the triflate complex ($PNP^{Ph}H$)$Ru(OTf)_2$ (**2**). Complex **1** was also treated with an excess of $NaBH_4$ to give a bimetallic complex [(PNP^{Ph})RuH_3]$_2$ (**3**). A number of methods, including X-ray crystallography, NMR spectroscopy, and computational studies, were used to probe the structure of **3**. Addition of Lewis bases to **3** resulted in octahedral complexes containing a hydride ligand *trans* to a dihydrogen ligand.

To my grandmother Gladdie Bertels, who taught me to be sassy

And my nieces Isobel, Lucia, and Remy Fasulo,
may you continue the tradition.

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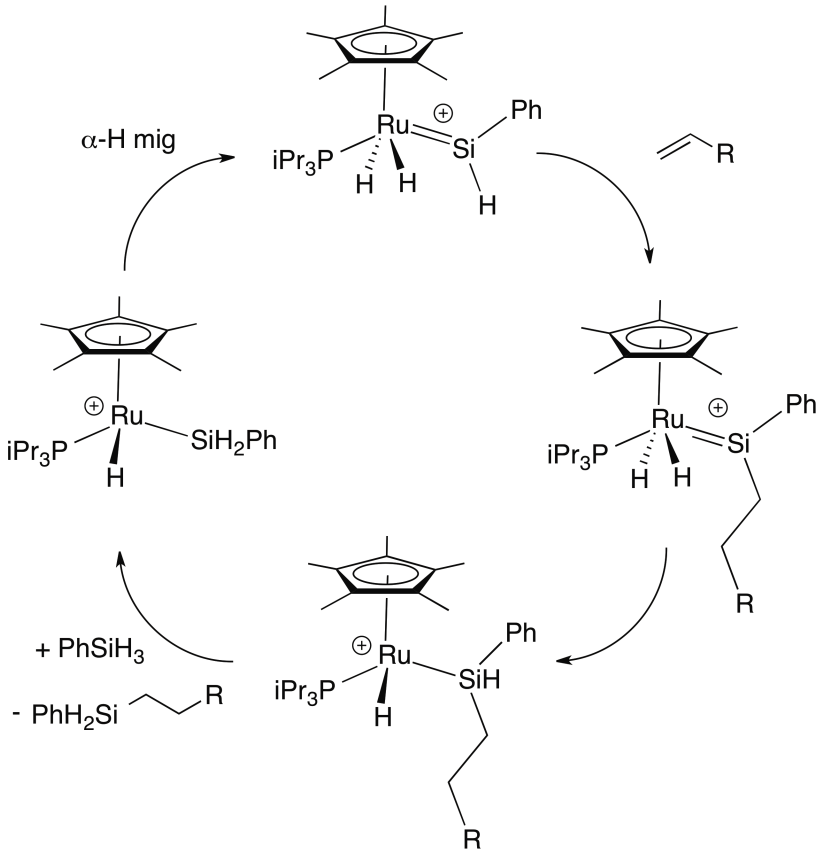
Chapter 1

$Cp^*(PiPr_3)RuOTf$: A Reagent for Access to Ruthenium Silylene Complexes

Introduction

Transition metal complexes with silylene ligands have been an active area of research for the last twenty years due to their potential applications in transformations involving organosilanes, such as hydrosilation and silane redistribution.[1] A silylene-mediated olefin hydrosilation mechanism that fundamentally differs from the Chalk-Harrod mechanism[2] has been proposed for two systems, involving $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh\bullet Et_2O)][B(C_6F_5)_4]$[3] and $[PNPIrH(=SiHPh)][B(C_6F_5)_4]$[4] (Scheme 1). These hydrosilations are selective for the anti-Markovnikov product and occur only with primary silanes. Importantly, the cationic sp^2-hybridized silicon center is required for this reactivity.[5]

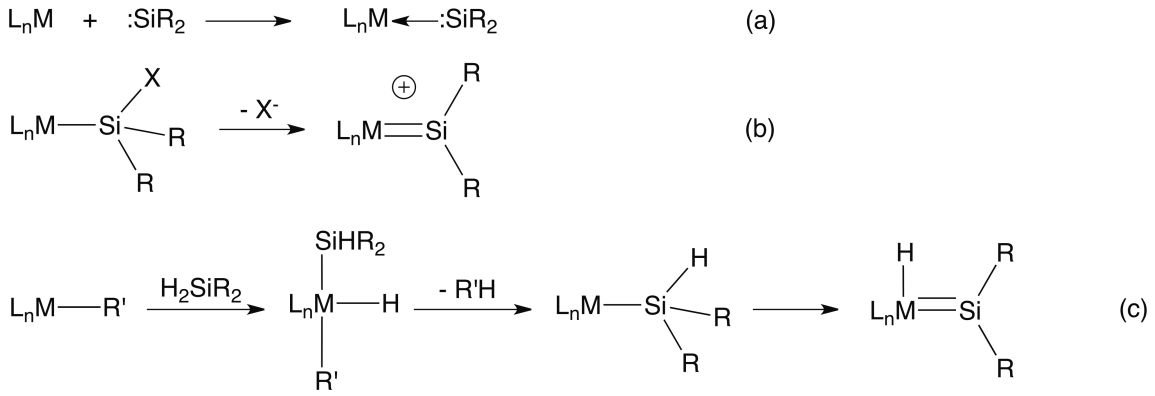
Scheme 1.



Several reliable synthetic routes to silylene complexes have been established, including the general reaction types of Scheme 2.[6] One straightforward strategy involves the coordination of a stable, free silylene to a transition metal fragment (Scheme 2a).[7] However, the reactivity of complexes synthesized via this method often result in displacement of the silylene ligand[7b] or the generation of tetravalent silicon.[7c] A widely employed procedure is based on abstraction of an anionic substituent, such as a halogen or triflate, from the silicon atom (Scheme 2b).[3,4,8] Recently, this chemistry has been extended to include abstraction of hydride from silicon.[4] Importantly, anion abstraction inherently yields cationic silylene species. Another effective approach has been termed "silylene extrustion," which involves two sequential Si – H activations (e.g., Scheme 2c).[9] In an example of this process, a silane reacts with a metal alkyl complex to undergo oxidative addition, followed by a C-H reductive elimination. Finally, an α-hydride

migration occurs to produce the silylene ligand. This methodology can result in cationic[9a] or neutral complexes.[9f]

Scheme 2.



Transition metal silylene complexes are extremely oxygen and moisture sensitive, and a number of examples are thermally unstable. This inherent instability has been assuaged by the use of bulky substituents on the metal fragment and the silicon atom.[10] Additionally, the use of electron-donating substituents on the silyl ligand allowed for the first base-free examples of silylenes.[11] Because the substituents at silicon play a strong role in determining stability and reactivity for a silylene complex, it is important to establish versatile synthetic methods that allow access to a wide range of new silylene complexes.

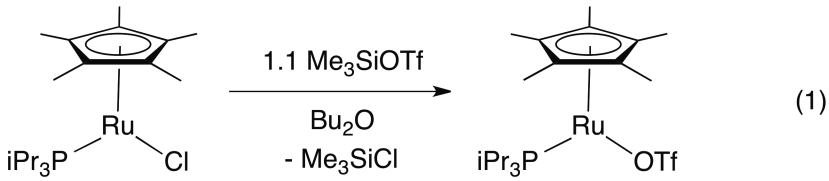
Herein we describe the synthesis and reactivity of Cp*($PiPr_3$)RuOTf (**1**), a new metal complex that activates a number of primary and secondary silanes. Several of the resulting metal silyl species have proven to be useful precursors to new ruthenium silylene complexes.

Results and Discussion

Synthesis, characterization, and reactivity of Cp*($PiPr_3$)RuOTf (1). The complex Cp*($PiPr_3$)RuCl has been shown to activate phenylsilane, and the resulting product, Cp*($PiPr_3$)RuHCl(SiH_2Ph), undergoes chloride abstraction to give a base-stabilized silylene complex that exhibits unusually high anti-Markovnikov regioselectivity as a catalyst for alkene hydrosilations.[3] Attempts to extend this methodology to additional catalysts of the type $[Cp^*(PiPr_3)Ru(H)_2(=SiHR)]^+$ have proven difficult, especially given the limited reactivity of Cp*($PiPr_3$)RuCl towards more sterically demanding primary silanes. Because the anion abstraction method to afford cationic silylene complexes has been successful for both Si – Cl and Si – OTf derivatives, Cp*($PiPr_3$)RuOTf was targeted as a potential starting material for access to new cationic silylene complexes.

Initial attempts to synthesize Cp*($PiPr_3$)RuOTf from the reaction of Cp*($PiPr_3$)RuCl with Me_3SiOTf at room temperature in diethyl ether for 24 h resulted in an inseparable mixture of starting material and product. Slow removal of volatile materials was somewhat successful in driving the reaction towards completion but paramagnetic side products and inconsistent yields were problematic. The use of a high boiling ether solvent such as Bu_2O (b.p. 143 °C) allowed for access to pure Cp*($PiPr_3$)RuOTf (**1**) (eq 1). After stirring Cp*($PiPr_3$)RuCl with 1.1 equiv Me_3SiOTf (b.p. 140 °C) at room temperature for 1 h, the volatile materials were slowly removed

under vacuum over 6 h. In this way, removal of Me_3SiCl, the volatile product of the reaction (b.p. 56 °C), forced the reaction to completion. Subsequent drying under vacuum gave **1** as a purple solid in high isolated yield (89%).



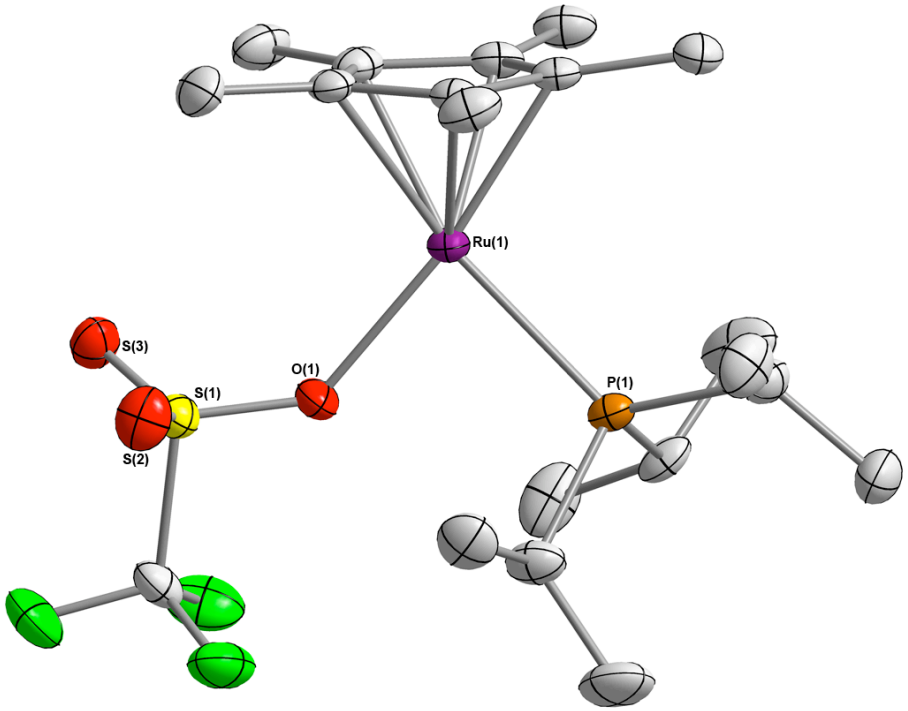
(1)

1

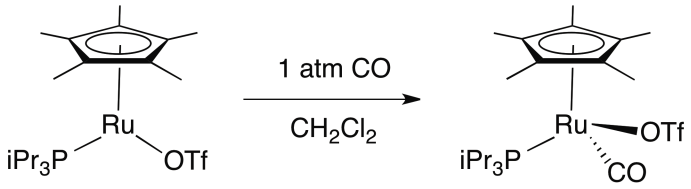
The ^1H NMR spectrum of **1** reveals a single peak for the Cp* methyl groups, a septet for the methine protons of the isopropyl groups, and a doublet of doublets for the methyl protons of the isopropyl groups, indicative of a highly symmetric molecule. The $^{31}P\{^1H\}$ NMR spectrum displays a single peak at 48.0 ppm that is downfield from that of free $PiPr_3$ (19.0 ppm). A single resonance at -76.7 ppm is observed by ^{19}F NMR spectroscopy. The multiple NMR active nuclei of **1** make for convenient NMR spectroscopic handles for exploring reactivity.

X-ray quality crystals were obtained as purple blocks from a solution of **1** in $(Me_3Si)_2O$ at -30 °C (Figure 1). The triflate ligand binds to the Ru center through one oxygen atom, with a Ru – O bond length of 2.136(2) Å. Although complex **1** formally possesses a 16 electron count, no additional inter- or intramolecular contacts are observed between the Ru center and the triflate ligand.

Figure 1. Molecular structure of **1** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1) – O(1) = 2.136(2), Ru(1) – P(1) = 2.4088(9), S(1) – O(1) = 1.474(2), S(1) – O(2) = 1.431(2), S(1) – O(3) = 1.434(2).



To verify that the bulky phosphine ligand would not preclude the formation of a complex containing more ligands, complex **1** in CH_2Cl_2 was exposed to 1 atm of CO gas (eq 2). At room temperature, the dark purple solution quickly faded to a dark yellow color. The presence of a CO ligand was observed in the infrared spectrum, as a ν(CO) stretch at 1945 cm^{-1}, indicating that there is less backbonding to the CO of **2** than in Cp*($PiPr_3$)RuCl(CO) (1910 cm^{-1}).[12] Additionally, an X-ray structure of **2** confirms the proposed structure.[13]

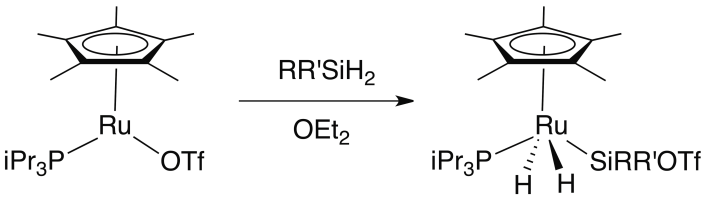


(2)

1 **2**

Complex **1** readily decomposes in the presence of many arenes to form complexes of the type [Cp*Ru(arene)][OTf].[14] These complexes precipitate from solution as white solids and can easily be differentiated from dark purple **1**. It is therefore important to avoid the use of arene solvents such as benzene and toluene during manipulations of **1**.

Synthesis and characterization of Cp*($PiPr_3$)Ru($H)_2$(SiRR′OTf) complexes. Complex **1** was found to react cleanly with one equiv of H_3SiPh at room temperature in ether in 30 min to give Cp*($PiPr_3$)Ru($H)_2$(SiHPhOTf) (**3**) as a light tan solid in very good yield (eq 3). Whereas the reaction of Cp*($PiPr_3$)RuCl with $PhSiH_3$ gives the simple oxidative addition product Cp*($PiPr_3$)RuHCl(SiH_2Ph),[15] the Ru(IV) complex **3** is the result of two Si – H bond cleavages and migration of the triflate anion to the Si center.



(3)

1

R = Ph, R' = H	(**3**)
R = Mes, R' = H	(**4**)
R = C_6F_5, R' = H	(**5**)
R = $SiPh_3$, R' = H	(**6**)
R = $Si(SiMe_3)_3$, R' = H	(**7**)
R = R' = Ph	(**8**)
R = Ph, R' = Me	(**9**)
R = R' = Et	(**10**)
R = R' = iPr	(**11**)
R = R' = Flu	(**12**)

Filtration of the reaction solution through a Celite plug and removal of solvent *in vacuo* resulted in analytically pure **3**. In an analogous manner, reactions of **1** with H_3SiMes, $H_3Si(C_6F_5)$, $H_3SiSiPh_3$, $H_3SiSi(SiMe_3)_3$, H_2SiPh_2, $H_2SiPhMe$, H_2SiEt_2, $H_2Si^iPr_2$, and 9-silafluorene gave complexes **4** – **12**, respectively. A number of these organosilanes do not react cleanly with

$Cp^*(PiPr_3)RuCl$ to afford similar complexes, and thus **1** allows for the synthesis of a number of silylene precursor complexes that were not previously accessible.

Due to the multiple NMR-active nuclei present in **3** – **12**, a large amount of structural information can be obtained for these complexes to support the structures proposed in eq 3. For example, the ^1H NMR spectrum for **4** reveals an Si – H group that gives rise to a resonance at 7.02 ppm, with a characteristically large J_{SiH} coupling constant of 215.4 Hz. The two hydride ligands (-11.81 and -12.86 ppm) are diastereotopic due to the chiral Si center and are associated with small J_{SiH} coupling constants (J_{SiH} = 11.4 Hz), indicating that there is not a strong interaction between the hydrides and the silicon center. The ^{29}Si NMR spectrum displays a single resonance at 62.4 ppm, in the region typical for a silyl ligand (SiR_3) bound to a transition metal.[16] The $^{31}P\{^1H\}$ NMR spectrum exhibits a resonance at 78.2 ppm that is downfield of that observed for **1** (48.0 ppm). Additionally, ^{19}F NMR spectroscopy confirms the presence of the triflate anion with a peak at -76.3 ppm. The NMR data for **3** – **12** follow similar trends and are tabulated in Table 1. Most noteworthy are the small J_{SiH} coupling constants observed for all complexes ($J_{SiH} \leq 20$ Hz) indicating very weak secondary interactions between the hydrides and the silicon. The range of ^{29}Si NMR resonances from 44.3 ppm for **5** to 118.9 ppm for **11** is typical of silyl ligands with a variety of substituents.

Table 1. NMR data for complexes **3** – **12**

Complex	δ ^1H (SiH) ($^2J_{SiH}$)	δ ^1H (RuH) ($^2J_{SiH}$)	δ ^{29}Si (RuSi)
$Cp^*(PiPr_3)RuH_2(SiHPhOTf)$ (**3**)	6.76 (211.5)	-11.51, -12.49 (18.8)	65.1
$Cp^*(PiPr_3)RuH_2(SiHMesOTf)$ (**4**)	7.02 (215.4)	-11.81, - 12.86 (10.4)	62.4
$Cp^*(PiPr_3)RuH_2(SiH(C_6F_5)OTf)$ (**5**)	6.75 (227.9)	-11.57, -12.26 (< 7)	44.3
$Cp^*(PiPr_3)RuH_2(SiH(SiPh_3)OTf)$ (**6**)	6.86 (188.6)	-10.96, -12.09 (21.8)	63.3
$Cp^*(PiPr_3)RuH_2(SiH(Si(SiMe_3)_3OTf)$ (**7**)	6.97 (192.5)	-10.98, -13.01 (11.4)	69.3
$Cp^*(PiPr_3)RuH_2(SiPh_2OTf)$ (**8**)	—	-11.56 (12.3)	83.4
$Cp^*(PiPr_3)RuH_2(SiPhMeOTf)$ (**9**)	—	-11.66, -13.52 (9.8)	84.1
$Cp^*(PiPr_3)RuH_2(SiEt_2OTf)$ (**10**)	—	-12.14 (12.5)	106.5
$Cp^*(PiPr_3)RuH_2(Si(iPr)_2OTf)$ (**11**)	—	-11.82 (12.3)	118.9
$Cp^*(PiPr_3)RuH_2(SiFluOTf)$ (**12**)	—	-11.17 (12.2)	77.9

Similar complexes containing a (triflate)silyl ligand have previously been synthesized, of the type $Cp^*(PMe_3)_2MSiR_2OTf$ (M = Ru, Os).[8b,17] For the complex M = Os and R = iPr, the triflate anion reversibly dissocates to provide access to the transient silylene complex, $[Cp^*(PMe_3)_2OsSi(^iPr)_2][OTf]$. The degree of dissociation was found to depend on the polarity of the solvent; the ^{29}Si NMR resonance for this compound in C_6D_6 (100 ppm) is at much higher field than that observed with CD_2Cl_2 solvent (223 ppm). This behavior is not observed for **3** – **12**, as NMR spectra for samples in C_6D_6 and CD_2Cl_2 are very similar. For example, complex **9** displays a ^{29}Si resonance at 84.1 ppm in C_6D_6 and at 87.4 ppm in CD_2Cl_2. Therefore, a transient silylene species does not appear to significantly contribute to the ^{29}Si NMR shifts of **3** – **12.**

Crystals of **8** suitable for X-ray crystallography were grown from a pentane solution at – 30 °C. Two independent molecules per asymmetric unit are present, and all hydride ligands were located (Figure 2). The silicon center is close to tetrahedral (sum of angles around Si = 343.4°) and displays a bonding interaction with the triflate anion. Additionally, the Ru – Si distance of 2.3138(17) Å is in the range expected for Ru – Si single bonds.[16] The Ru – H ··· Si distances are all greater than 2 Å, indicating that full oxidative addition has occurred. However, the hydride ligands are somewhat canted towards the silyl ligands and away from the phosphine, as indicated by the average P-Ru-H angle of 77.7° which is greater than the average Si-Ru-H angle of 63.7°. The short Si – O(1) bond length (1.815(3) Å) further suggests that this complex possesses little silylene character. The solid-state structure of **12** varies little from that of **8** (Figure 3). Additionally, the solid-state structures of **8** and **12** are remarkably similar to that of $Cp^*(PiPr_3)Ru(H)_2(SiHMesCl)$, indicating that the anionic substituent (Cl^- or OTf^-) on silicon does not significantly influence the solid-state molecular geometry.[18]

Figure 2. Molecular structure of **8** displaying thermal ellipsoids at the 50% probability level. One molecule and selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1) – Si(1) = 2.3138(17), Ru(1) – P(1) = 2.3338(14), Ru(1) – H(1) = 1.41(4), Ru(1) – H(2) = 1.51(5), Si(1) – O(1) = 1.815(3).

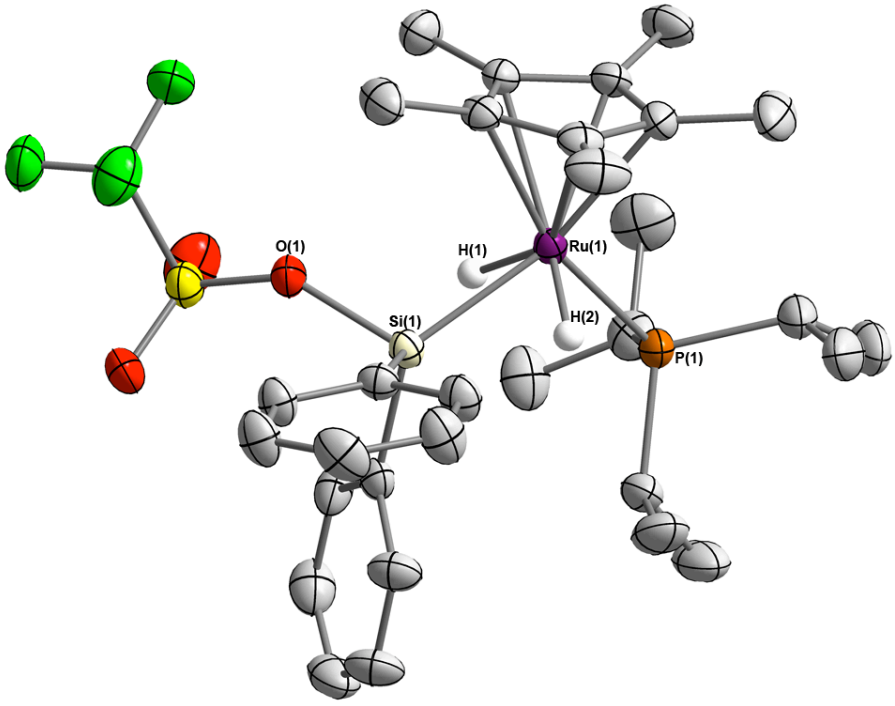
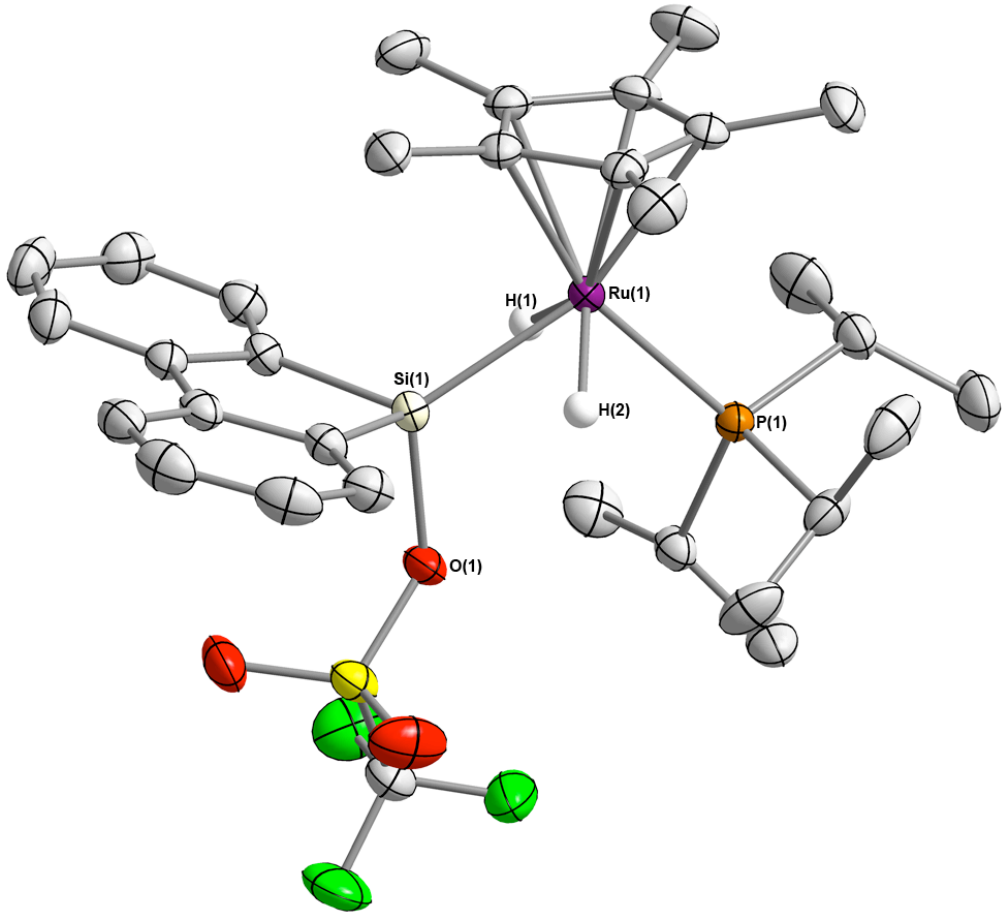


Figure 3. Molecular structure of **12** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1) – Si(1) = 2.2986(9), Ru(1) – P(1) = 2.3369(8), Ru(1) – H(1) = 1.56(3), Ru(1) – H(2) = 1.54(3), Si(1) – O(1) = 1.8108(16).

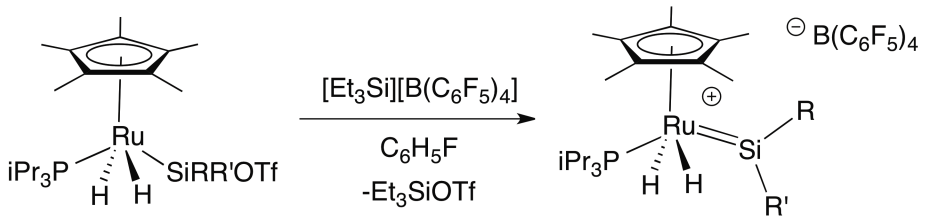


Synthesis and characterization of ruthenium silylene complexes [Cp*(PiPr$_3$)Ru(H)$_2$(=SiRR′)][B(C$_6$F$_5$)$_4$]. A number of cationic silylene complexes have been synthesized via an anion or hydride abstraction, and the triflate complexes **3** – **12** seemed potentially suitable for this purpose. Initial attempts to replace the triflate anion with a more weakly coordinating counterion focused on use of the Li(Et$_2$O)$_2$[B(C$_6$F$_5$)$_4$] salt. Addition of 1 equiv of Li(Et$_2$O)$_2$[B(C$_6$F$_5$)$_4$] to **8** in C$_6$D$_5$Br produced a bright orange solution and ^{1}H NMR spectroscopy revealed quantitative conversion to a new species. However, the ^{29}Si resonance at 127.8 ppm indicated the likely formation of a base-stabilized silylene complex, with diethyl ether acting as the base. Subsequent exposure to vacuum was not successful in removing the ether.

To avoid the introduction of coordinating solvents during the synthesis of silylene complexes, an ether-free [B(C$_6$F$_5$)$_4$]$^-$ reagent capable of removing triflate was required. Thus, the ability of [Et$_3$Si•toluene][B(C$_6$F$_5$)$_4$][19] to afford the desired solvate-free silylenes was explored with **3** – **12**. The compound [Et$_3$Si•toluene][B(C$_6$F$_5$)$_4$] is an interesting reagent because it can act as either an anion abstraction reagent (with loss of Et$_3$SiX) or a hydride abstraction reagent (with

loss of Et_3SiH). Both anion and hydride abstraction have proven to be effective strategies for generation of silylene complexes.[6]

The reactivity of $[Et_3Si•toluene][B(C_6F_5)_4]$ was first examined with **4**, which possesses an Si – H and Si – OTf group that could potentially be susceptible to abstraction. A solution of 1 equiv of $[Et_3Si•toluene][B(C_6F_5)_4]$ in C_6H_5F was added to a solution of **4** in C_6H_5F, resulting in an immediate color change from pale yellow to bright orange (eq 4). Complex **13**, $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$, was isolated as an orange solid.



(4)

R = Mes, R' = H	(**4**)	R = Mes, R' = H	(**13**)
R = Si(SiMe$_3$), R' = H	(**7**)	R = Si(SiMe$_3$), R' = H	(**14**)
R = R' = Ph	(**8**)	R = R' = Ph	(**15**)
R = Ph, R' = Me	(**9**)	R = Ph, R' = Me	(**16**)
R = R' = Flu	(**12**)	R = R' = Flu	(**17**)

Multinuclear NMR spectroscopy confirms the identity of **13** as a hydrogen-substituted ruthenium silylene complex. ^{1}H NMR spectroscopy reveals an Si – H resonance at 7.99 ppm, shifted downfield relative to that of the silyl complex **4** (7.02 ppm) and in a region typical for H-substituted silylene complexes.[4,9b,9c,10] The two hydride ligands of **13** (-11.47 ppm) are equivalent and exhibit a strong coupling to the silicon atom ($^2J_{SiH}$ = 58.2 Hz). The downfield ^{29}Si NMR resonance at 228.9 ppm is characteristic of a silylene ligand. The ^{19}F NMR spectrum reveals three resonances at -132.2, -162.7, and -166.5 ppm that are characteristic of the $[B(C_6F_5)_4]^-$ counterion and a peak associated with triflate (-76.0 ppm for **4**) is absent.

Complex **13** displays very limited solubility in non-coordinating solvents, which necessitated the use of polar solvents. To reduce the possibility of reaction with the solvent, C_6H_5F and C_6D_5Br were used exclusively for synthesis and characterization. In solution, **13** decomposes within 24 h to multiple unidentified species, and the characteristic bright orange color fades to pale brown. However, as a solid, **13** can be stored at -30 °C for one to two weeks without decomposition.

Several previously reported silylene complexes have been found to have observable secondary interactions between M – H and the silylene ligand, as indicated by a J_{SiH} greater than 20 Hz.[9b,9c,20] For example, the family of neutral silylene complexes Cp*(dmpe)Mo(H)(=SiRR') exhibit J_{SiH} values of 30 – 48 Hz and an H···Si interaction is confirmed by a neutron structure.[9b] The degree of H···Si interaction for the cationic silylyne-hydride complex $[Cp^*(dmpe)(H)Mo{\equiv}SiMes][B(C_6F_5)_4]$ is somewhat ambiguous based on NMR data (J_{SiH} = 15 Hz) and X-ray crystallography, but appears to be rather weak.[20] Another Group 6 neutral silylene complex synthesized by Tobita and co-workers, $[Cp^*(CO)_2(H)W=Si(H)\{C(SiMe_3)_3\}]$, also has a high J_{SiH} of 28.6 Hz.[9c] Interestingly, the analogous ruthenium complex, $[Cp^*(CO)(H)Ru=Si(H)\{C(SiMe_3)_3\}]$, does not display such an interaction.[10] The J_{SiH} value for **13** is significantly higher than that observed for other complexes, indicative of a stronger H···Si interaction. This type of interaction was predicted based on theoretical calculations by Beddie

and Hall with a simplified system, $[Cp(PH_3)RuH_2(=SiH_2)]^+$, but is not observable for the previously synthesized, ether-stabilized silylene complex $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh•Et_2O)][B(C_6F_5)_4]$.[3, 6b]

Anion abstraction was utilized for synthesis of the disubstituted silylene complex $[Cp^*(PiPr_3)Ru(H)_2(=SiPh_2)][B(C_6F_5)_4]$ (**15**). Complex **8** was treated with 1 equiv $[Et_3Si•toluene][B(C_6F_5)_4]$ in C_6H_5F and the product (**15**) precipitated from pentane at -30 °C as a bright yellow solid. The ^{1}H NMR spectrum for **15** differs very little from that of **8**. Most notably, the resonance for the hydride ligands of **15** is further downfield at -9.11 ppm (relative to -11.56 ppm for **8**). The presence of the silylene ligand was confirmed with ^{29}Si NMR spectroscopy by a resonance at 339.0 ppm. No silicon satellites were detected for the ruthenium hydride resonance via a ^{29}Si–filtered ^{1}H NMR experiment optimized for a variety of $^2J_{SiH}$ values, suggesting the absence of a significant interaction between the hydride ligand and the silicon center. As determined by structural investigations of Cp*(dmpe)MoH(=ERR') (E = Si, Ge) complexes, such H···Si interactions can be quite sensitive to steric influences, and in particular by rotation about the M – Si bond.[21] The $[B(C_6F_5)_4]^-$ anion displays three characteristic resonances in the ^{19}F NMR spectrum (-132.6, -163.1, and -166.8 ppm), and full conversion from the triflate was further supported by the absence of the downfield triflate peak at (-75.7 ppm for **8**). Complexes **14**, **16**, and **17** display similar spectroscopic properties, which are tabulated in Table 2.

Table 2. NMR data for complexes **13 – 17**

Complex	δ ^{1}H (SiH) ($^2J_{SiH}$)	δ ^{1}H (RuH) ($^2J_{SiH}$)	δ ^{29}Si (RuSi)
$[Cp^*(PiPr_3)RuH_2(=SiHMes)][B(C_6F)_4]$ (**13**)	7.99 (226.5)	-11.46 (58.2)	228.9
$Cp^*(PiPr_3)RuH_2(=SiH(Si(SiMe_3)_3)][B(C_6F)_4]$ (**14**)	7.42 (214.9)	-7.08 (37.1)	241.0
$[Cp^*(PiPr_3)RuH_2(=SiPh_2)][B(C_6F)_4]$ (**15**)	—	-9.11 (not observed)	339.0
$[Cp^*(PiPr_3)RuH_2(=SiPhMe)][B(C_6F)_4]$ (**16**)	—	-9.88 (not observed)	275.9
$[Cp^*(PiPr_3)RuH_2(=SiFlu)][B(C_6F)_4]$ (**17**)	—	-8.69 (not observed)	328.8

Reactions to access silylene complexes were also attempted with **3**, **5**, **6**, **10**, and **11**. For example, 1 equiv of $Li(Et_2O)_2[B(C_6F_5)_4]$ was added to **5** in C_6D_5Br at room temperature to give an orange solution. Immediate characterization by multi-nuclear NMR spectroscopy revealed multiple hydride-containing species and several silicon species. Analogous attempts with $[Et_3Si•toluene][B(C_6F_5)_4]$ resulted in similar mixtures of products. Attempted purification of the reaction mixtures by crystallization yielded impure oils. Interestingly, the reaction of **3** with 1 equiv $[Et_3Si][B(C_6F_5)_4]$ yielded the diphenyl silylene **15** (45% yield) and several unidentified Cp*-containing species (by ^{1}H, ^{31}P, and ^{29}Si NMR spectroscopy). All attempts to isolate or observe $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh)][B(C_6F_5)_4]$ resulted only in observation of **15**. The

transformation of $Cp^*(PiPr_3)RuH_2SiHPhOTf$ to $[Cp^*(PiPr_3)RuH_2(=SiPh_2)]^+$ upon reaction with $[Et_3Si][B(C_6F_5)_4]$ would appear to involve a silylene-mediated redistribution at silicon. This might occur via a bimolecular exchange of groups between silyl and silylene complexes of ruthenium, as has been previously characterized for the related $Cp^*(PMe_3)Ru$ fragment.[22]

Conclusion

$Cp^*(PiPr_3)RuOTf$ (**1**) represents a new electrophilic ruthenium complex that readily activates primary and secondary organosilanes. More generally, it should prove to be a useful starting material for investigations of bond activations at ruthenium. As compared to the similar complex $Cp^*(PiPr_3)RuCl$, **1** tolerates silanes with a significantly wider variety of substitution patterns to give silyl triflate complexes. The reagent $[Et_3Si][B(C_6F_5)_4]$ selectively acts as a triflate abstraction reagent even in the presence of Si – H bonds to yield new ruthenium silylene complexes. The complex $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)]^+$ (**13**) displays significant interactions between the ruthenium hydride ligands and the silicon center by NMR spectroscopy. Significantly, related interactions were previously predicted by Hall and co-workers but had not been experimentally observed.[5b] Interestingly, secondary silylenes such as complex $[Cp^*(PiPr_3)Ru(H)_2(=SiPh_2)]^+$ (**22**) do not appear to have such significant Ru – H ··· Si interactions, but this is probably the result of unfavorable H–Ru–Si–C torsion angles. Stoichiometric and catalytic reactivity studies of silylene complexes **13** – **17** are currently underway, as well as further E – H bond activiation studies with **1**.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and then $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene and toluene were then dried over $CaCl_2$ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Fluorobenzene was dried over P_2O_5, degassed and distilled under N_2. Methylene chloride-d_2 was dried by vacuum distillation from CaH_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Bromobenzene-d_5 was refluxed over CaH_2 for 20 h and then distilled under nitrogen. $Cp^*(PiPr_3)RuCl$[15] an $[Et_3Si][B(C_6F_5)_4]$[18] were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{19}F\{^1H\}$ spectra were referenced relative to a C_6F_6 external standard. $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^1H ^{29}Si HMBC unless specified otherwise. The following abbreviations have been used to describe peak multiplicities in the reported NMR spectroscopic data: “m” for

complex multiplet, and "br" for broadened resonances. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

Cp*(PiPr$_3$)RuOTf (1). To a stirred solution of Cp*(PiPr$_3$)RuCl (3.12 g, 7.24 mmol) in Bu_2O was added Me_3SiOTf (1.44 mL, 7.96 mmol) dropwise over a period of 5 min. The purple solution was allowed to stir for 4 h, and then placed under vacuum for 12 h. After the reaction mixture was stripped to dryness, the purple solid was collected to give **1** in 89% yield (3.50 g). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 1.92 (3H, septet, J = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.35 (15H, s, C$_5$*Me$_5$*), 0.95 (18H, dd, J = 6.9 Hz, J_{PH} = 13.1 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150.9 MHz): 75.2 (*C*$_5$Me$_5$), 25.3 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 19.8 Hz), 19.5 (CH(*C*H$_3$)$_2$), 12.8 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 163.0 MHz): δ 48.0. ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz): δ -76.7. Anal. Calcd for $C_{20}H_{36}F_3O_3PRuS$: C, 44.03; H, 6.65. Found: C, 44.12; H, 6.76.

Cp*(PiPr$_3$)Ru(CO)OTf (2). A 1:1 pentane/ether solution of **1** (0.42 g, 0.77 mmol) was degassed and cooled to 0 °C. The solution was exposed to 1 atm of CO and stirred for 1 h to give an orange-yellow solution. The reaction mixture was filtered through Celite and then cooled to -30 °C to give **2** as orange crystals in 51% yield (0.23 g). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 2.78 (3H, septet, J = 7.3 Hz, C*H*(CH$_3$)$_2$), 2.04 (15H, s, C$_5$*Me$_5$*), 1.47 (18H, dd, J = 7.3 Hz, J_{PH} = 17.6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150.9 MHz): 208.5 (*C*O, d, J_{PC} = 20.1 Hz), 94.9 (*C*$_5$Me$_5$), 25.6 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 22.6 Hz), 19.6 (CH(*C*H$_3$)$_2$), 10.2 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 163.0 MHz): δ 57.3. ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz): δ -75.9. IR (cm^{-1}): ν(CO) 1945. Anal. Calcd for $C_{21}H_{36}F_3O_4PRuS$: C, 43.97; H, 6.33. Found: C, 43.96; H, 6.20.

Cp*(PiPr$_3$)Ru(H)$_2$(SiHPhOTf) (3). A solution of $PhSiH_3$ (0.020 g, 0.18 mmol) in 1 mL of diethyl ether was added to a solution of Cp*(PiPr$_3$)RuOTf (0.10 g, 0.18 mmol) in 2 mL of diethyl ether. The reaction solution was stirred for 20 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a light yellow solid (0.095 g, 79% yield). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.07 (2H, d, J = 7.5 Hz, Ph*H*), 7.33 (2H, t, J = 7.5 Hz, Ph*H*), 7.19 (1H, t, J = 7.5 Hz, Ph*H*), 6.76 (1H, t, J_H = 4.7 Hz, $^1J_{SiH}$ = 211.5 Hz, Si*H*), 1.84 (3H, septet, J = 7.4 Hz, C*H*(CH$_3$)$_2$), 1.57 (15H, s, C$_5$*Me$_5$*), 1.01 (9H, dd, J = 7.4 Hz, J_{PH} = 13.4 Hz, CH(C*H*$_3$)$_2$), 0.94 (9H, dd, J = 7.4 Hz, J_{PH} = 13.5 Hz, CH(C*H*$_3$)$_2$), -11.51 (1H, d, $^2J_{PH}$ = 27.3 Hz, $^2J_{SiH}$ = 18.8 Hz, J_H = 4.7 Hz, Ru*H*), -12.49 (1H, d, $^2J_{PH}$ = 26.6 Hz, $^2J_{SiH}$ = 18.8 Hz, J_H = 4.7 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 141.1 (Ar*C*), 133.4 (Ar*C*), 128.6 (Ar*C*), 127.9 (Ar*C*), 95.9 (*C*$_5$Me$_5$), 26.7 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 26.8 Hz), 19.0 (CH(*C*H$_3$)$_2$), 18.8 (CH(*C*H$_3$)$_2$), 10.8 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 79.4. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 65.1. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -78.0. Anal. Calcd for $C_{24}H_{44}F_3O_3PRuSSi$: C, 47.76; H, 6.78. Found: C, 48.08; H, 7.00.

Cp*(PiPr$_3$)Ru(H)$_2$(SiHMesOTf) (4). By a procedure analogous to that for **3**, complex **4** was obtained as a light tan solid in 90% yield (0.115 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.02 (1H, m, J_H = 7.2 Hz, $^1J_{SiH}$ = 215.4 Hz, Si*H*), 6.70 (2H, s, Ar*H*), 2.67 (6H, s, ArC*H$_3$*), 2.11 (3H, s, ArC*H$_3$*), 1.72 (15H, s, C$_5$*Me$_5$*), 1.59 (3H, septet, J = 7.2 Hz, C*H*(CH$_3$)$_2$), 0.90 (9H, dd, J = 7.1 Hz, J_{PH} = 13.5 Hz, CH(C*H*$_3$)$_2$), 0.68 (9H, dd, J = 7.1 Hz, J_{PH} = 13.0 Hz, CH(C*H*$_3$)$_2$), -11.81 (1H, d, $^2J_{PH}$ = 26.1 Hz, $^2J_{SiH}$ = 10.4 Hz, J_H = 7.2 Hz, Ru*H*), -12.86 (1H, d, $^2J_{PH}$ = 24.9 Hz, $^2J_{SiH}$ = 10.4 Hz, J_H = 7.2 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 143.1 (Ar*C*), 138.5 (Ar*C*), 136.4 (Ar*C*), 129.1 (Ar*C*), 96.5 (*C*$_5$Me$_5$), 27.3 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 25.7 Hz), 22.8 (Ar*Me*), 21.1

(Ar*Me*), 19.9 (CH(*C*H$_3$)$_2$), 18.6 (CH(*C*H$_3$)$_2$), 11.2 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 163.0 MHz): δ 78.2. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 62.4. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.5 MHz): δ -76.3. Anal. Calcd for $C_{29}H_{50}F_3O_3PRuSSi$: C, 50.05; H, 7.24. Found: C, 50.38; H, 7.51.

Cp*(PiPr$_3$)Ru(H)$_2$(SiH(C$_6$F$_5$)OTf) (5). By a procedure analogous to that for **3**, complex **5** was obtained as a light orange solid in 22% yield (0.030 g). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 6.75 (1H, s, $^1J_{SiH}$ = 227.9 Hz, Si*H*), 1.79 (3H, septet, *J* = 7.4 Hz, C*H*(CH$_3$)$_2$), 1.55 (15H, s, C$_5$*Me$_5$*), 0.92 (18H, m, CH(C*H*$_3$)$_2$), -11.57 (1H, d, $^2J_{PH}$ = 25.1 Hz, $^2J_{SiH}$ = < 7 Hz, Ru*H*), -12.26 (1H, d, $^2J_{PH}$ = 28.2 Hz, $^2J_{SiH}$ = < 7, Ru*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 137.9 (Ar*C*), 136.2 (Ar*C*), 120.3 (Ar*C*), 118.2 (Ar*C*), 96.8 (*C*$_5$Me$_5$), 26.3 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 26.0 Hz), 18.8 (CH(*C*H$_3$)$_2$), 18.7 (CH(*C*H$_3$)$_2$), 10.5 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 163.0 MHz): δ 77.0. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 44.3. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.5 MHz): δ -78.3, -129.9, -154.0, -163.0. Anal. Calcd for $C_{26}H_{39}F_8O_3PRuSSi$: C, 41.99; H, 5.29. Found: C, 42.36; H, 5.66.

Cp*(PiPr$_3$)Ru(H)$_2$(SiH(SiPh$_3$)OTf) (6). By a procedure analogous to that for **3**, complex **6** was obtained as a light orange solid in 40% yield (0.061 g). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 7.97 (6H, d, *J* = 6.9 Hz, Ph*H*), 7.26 (6H, t, *J* = 6.9 Hz, Ph*H*), 7.20 (3H, t, *J* = 6.9 Hz, Ph*H*), 6.86 (1H, br s, $^1J_{SiH}$ = 188.6 Hz, Si*H*), 1.85 (3H, septet, *J* = 7.9 Hz, C*H*(CH$_3$)$_2$), 1.67 (15H, s, C$_5$*Me$_5$*), 0.97 (9H, dd, *J* = 7.9 Hz, J_{PH} = 13.9 Hz, CH(C*H*$_3$)$_2$), 0.74 (9H, dd, *J* = 7.9 Hz, J_{PH} = 13.4 Hz, CH(C*H*$_3$)$_2$), -10.96 (1H, d, $^2J_{PH}$ = 27.6 Hz, $^2J_{SiH}$ = 21.8 Hz, Ru*H*), -12.09 (1H, d, $^2J_{PH}$ = 27.6 Hz, $^2J_{SiH}$ = 21.8 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 137.0 (Ar*C*), 135.9 (Ar*C*), 129.7 (Ar*C*), 129.2 (Ar*C*), 97.0 (*C*$_5$Me$_5$), 26.6 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 24.8 Hz), 19.0 (CH(*C*H$_3$)$_2$), 18.8 (CH(*C*H$_3$)$_2$), 11.3 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 163.0 MHz): δ 77.8. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 63.3, -24.9. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.5 MHz): δ -78.0. Anal. Calcd for $C_{38}H_{54}F_3O_3PRuSSi_2$•1/2($C_6H_5F$): C, 55.70; H, 6.44. Found: C, 55.64; H, 6.50.

Cp*(PiPr$_3$)Ru(H)$_2$(SiH(Si(SiMe$_3$)$_3$)OTf) (7). By a procedure analogous to that for **3**, complex **7** was obtained as a light pink solid in 22% yield (0.030 g). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 6.97 (1H, s, $^1J_{SiH}$ = 192.5 Hz, Si*H*), 1.89 (3H, septet, *J* = 7.3 Hz, C*H*(CH$_3$)$_2$), 1.81 (15H, s, C$_5$*Me$_5$*), 1.03 (9H, dd, *J* = 7.3 Hz, J_{PH} = 13.6 Hz, CH(C*H*$_3$)$_2$), 0.96 (9H, dd, *J* = 7.3 Hz, J_{PH} = 13.7 Hz, CH(C*H*$_3$)$_2$), 0.49 (27H, s, Si*Me$_3$*), -10.98 (1H, d, $^2J_{PH}$ = 28.5 Hz, $^2J_{SiH}$ = 11.4 Hz, Ru*H*), -13.01 (1H, d, $^2J_{PH}$ = 26.5 Hz, $^2J_{SiH}$ = 11.4, Ru*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 96.3 (*C*$_5$Me$_5$), 26.7 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 22.5 Hz), 19.5 (CH(*C*H$_3$)$_2$), 19.0 (CH(*C*H$_3$)$_2$), 11.5 (C$_5$*Me$_5$*), 3.3 (Si*Me$_3$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 163.0 MHz): δ 77.8. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 69.3, -9.2, -118.4. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.5 MHz): δ -77.3. Anal. Calcd for $C_{29}H_{66}F_3O_3PRuSSi_5$: C, 42.25; H, 8.07. Found: C, 42.54; H, 7.88.

Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$OTf) (8). By a procedure analogous to that for **3**, complex **8** was obtained as a light brown solid in 59% yield (0.079 g). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 8.15 (4H, d, *J* = 7.2 Hz, Ph*H*), 7.26 (4H, t, *J* = 7.2 Hz, Ph*H*), 7.14 (2H, t, *J* = 7.2 Hz, Ph*H*), 1.57 (18H, s, C$_5$*Me$_5$* + C*H*(CH$_3$)$_2$), 0.94 (18H, dd, *J* = 7.2 Hz, J_{PH} = 13.4 Hz, CH(C*H*$_3$)$_2$), -11.56 (2H, d, $^2J_{PH}$ = 26.5 Hz, $^1J_{SiH}$ = 12.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 142.8 (Ph*C*), 135.3 (Ph*C*), 128.7 (Ph*C*), 127.0 (Ph*C*), 99.2 (*C*$_5$Me$_5$), 27.1 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 22.6 Hz), 19.2 (CH(*C*H$_3$)$_2$), 10.7 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 163.0 MHz): δ 77.5. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 83.4. ^{19}F{^{1}H} NMR (C$_6$D$_6$, 376.5 MHz): δ -75.7. Anal. Calcd for $C_{32}H_{48}F_3O_3PRuSSi$: C, 52.66; H, 6.63. Found: C, 52.45; H, 6.40.

Cp*(PiPr$_3$)Ru(H)$_2$(SiPhMeOTf) (9). By a procedure analogous to that for **3**, complex **9** was obtained as a light peach solid in 81% yield (0.099 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.03 (2H, d, *J* = 7.3 Hz, Ph*H*), 7.35 (2H, t, *J* = 7.3 Hz, Ph*H*), 7.21 (1H, t, *J* = 7.3 Hz, Ph*H*), 1.81 (3H, septet, *J* = 7.4 Hz, C*H*(CH$_3$)$_2$), 1.54 (15H, s, C$_5$*Me$_5$*), 1.02 (18H, m, CH(C*H*$_3$)$_2$), 0.89 (3H, s, C*H*-$_3$), -11.66 (1H, d, $^2J_{PH}$ = 26.8 Hz, $^1J_{SiH}$ = 9.8 Hz, Ru*H*), -13.52 (1H, d, $^2J_{PH}$ = 26.4 Hz, $^1J_{SiH}$ = 9.8 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 145.1 (Ph*C*), 132.8 (Ph*C*), 128.0 (Ph*C*), 127.0 (Ph*C*), 95.9 (*C*$_5$Me$_5$), 27.8 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 26.9 Hz), 19.4 (CH(*C*H$_3$)$_2$), 18.7 (CH(*C*H$_3$)$_2$), 13.7 (Si*Me*), 10.5 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 79.8. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 84.1. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -76.4. Anal. Calcd for $C_{27}H_{46}F_3O_3PRuSSi$: C, 48.56; H, 6.94. Found: C, 48.94; H, 7.04.

Cp*(PiPr$_3$)Ru(H)$_2$(SiEt$_2$OTf) (10). By a procedure analogous to that for **3**, complex **10** was obtained as a light pink-brown solid in 56% yield (0.065 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 1.81 (3H, septet, *J* = 7.2 Hz, C*H*(CH$_3$)$_2$), 1.61 (15H, s, C$_5$*Me$_5$*), 1.34 (6H, m, C*H*$_2$C*H*$_3$), 1.13 (4H, m, C*H*$_2$C*H*$_3$), 1.00 (18H, dd, *J* = 7.2 Hz, J_{PH} = 13.1 Hz, PCH(C*H*$_3$)$_2$), -12.14 (2H, d, $^2J_{PH}$ = 26.8 Hz, $^1J_{SiH}$ = 12.5 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 95.4 (*C*$_5$Me$_5$), 27.6 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 23.3 Hz), 19.1 (CH(*C*H$_3$)$_2$), 16.4 (*C*H$_2$CH$_3$), 10.7 (C$_5$*Me$_5$*), 8.3 (CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 79.3. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 106.5. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -76.6. Anal. Calcd for $C_{24}H_{48}F_3O_3PRuSSi$: C, 45.48; H, 7.63. Found: C, 45.63; H, 7.70.

Cp*(PiPr$_3$)Ru(H)$_2$(Si^{i}Pr$_2$OTf) (11). By a procedure analogous to that for **3**, complex **11** was obtained as a light pink solid in 53% yield (0.064 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 1.87 (3H, septet, *J* = 7.1 Hz, PC*H*(CH$_3$)$_2$), 1.70 (2H, septet, *J* = 7.4 Hz, SiC*H*(CH$_3$)$_2$), 1.58 (15H, s, C$_5$*Me$_5$*), 1.54 (6H, d, *J* = 7.4 Hz, SiCH(C*H*$_3$)$_2$), 1.40 (6H, dd, *J* = 7.4 Hz, SiCH(C*H*$_3$)$_2$), 1.06 (18H, dd, *J* = 7.1 Hz, J_{PH} = 13.2 Hz, PCH(C*H*$_3$)$_2$), -11.82 (2H, d, $^2J_{PH}$ = 27.0 Hz, $^1J_{SiH}$ = 12.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 95.6 (*C*$_5$Me$_5$), 27.9 (PCH(CH$_3$)$_2$, d, $^1J_{PC}$ = 22.8 Hz), 23.6 (Si*C*H(CH$_3$)$_2$), 19.7 (SiCH(*C*H$_3$)$_2$), 19.6 (SiCH(*C*H$_3$)$_2$), 19.4 (PCH(*C*H$_3$)$_2$), 11.3 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 77.8. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 118.9. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -75.0. Anal. Calcd for $C_{26}H_{52}F_3O_3PRuSSi$: C, 47.18; H, 7.92. Found: C, 47.47; H, 8.19.

Cp*(PiPr$_3$)Ru(H)$_2$(SiFluOTf) (12). By a procedure analogous to that for **3**, complex **12** was obtained as a colorless solid in 42% yield (0.056 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.96 (2H, m, Ar*H*), 7.69 (2H, m, Ar*H*), 7.30 (4H, m, Ar*H*), 2.05 (3H, septet, *J* = 7.1 Hz, C*H*(CH$_3$)$_2$), 1.29 (15H, s, C$_5$*Me$_5$*), 1.16 (18H, dd, *J* = 7.1 Hz, J_{PH} = 13.0 Hz, CH(C*H*$_3$)$_2$), -11.17 (2H, d, $^2J_{PH}$ = 25.9 Hz, $^1J_{SiH}$ = 12.2 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 146.6 (Ar*C*), 140.4 (Ar*C*), 132.9 (Ar*C*), 130.4 (Ar*C*), 120.2 (Ar*C*), 95.4 (*C*$_5$Me$_5$), 27.4 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 22.7 Hz), 19.2 (CH(*C*H$_3$)$_2$), 10.2 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 79.1. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 77.9. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -76.4. Anal. Calcd for $C_{32}H_{46}F_3O_3PRuSSi$: C, 52.80; H, 6.37. Found: C, 52.70; H, 6.17.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiHMes)][B(C$_6$F)$_4$] (13). A solution of [Et$_3$Si•toluene][B(C$_6$F$_5$)$_4$] (0.055 g, 0.07 mmol) in 0.5 mL of C$_6$H$_5$F was added to a solution of **4** (0.050 g, 0.07 mmol) in 1 mL of C$_6$H$_5$F. After stirring for 5 min at room temperature, 15 mL of pentane was added to the bright orange solution and the reaction vessel was placed in the −30 °C freezer. After 1 h, an orange oil

settled to the bottom of the vial. The solution was carefully decanted and the resulting orange oil was dried under vacuum for 1 h to afford **13** as an orange solid in 53% yield (0.048 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.99 (1H, br s, $^{1}J_{SiH}$ = 226.5 Hz, Si*H*), 6.93 (2H, s, Ar*H*), 2.42 (6H, s, ArC*H*$_3$), 2.38 (3H, s, ArC*H*$_3$), 2.06 (3H, septet, *J* = 7.1 Hz, C*H*(CH$_3$)$_2$), 1.58 (15H, s, C$_5$*Me*$_5$), 1.09 (18H, dd, *J* = 7.1 Hz, J_{PH} = 13.8 Hz, CH(C*H*$_3$)$_2$), -11.47 (2H, d, $^{2}J_{PH}$ = 14.1 Hz, $^{2}J_{SiH}$ = 58.2 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.6 (B(*C*$_6$F)$_4$), 148.2 (B(*C*$_6$F)$_4$), 142.9 (Ar*C*), 140.0 (Ar*C*), 137.7 (B(*C*$_6$F)$_4$), 135.9 (B(*C*$_6$F)$_4$), 129.0 (Ar*C*), 97.4 (*C*$_5$Me$_5$), 26.1 (*C*H(CH$_3$)$_2$, d, $^{1}J_{PC}$ = 19.6 Hz), 21.9 (Ar*Me*), 21.5 (Ar*Me*), 19.1 (CH(*C*H$_3$)$_2$), 10.6 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 66.2. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 228.9. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.2, -162.7, -166.5. Anal. Calcd for $C_{52}H_{50}BF_{20}PRuSi$: C, 50.95; H, 4.11. Found: C, 50.66; H, 4.50.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiH(Si(SiMe$_3$)$_3$)][B(C$_6$F)$_4$] (14). By a procedure analogous to that for **13**, complex **14** was obtained as a bright red solid in 63% yield (0.031 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.42 (1H, s, $^{1}J_{SiH}$ = 214.9 Hz, Si*H*), 1.88 (15H, s, C$_5$*Me*$_5$), 1.64 (3H, m, C*H*(CH$_3$)$_2$), 1.12 (18H, dd, *J* = 7.2 Hz, J_{PH} = 14.8 Hz, CH(C*H*$_3$)$_2$), 0.47 (27H, s, Si*Me*$_3$), -7.08 (2H, d, $^{2}J_{PH}$ = 24.9 Hz, $^{2}J_{SiH}$ = 37.1 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 149.6 (B(*C*$_6$F)$_4$), 148.0 (B(*C*$_6$F)$_4$), 137.6 (B(*C*$_6$F)$_4$), 136.0 (B(*C*$_6$F)$_4$), 97.8 (*C*$_5$Me$_5$), 30.4 (*C*H(CH$_3$)$_2$), 19.7 (CH(*C*H$_3$)$_2$), 19.0 (CH(*C*H$_3$)$_2$), 11.6 (C$_5$*Me*$_5$), 3.1 (Si*Me*$_3$), 2.3 (Si*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 83.8. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 241.0, -7.1, -46.4. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -132.2, -162.5, -166.4. Anal. Calcd for $C_{29}H_{66}BF_{20}PRuSi_5$: C, 46.12; H, 4.91. Found: C, 46.45; H, 4.54.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiPh$_2$)][B(C$_6$F)$_4$] (15). By a procedure analogous to that for **13**, complex **15** was obtained as a bright yellow solid in 57% yield (0.048 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.88 (4H, d, *J* = 7.3 Hz, Ph*H*), 7.63 (2H, t, *J* = 7.3 Hz, Ph*H*), 7.58 (4H, t, *J* = 7.3 Hz, Ph*H*), 1.77 (15H, s, C$_5$*Me*$_5$), 1.69 (3H, septet, *J* = 7.0 Hz, C*H*(CH$_3$)$_2$**)**, 0.98 (18H, dd, *J* = 7.0 Hz, J_{PH} = 14.5 Hz, CH(C*H*$_3$)$_2$), -9.11 (2H, d, $^{2}J_{PH}$ = 25.5 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.3 (B(*C*$_6$F)$_4$), 147.7 (B(*C*$_6$F)$_4$), 141.8 (Ar*C*), 139.1 (Ar*C*), 137.4 (B(*C*$_6$F)$_4$), 135.9 (Ar*C*), 135.6 (B(*C*$_6$F)$_4$), 133.6 (Ar*C*), 199.1 (*C*$_5$Me$_5$), 27.4 (*C*H(CH$_3$)$_2$, d, $^{1}J_{PC}$ = 24.8 Hz), 19.2 (CH(*C*H$_3$)$_2$), 11.0 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 81.0. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 339.0. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.6, -163.1, -166.8. Anal. Calcd for $C_{55}H_{48}BF_{20}PRuSi$: C, 52.43; H, 3.84. Found: C, 52.06; H, 3.89.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiPhMe)][B(C$_6$F)$_4$] (16). By a procedure analogous to that for **13**, complex **16** was obtained as a light brown solid in 52% yield (0.033 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.95 (2H, m, Ph*H*), 7.58 (2H, m, Ph*H*), 7.41 (1H, m, Ph*H*), 1.78 (15H, s, C$_5$*Me*$_5$), 1.71 (3H, septet, *J* = 7.0 Hz, C*H*(CH$_3$)$_2$**)**, 1.52 (3H, s, C*H*$_3$), 0.99 (18H, dd, *J* = 7.0 Hz, J_{PH} = 14.3 Hz, CH(C*H*$_3$)$_2$), -9.88 (2H, d, $^{2}J_{PH}$ = 25.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 149.7 (B(*C*$_6$F)$_4$), 148.1 (B(*C*$_6$F)$_4$), 139.5 (Ar*C*), 137.6 (B(*C*$_6$F)$_4$), 135.9 (B(*C*$_6$F)$_4$), 134.1 (Ar*C*), 128.3 (Ar*C*), 124.3 (Ar*C*), 97.2 (*C*$_5$Me$_5$), 27.9 (*C*H(CH$_3$)$_2$, d, $^{1}J_{PC}$ = 22.0 Hz), 19.6 (CH(*C*H$_3$)$_2$), 11.3 (C$_5$*Me*$_5$), 10.8 (Si*Me*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 81.2. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 275.9. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -132.2, -162.8, -166.6. Anal. Calcd for $C_{50}H_{46}BF_{20}PRuSi$: C, 50.14; H, 3.87. Found: C, 50.02; H, 4.25.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiFlu)][B(C$_6$F)$_4$] (17). By a procedure analogous to that for **13**, complex **17** was obtained as a bright yellow solid in 69% yield (0.036 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.93 (2H, d, Ar*H*), 7.55 (4H, m, Ar*H*), 7.46 (2H, m, Ar*H*), 1.84 (15H, s, C_5Me_5), 1.67 (3H, septet, J = 7.0 Hz, C*H*(CH_3)$_2$), 0.97 (18H, dd, J = 7.0 Hz, J_{PH} = 14.6 Hz, CH(C*H*$_3$)$_2$), -8.69 (2H, br s). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 149.7 (B(*C*$_6$F)$_4$), 148.1 (B(*C*$_6$F)$_4$), 139.4 (Ar*C*), 137.6 (B(*C*$_6$F)$_4$), 136.5 (Ar*C*), 135.9 (B(*C*$_6$F)$_4$), 135.7 (Ar*C*), 134.7 (Ar*C*), 121.3 (Ar*C*), 99.7 (*C*$_5$Me$_5$), 27.9 (*C*H(CH$_3$)$_2$, d, $^1J_{PC}$ = 25.2 Hz), 19.6 (CH(*C*H$_3$)$_2$), 11.7 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 84.6. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 328.8. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -132.3, 162.8, 166.6. Anal. Calcd for $C_{55}H_{46}BF_{20}PRuSi$: C, 52.52; H, 3.69. Found: C, 52.28; H, 4.03.

X-ray Crystallography. The single-crystal X-ray analysis of compounds **1**, **8**, and **12** were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data was integrated and analyzed for agreement using Bruker APEX2 v. 2009.1.[23] Empirical absorption correction were made using SADABS.[24] Structures were solved by direct methods using the SHELX program package.[25]

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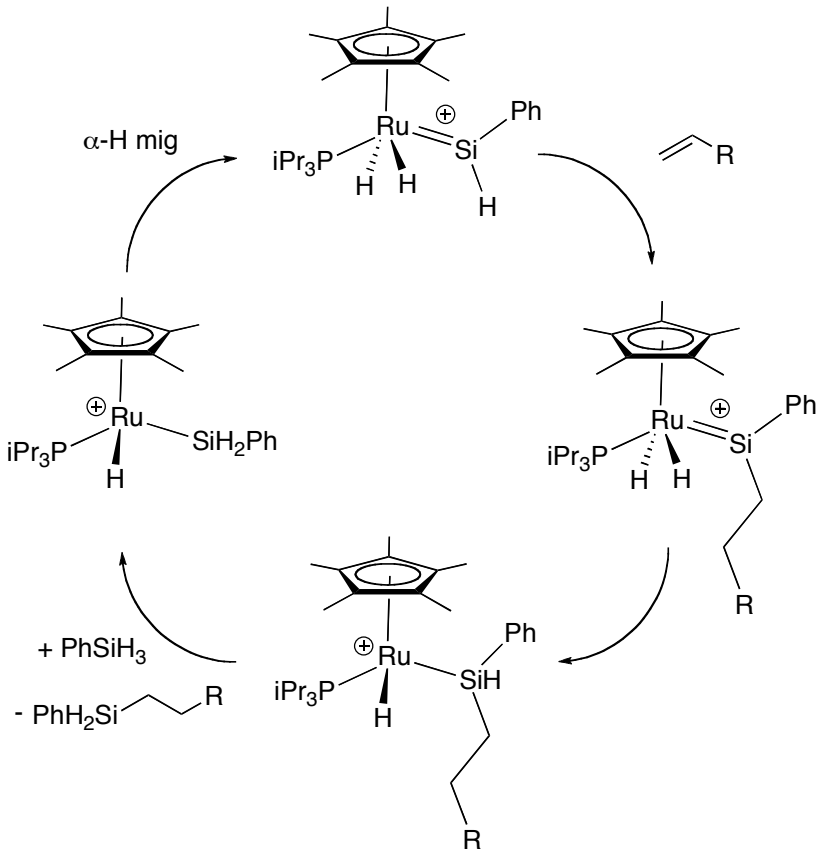
Chapter 2

Mechanism of Catalytic Alkene Hydrosilation by a Cationic Hydrogen-Substituted Ruthenium Silylene Complex

Introduction

Hydrosilation, the addition of an Si–H bond across an unsaturated bond (C=C, C=O, C=N, etc.), is an extremely important chemical transformation in the laboratory and in large-scale industrial applications.[1] Commercial processes utilize expensive platinum-based catalysts, which are highly effective but somewhat limited with respect to selectivities and substrate scope.[2] The performance of these catalysts are generally understood within the context of the Chalk-Harrod or modified Chalk-Harrod mechanisms, which account for the observed activity as well as the side reactions which lower selectivity.[3] Recent efforts to advance hydrosilation catalysis have resulted in several systems that exhibit high selectivities for particular products, and employ less expensive metals.[4] In some cases, it seems that the new hydrosilation catalysts operate via mechanisms distinct from those associated with platinum, and the discovery of new catalytic mechanisms is expected to enable the design of new catalysts.

Scheme 1.



Several recent investigations point to the potential utility of transition metal silylene complexes as reactive intermediates in the catalytic hydrosilation of olefins.[5-9] The initial discovery of hydrosilation catalyzed by a silylene complex, $[Cp^*(PiPr_3)Ru(H)_2(SiHPh\bullet Et_2O)][B(C_6F_5)_4]$[6] (**1**), implicated a new hydrosilation mechanism involving direct addition of the silylene Si–H bond to an olefin (Scheme 1). In addition, the silylene ligand appears to be regenerated in the catalytic cycle by oxidative addition of an Si–H bond, followed by 1,2-migration of a second hydrogen from silicon to ruthenium. The silylene functionality appears to be necessary for catalysis, since the related silyl complexes

$Cp^*(PiPr_3)Ru(H)_2(SiHPhOTf)$ and $Cp^*(PiPr_3)Ru(H)Cl(SiH_2Ph)$ are not active catalysts. This catalysis features a strict selectivity for primary silanes (to exclusively give secondary silane products), and no reactivity is observed with secondary and tertiary silanes. Additionally, olefin hydrosilations are highly selective in exclusively producing anti-Markovnikov secondary silane products. Typical byproducts of hydrosilation catalysis, such as vinyl silanes, isomerized olefin, and silane redistribution products, are not observed. Studies with analogous osmium silylene complexes indicate that the cationic nature of the catalytic species is required for insertion of the olefin into the Si–H bond.[7]

Given the potential importance of new catalysis based on reactions of a silylene ligand, it is important to obtain detailed mechanistic information for hydrosilations catalyzed by **1** and related complexes. Current understanding of the mechanism is based on studies of relevant stoichiometric transformations and by DFT investigations.[8] Significantly, kinetic studies of the catalytic process have not been reported, and structural information on key catalytic species of the type $[Cp^*(PiPr_3)Ru(H)_2(=SiHR)]^+$ has not been available. Interestingly, DFT calculations on $[Cp(PH_3)Ru(H)_2(=SiHR)]^+$ (R = H,[8a] Ph[8b]) complexes indicate the presence of two strong ruthenium hydride–silicon interactions in such catalytic species. However, structural information on **1** has not been available since repeated efforts to obtain X-ray-quality crystals of this sticky yellow solid have not been successful. In addition, kinetic studies on catalysis by **1** has been complicated by lack of a suitable solvent that is unreactive and nonvolatile over an appropriate temperature range. Here, we report the synthesis and structural characterization of $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][CB_{11}H_6Br_6]$ (**2**), a hydrosilation catalyst and model for the key silylene intermediate. Furthermore, kinetic studies with this type of silylene complex have now provided significant new insights into how this catalysis operates.

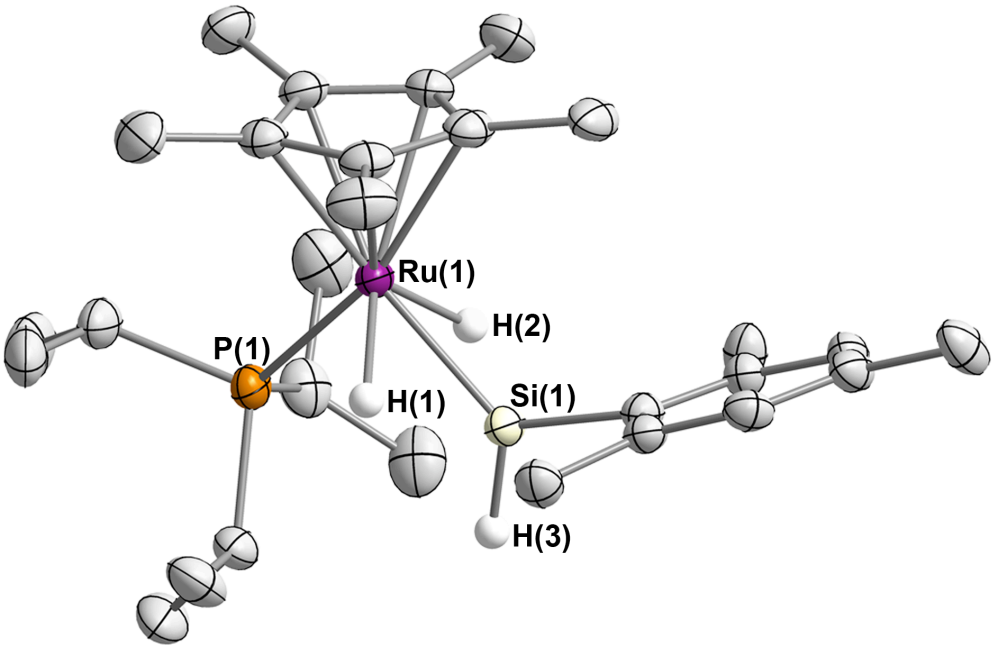
Results and Discussion

Structural characterization of cationic silylene complex 2. In general, cationic silylene complexes containing the $[B(C_6F_5)_4]^-$ anion do not readily crystallize to produce well-formed crystals. To obtain X-ray quality crystals of a $[Cp^*(PiPr_3)Ru(H)_2(=SiHR)]^+$ complex, a weakly coordinating anion other than $[B(C_6F_5)_4]^-$ was sought. In this context, the carborane anion $[CB_{11}H_6Br_6]^-$ has proven useful in providing crystalline samples of iridium silylene complexes and other cationic silicon species.[10] Reaction of $Cp^*(PiPr_3)Ru(H)_2(SiHMesOTf)$[11] with $[Et_3Si][CB_{11}H_6Br_6]$[12] in C_6H_5F followed by precipitation with pentane provided $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][CB_{11}H_6Br_6]$ (**2**) as an orange solid. The ^{29}Si NMR spectrum reveals a resonance at 228.7 ppm, and in the ^1H NMR spectrum the ruthenium hydride ligands at -11.35 ppm display a $^2J_{SiH}$ coupling constant of 62.3 Hz. These values are nearly identical to those observed for the analogous complex $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$ (^{29}Si = 228.9 ppm, $^2J_{SiH}$ = 58.2 Hz).[11] While $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$ can be stored for 1 to 2 weeks at -35 °C before significant decomposition, **2** can be stored for 2 months at -35 °C without decomposition and is stable in C_6D_5Br solution at room temperature for *ca.* one week.

Single crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a solution of **2** in C_6H_5F over 48 h at -35 °C (Figure 1). No interactions are observed between the carborane anion and the silicon center. The Ru–Si bond distance of 2.246(1) Å is slightly longer than analogous distances in the neutral ruthenium silylene complexes $Cp^*(CO)(H)Ru{=}SiH[C(SiMe_3)_3]$ (2.220(2) Å)[13] and $Cp^*(iPr_2MeP)(H)Ru{=}SiH(Trip)$ (2.205(1) Å)[14] but is similar to that found in the cationic complex $[Cp^*(Me_3P)_2Ru{=}SiMe_2][B(C_6F_5)_4]$

(2.238(3) Å).[15] The observed bond lengthening may be attributed to an increased Ru–H ··· Si interaction for **2**. The ruthenium hydride ligands were located in the Fourier difference map. However, the position of H(2) was not stable under refinement and was fixed in position, so metrical parameters of H(2) will not be discussed. The Ru–H(1) distance of 1.73(6) Å is longer than the Ru–H distances observed in $Cp^*(PiPr_3)Ru(H)_2(SiHMesCl)$[16] (Ru–H(1) = 1.50(9) Å; Ru–H(2) = 1.59(7) Å) and $Cp^*(PiPr_3)Ru(H)_2(SiPh_2OTf)$[11] (Ru–H(1) = 1.41(4) Å; Ru–H(2) = 1.51(5) Å), and the Si···H(1) distance of 1.74(6) Å is remarkably short, indicating a relatively strong Ru–H···Si interaction in **2**. For comparison, the neutral complex $Cp^*(iPr_2MeP)(H)Ru{=}SiH(Trip)$ displays a Ru–H···Si distance of 2.21(4) Å.[14] The strong distortion of **2** away from an idealized four-legged piano stool structure, with the hydride ligands significantly displaced toward silicon, is a feature that is often observed for piano-stool silyl hydride complexes of ruthenium and is attributed to donation of hydride electron density to the electrophilic silicon center.[17] For $Cp^*(PiPr_3)Ru(H)_2(SiHMesCl)$, this distortion results in different sets of P-Ru-H (78, 79°) and Si-Ru-H (60, 64°) angles. The stronger distortion for **2**, reflected in a greater difference in P-Ru-H (80, 85°) and Si-Ru-H (50, 54°) angles, appears to reflect the more strongly electrophilic nature of the sp^2-hybridized silicon center in this type of cationic structure.[18] In addition, the small hydrogen substituent at the silicon of **2** appears to allow the complex to readily adopt a conformation that maximizes interactions of the hydrides with the formally empty p orbital at silicon.[19]

Figure 1. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms, carborane anion, and fluorobenzene molecule have been omitted for clarity. Selected bond lengths (Å): Ru(1)-Si(1) = 2.2461(13), Ru(1)-P(1) = 2.3662(12), Ru(1)-H(1) = 1.73(6), Ru(1)-H(2) = 1.5981(4), Si(1)-H(3) = 1.32(6).



Catalytic hydrosilation with 2. Compound **2** was evaluated as a catalyst for hydrosilation of a variety of olefins, with the primary silanes $PhSiH_3$ and $CySiH_3$ (Table 1). In a typical hydrosilation experiment, equimolar amounts of the primary silane and the olefin were

added to a C_6D_5Br solution containing 1 mol % loading of **2** and an internal standard. The reaction temperature was then raised to 80 °C, and reactions were allowed to proceed for 1 h. As observed for both $[Cp^*(PiPr_3)Ru(H)_2(SiHPh•Et_2O)][B(C_6F_5)_4]$[6] and $[(PNP)(H)Ir{=}Si(H)Mes][B(C_6F_5)_4]$,[20] the catalysis is regioselective and exclusively produces the anti-Markovnikov, secondary silane product (H_2SiRR'), which is inactive to further hydrosilation.

Table 1. Catalytic Hydrosilation by **2**[a].

silane	**alkene**	**yield**
$PhSiH_3$	1-octene	73%
	1-hexene	60%
	cyclopentene	67%
	cyclohexene	79%
	t-butylethylene	79%
$CySiH_3$	1-octene	>98%
	1-hexene	97%
	cyclopentene	>98%
	cyclohexene	94%
	t-butylethylene	>98%

a. Reactions were conducted with 1 mol % of **2** in 0.5 mL of C_6D_5Br at 80 °C for 1 h.

Unlike **1**, compound **2** catalyzes silane redistribution under these reaction conditions. This side reaction results in lowered yields for the main hydrosilation product when **2** is used as the catalyst. For example, the catalytic reaction mixture of $PhSiH_3$ and 1-hexene after 1 h at 80 °C in C_6D_5Br contains $PhHexSiH_2$ (60%), $PhSiH_3$ (8%), $HexSiH_3$ (19%), and Ph_2SiH_2 (10%). However, the alkylsilane substrate $CySiH_3$ results in no redistribution products under the same conditions. Furthermore, the $B(C_6F_5)_4^-$ analogue of **2**, $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$,[11] produces only the hydrosilation product $PhHexSiH_2$ (98%) under the same reaction conditions. In the absence of olefin, **2** reacted with 10 equiv of $PhSiH_3$ at 80 °C in C_6D_5Br over 1 h to give Ph_3SiH (16%), Ph_2SiH_2 (27%), $PhSiH_3$ (27%), and SiH_4 (30%). Under analogous conditions, no redistribution is observed for $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$ with 10 equiv of $PhSiH_3$. These interesting results imply that the anion plays a crucial role in defining the catalytic chemistry. A detailed explanation for this difference is currenty lacking, but it would seem to reflect the nature of cation-anion interactions in solution. In this context, note that redistribution at silicon has been shown to occur via bimolecular reactions of neutral silyl and cationic silylene complexes in solution.[21] Interestingly, a ten-fold decrease in the concentration of **2** gave much lower conversion of 10 equiv of $PhSiH_3$ at 80 °C in C_6D_5Br over 1 h to redistribution products (Ph_2SiH_2 (5%), $PhSiH_3$ (93%), and SiH_4 (3%)).

Mechanistic studies on hydrosilation with $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)]^+$. Mechanistic studies were undertaken using $CySiH_3$ and 1-octene as substrates, to avoid possible

complications from silane redistribution. Kinetic measurements were monitored by loss of silane at 80 °C in bromobenzene-d_5, and the appearance of product correlates with silane loss. First-order dependence of the reaction rate on the concentration of **2** was established by varying the loading of catalyst **2** from 1 to 4 mol % (Figure 2). Preliminary studies indicated that the reaction is not first order in olefin and suggested an inverse dependence. To determine the reaction order in olefin more precisely, pseudo-first order reaction conditions were established for various concentrations of olefin (3.2 – 7.5 M) with 0.16 M silane and 1 mol % catalyst **2**. Under these conditions, plots of [olefin] vs. $1/k_{obs}$ were linear, indicating an inverse-order dependence on olefin (Figure 3). Additionally, the reaction order in silane was determined to be first order based on the linear plots of ln[silane] vs. time (Figure 4) under pseudo-first order conditions, measured over 4 half-lives. While first order dependence on both [**2**] and [silane] might be expected on the basis of the simple mechanism previously reported,[6] the inverse order dependence on [olefin] indicates that the initially proposed mechanism requires refinement.

Figure 2. Plot of rate versus [**2**].

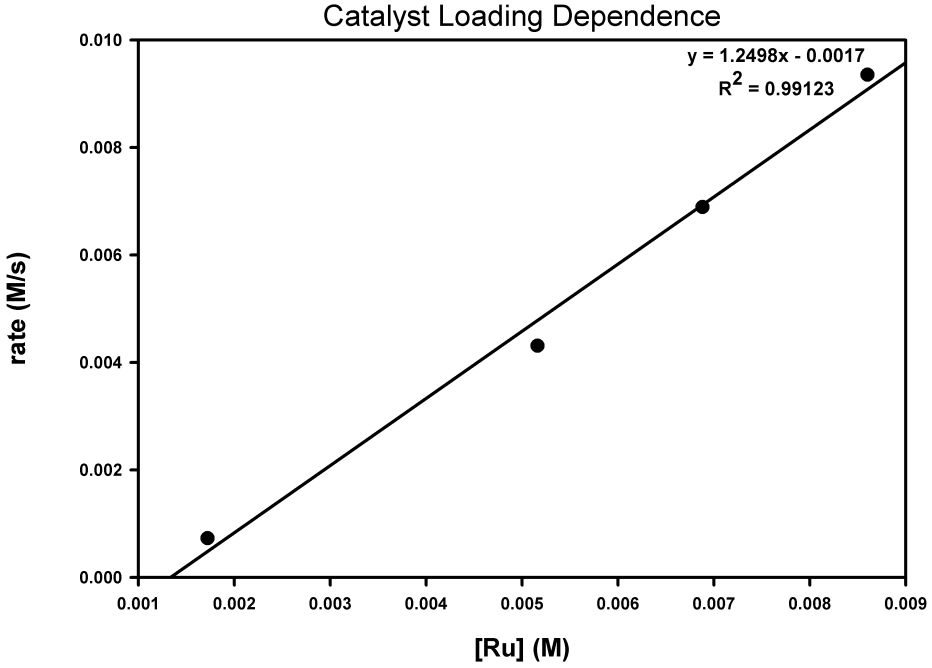


Figure 3. Plot of 1/rate versus [olefin].

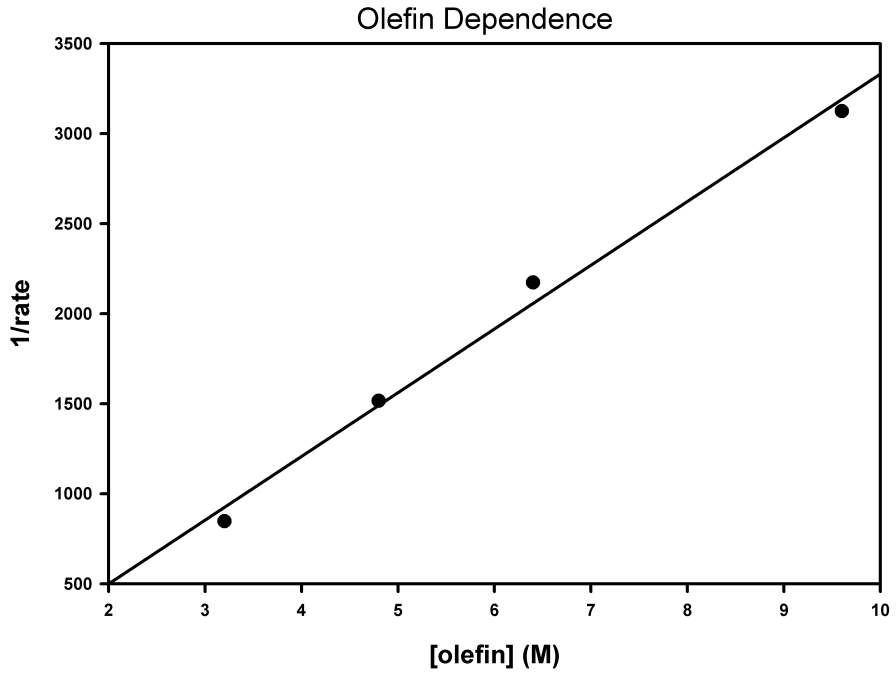
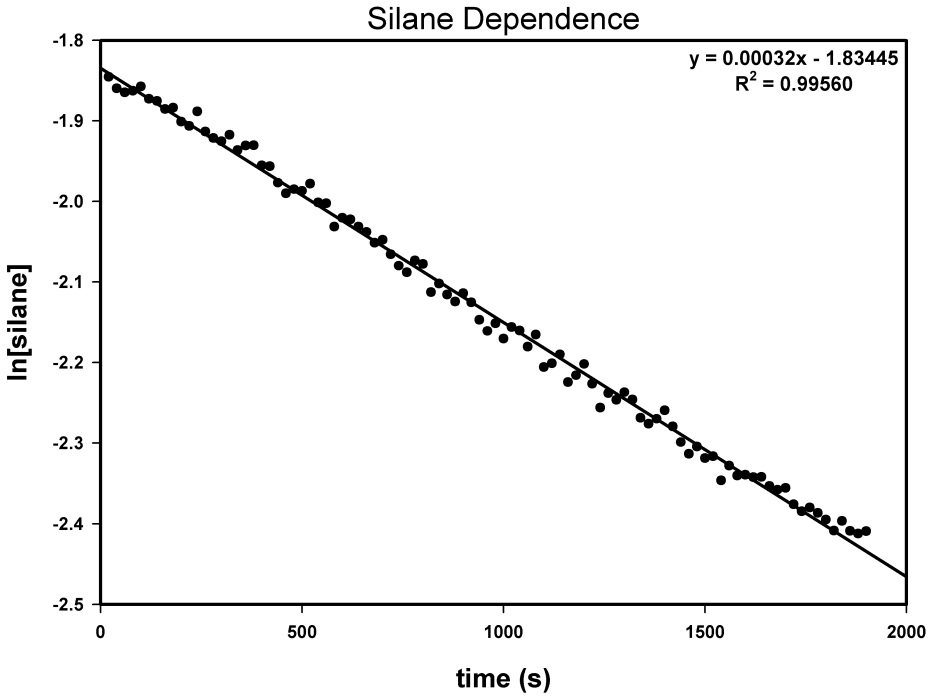
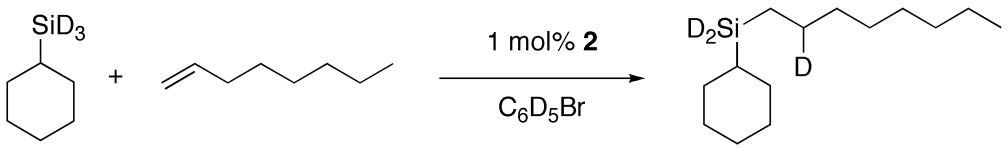


Figure 4. Sample first order plot of ln[silane] versus time.

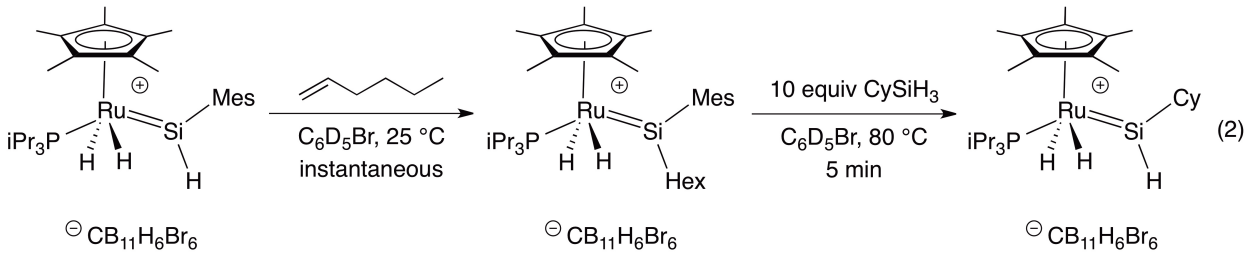


Further investigation of the catalytic mechanism involved a series of isotopic labeling experiments. An experiment to determine the kinetic isotope effect (KIE) for the catalytic reaction involved reaction of 1 equiv of 1-octene, 10 equiv of $CySiH_3$, and 10 equiv of $CySiD_3$ with 1 mol % of **2** in C_6D_5Br at 80 °C over 1 h. The KIE was found to be $k_H/k_D = 1.5(1)$, which suggests that an Si–H bond is broken during the rate determining step (RDS). Based on the previously suggested mechanism, there are three steps that may involve cleavage of an Si–H bond: initial activation of the silane at the metal center, α-H migration from silicon to ruthenium to produce the silylene ligand, and insertion of an olefin into the H-substituted silylene ligand. For only the olefin insertion step, the related complex $[Cp^*(PiPr_3)(H)_2Os{=}SiH(trip)][B(C_6F_5)_4]$[7] was reported to exhibit an inverse KIE of $k_H/k_D = 0.8(1)$. A competition experiment between **2** and $[Cp^*(PiPr_3)Ru(D)_2(=SiDMes)][CB_{11}H_6Br_6]$ (**2**-d_3) was performed by combining 1 equiv of **2** with 1 equiv of **2**-d_3 in C_6D_5Br, followed by 0.5 equiv of 1-octene and the internal standard $Ph_2Si(CH_3)(CD_3)$. After 5 min at room temperature, NMR spectra were recorded to give a KIE of $k_H/k_D = 0.77(4)$. The observed difference between the KIE for the overall reaction and that for olefin insertion indicates that the latter is not the RDS. Additionally, the catalytic reaction of 1-octene and $CySiD_3$ by **2** in C_6D_5Br resulted in a single isotopomer by ^1H and ^2H NMR spectroscopy, consistent with a concerted reaction (eq 1). The competiton experiment of 10 equiv of $CySiH_3$, 10 equiv of $CySiD_3$, 100 equiv of 1-octene, and 1 equiv of **2** in C_6D_5Br at 80 °C for 1 h gave a mixture of isotopomers.



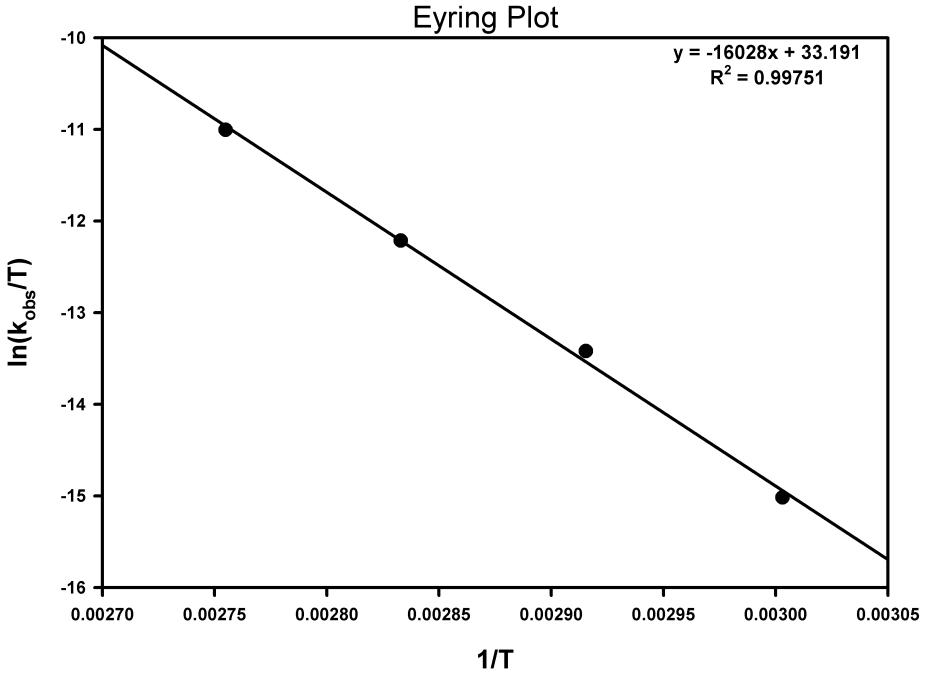
(1)

Qualitative observations provide further evidence that initial silane activation accompanied by product elimination to regenerate the H-substituted silylene complex is the RDS. The stoichiometric reaction of **2** with 1 equiv of 1-hexene in C_6D_5Br at room temperature proceeds instantaneously with a color change from bright orange to bright yellow to give the secondary silylene complex $[Cp^*(PiPr_3)Ru(H)_2(=SiMes(Hexyl))][CB_{11}H_6Br_6]$ (**3**) (eq 2). The ^{29}Si NMR spectrum reveals a resonance at 264.7 ppm, and in the ^1H NMR spectrum the ruthenium hydride ligands at -11.62 ppm do not display a $^2J_{SiH}$ coupling constant. The lack of observable $^2J_{SiH}$ coupling indicates little or no Ru–H···Si interaction in this complex. Addition of 10 equiv of $CySiH_3$ to **3** in C_6D_5Br resulted in no reaction after 3 h at room temperature. However, heating this reaction mixture at 80 °C for 5 min resulted in complete conversion to $[Cp^*(PiPr_3)Ru(H)_2(=SiHCy)][CB_{11}H_6Br_6]$ (eq 2). Efforts to observe an intermediate in the reaction of **3** with 1 – 10 equiv of $CySiH_3$ by monitoring NMR spectra were unsuccessful. In order to probe the reversibility of product release, a model reaction involving 20 equiv of $H_2SiMesHex$ and the silylene complex $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][CB_{11}H_6Br_6]$ (**2**) in C_6D_5Br solution was monitored by NMR spectroscopy. After 1 h at room temperature, an equilibrium mixture of **2** and **3** (10:1) was established, indicating that product formation is somewhat reversible ($K_{eq} \approx 2000$), and 0.1 equiv of free H_3SiMes was observed in solution.



Activation parameters for the catalytic reaction were determined by collecting kinetic measurements over the temperature range of 60 – 90 °C. The Eyring plot provides the values $\Delta H^{\ddagger}$ = 32(2) kcal/mol, $\Delta S^{\ddagger}$ = 19(1) eu, and $\Delta G^{\ddagger}$ = 25(2) kcal/mol (at 80 °C) (Figure 5). The relatively large, positive value for $\Delta S^{\ddagger}$ suggests that the rate determining step involves dissociation of the product silane from the ruthenium center after initial coordination of H_3SiCy, resulting in free H_2SiCyR. In additon, the KIE of 1.5(1) suggests that the dissociation of H_2SiCyR must be concomitant with the Si-H activation of H_3SiCy.

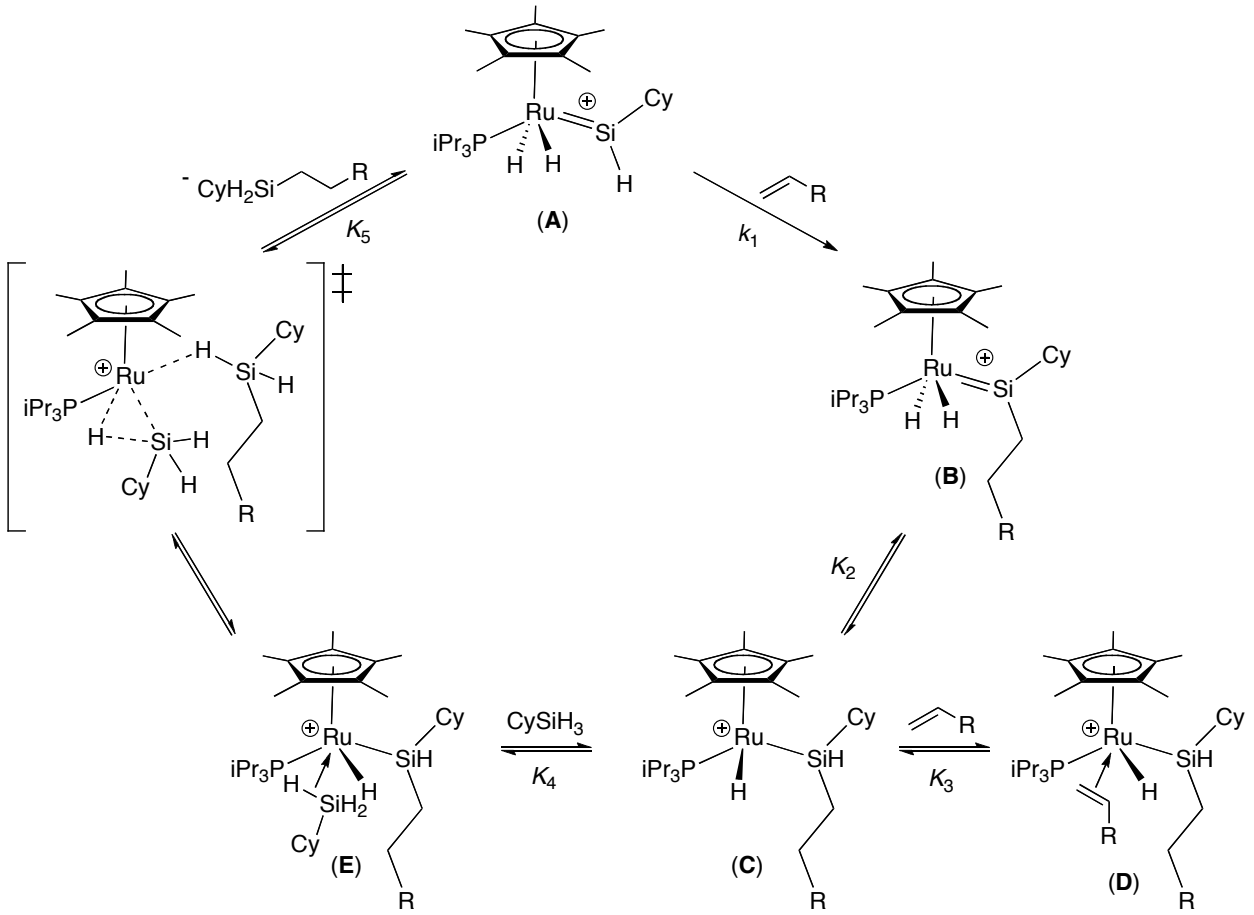
Figure 5.



Taken together, the above kinetic data suggests a revision to the previously proposed catalytic cycle (Scheme 2). The first step involves the concerted insertion of the olefin substrate into the Si – H bond of the H-substituted silylene complex (**A**) to give a disubstituted silylene complex (**B**). Next, α-hydride migration from the Ru center to the Si center results in an unsaturated cationic Ru silyl complex (**C**). This species is likely in equilibrium with the disubstituted silylene complex and can be trapped by excess olefin (**D**). This non-productive equilibrium established by the binding of olefin to the Ru species could lead to the observation of inverse-order rate dependence on olefin. Experiments to observe complex **D** were conducted

with **3** and 1 – 20 equiv of 1-octene from 25 to -30 °C in C_6D_5Br, but these were unsuccessful and limited by the freezing point of C_6D_5Br (-30.8 °C).

Scheme 2.



In the product-forming pathway, the 16-electron intermediate **C** is trapped by the H_3SiCy substrate, to initially produce the silane complex represented by **E**. The kinetic data given above, and computational results described by Beddie and Hall[8a] (*vide infra*), are consistent with a concerted process in which the incoming silane displaces the secondary silane product *via* Si···H bond formation as the product is eliminated and the incoming silane is activated. This process is reversible, as indicated by the observed reaction of **3** with $H_2SiMesHex$, and is described in Scheme 2 as the two-step equilibrium (K_4) that converts **C** and H_3SiCy to the silane product with regeneration of **A** by way of transition state **F**.

The rate law expression derived from this mechanism (eq 3) is consistent with the kinetic data discussed above. In the derivation of the rate law, the insertion of olefin into the Si–H bond of the silylene ligand is assumed to be fast. This rate law predicts that at high silane concentration, saturation may be observed due to the presence of [silane] in both the numerator and denominator. Further data was collected in search of evidence for saturation behavior with increasing concentrations of silane, and the maximum reaction rate was observed at concentrations of 3.5 M silane and greater (Figure 6). Additionally, a double-reciprocal plot of the proposed rate law ([olefin]/[silane] vs. [2]/rate) is linear (Figure 7).

$$\text{rate} = (K_2K_4[\text{silane}][\mathbf{2}]) / (K_3[\text{olefin}] + K_4[\text{silane}]) \quad (3)$$

Figure 6. Plot of rate versus [silane].

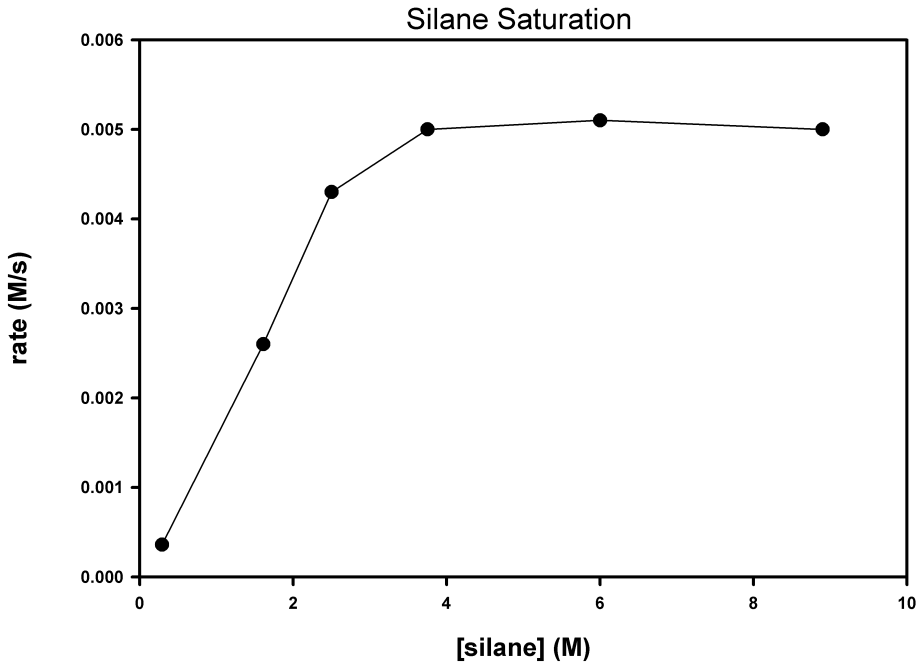
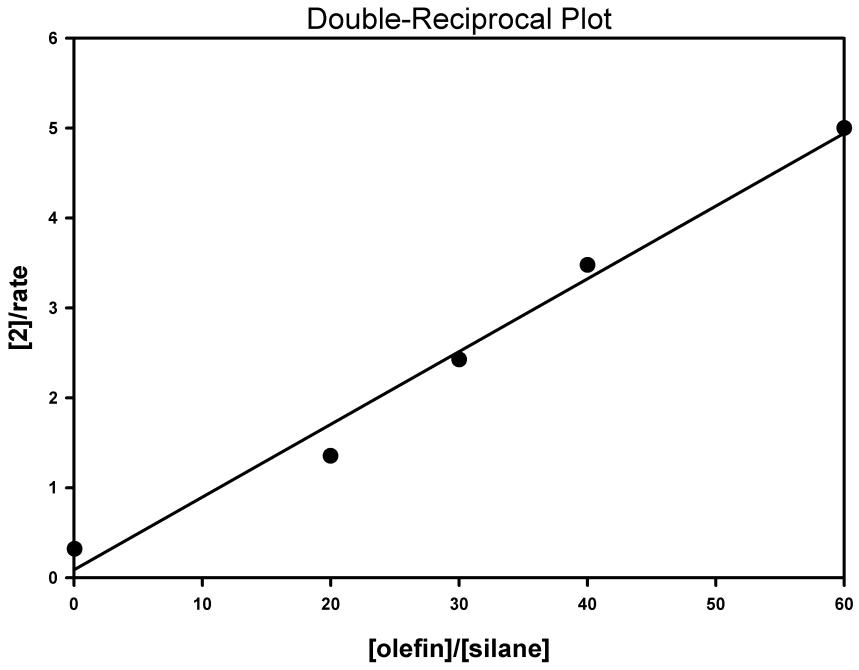


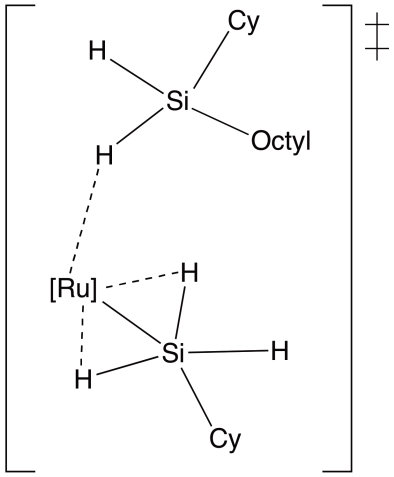
Figure 7. Double-reciprocal plot.



The resting state of the catalyst was determined to be species **B** by monitoring the ^{1}H NMR spectrum during catalysis. Thus, the RDS is hypothesized to be the release of the secondary silane product ($CyH_2SiCH_2CH_2R$) and reformation of the H-substituted silylene complex **A**. The binding of $CySiH_3$ to the Ru complex must occur before the RDS in order for [$CySiH_3$] to appear in the rate law. Therefore, this eliminates the possibility that the product is released to give an intermediate $[Cp^*(PiPr_3)Ru]^+$ complex that then reacts with $CySiH_3$ to give **A**.[6]

Theoretical studies by Hall and Beddie, based on the simplified catalyst $Cp(PH_3)Ru(H)_2(=SiH_2)^+$, also predict that silane displacement is involved in the RDS.[8a] This study also proposed a series of related intermediates and transition states involving two silicon-containing ligands for the rate-determining transformation, and an associated, high-energy transition state that involves activation of the incoming silane during elimination of the product.[8a] This transition state (analogous to the simpler transition state structure **F** of Scheme 2) features a partially activated Si–H bond, accompanied by a secondary, agostic Si–H interaction with the metal center (Figure 8). The experimental findings presented herein support this previously proposed transition state for the transformation of **E** to **A** (Scheme 2), but do not provide enough detail to address the proposed, simultaneous interaction of two Si–H bonds of the incoming silane with the metal.

Figure 8. Proposed transition state for product formation in the transformation of **E** to **A**, based on calculations for a model system by Beddie and Hall (ref 8a).



Concluding Remarks

In conclusion, use of the anion $[CB_{11}H_6Br_6]^-$ has enabled a structural analysis of the cationic silylene complex $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][CB_{11}H_6Br_6]$ (**2**), which exhibits short Ru–H···Si distances. These short contacts appear to reflect the electrophilicity of the silicon center, which is a key chemical property associated with hydrosilation activity.[6-8] Additionally, complex **2** displays greater thermal stability relative to that of the $[B(C_6F_5)_4]^-$ analogue **1**, allowing for in-depth kinetic and mechanistic studies. These experiments have resulted in further understanding of the first reported silylene-mediated alkene hydrosilation catalytic cycle. Interestingly, activation of the olefin is relatively rapid in this catalysis, and the rate-determining

process is associated with activation of the silane substrate. Importantly, these studies provide a working model for the design of a wider range of catalysts that may operate via related mechanisms.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and then $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene and toluene were then dried over $CaCl_2$ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Fluorobenzene was dried over P_2O_5, degassed and distilled under N_2. Methylene chloride-d_2 was dried by vacuum distillation from CaH_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Bromobenzene-d_5 was refluxed over CaH_2 for 20 h and then distilled under nitrogen. Cp*(PiPr$_3$)Ru(H)$_2$(SiHMesOTf)[11] and [Et$_3$Si][B(C$_6$F$_5$)$_4$][12] were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^{1}H. ^{31}P{^{1}H} NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). ^{19}F{^{1}H} spectra were referenced relative to a C_6F_6 external standard. ^{13}C{^{1}H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For ^{13}C{^{1}H} NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^{1}H ^{29}Si HMBC unless specified otherwise. The following abbreviations have been used to describe peak multiplicities in the reported NMR spectroscopic data: "m" for complex multiplet, and "br" for broadened resonances. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiHMes)][CB$_{11}$H$_6$Br$_6$] (2). A solution of [Et$_3$Si][CB$_{11}$H$_6$Br$_6$] (0.052 g, 0.07 mmol) in 0.5 mL of C_6H_5F was added to a solution of Cp*(PiPr$_3$)Ru(H)$_2$(SiHMesOTf) (0.050 g, 0.07 mmol) in 1 mL of C_6H_5F. After stirring 5 min at rt, 15 mL of pentane was added to the bright orange solution and placed in the −30 °C freezer. After 1 h, an orange solid settled to the bottom of the vial. The solution was carefully decanted and the resulting orange solid was dried under vacuum for 1 h to afford **2** in 89% yield (0.075 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 8.15 (1H, br s, $^1J_{SiH}$ = 224.5 Hz, Si*H*), 6.97 (2H, s, Ar*H*), 3.17 – 2.97 (6H, br s, carborane), 2.43 (6H, s, ArC*H*$_3$), 2.41 (3H, s, ArC*H*$_3$), 2.11 (3H, sept, J = 7.1 Hz, C*H*(CH$_3$)$_2$), 1.59 (15H, s, C$_5$*Me*$_5$), 1.13 (18H, dd, J = 7.1 Hz, J_{PH} = 13.9 Hz, CH(C*H*$_3$)$_2$), -11.35 (2H, d, $^2J_{PH}$ = 14.5 Hz, $^2J_{SiH}$ = 62.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 144.7 (Ar*C*), 143.2 (Ar*C*), 139.8 (Ar*C*), 97.7 (*C*$_5$Me$_5$), 41.3 (carborane), 26.1 (*C*H(CH$_3$)$_2$), 25.9 (*C*H(CH$_3$)$_2$), 22.3 (Ar*Me*), 21.7 (Ar*Me*), 19.4 (CH(*C*H$_3$)$_2$), 11.0 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 65.1. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 228.7. Anal. Calcd for $C_{29}H_{56}B_{11}Br_6PRuSi$: C, 29.94; H, 4.85. Found: C, 29.64; H, 4.65.

[Cp*(PiPr$_3$)Ru(D)$_2$(=SiDMes)][CB$_{11}$H$_6$Br$_6$] (2-*d*$_3$). By a procedure analogous to that for **2**, complex **2-*d*$_3$** was obtained using MesSiD$_3$.

[Cp*(PiPr$_3$)Ru(H)$_2$(=SiMes(Hex)][CB$_{11}$H$_6$Br$_6$] (3). An excess of 1-hexene (0.008 g, 0.04 mmol) was added to a solution of **2** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a yellow solution. After 5 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a yellow solid in 96% yield (0.055 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 6.96 (2H, s, Ar*H*), 3.16 – 2.81 (6H, br s, carborane), 2.60 (3H, m, C*H*$_3$), 2.49 (6H, s, ArC*H*$_3$), 2.38 (3H, s, ArC*H*$_3$), 2.09 (3H, sept, J = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.60 (15H, s, C$_5$*Me*$_5$), 1.35 (4H, m, C*H*$_2$), 1.28 (6H, m, C*H*$_2$), 1.17 (18H, dd, J = 6.8 Hz, J_{PH} = 13.7 Hz, CH(C*H*$_3$)$_2$), -11.62 (2H, d, $^2J_{PH}$ = 15.6 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 142.1 (Ar*C*), 138.7 (Ar*C*), 132.9 (Ar*C*), 98.4 (*C*$_5$Me$_5$), 41.4 (carborane), 32.7 (*C*H$_2$), 31.3 (*C*H$_2$), 27.5 (*C*H(CH$_3$)$_2$), 27.3 (*C*H(CH$_3$)$_2$), 24.0 (*C*H$_2$), 23.3 (*C*H$_2$), 22.7 (Ar*Me*), 21.6 (Ar*Me*), 19.8 (CH(*C*H$_3$)$_2$), 17.6 (*C*H$_3$), 11.1 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 68.9. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 264.7. Anal. Calcd for $C_{35}H_{68}B_{11}Br_6PRuSi$: C, 33.70; H, 5.49. Found: C, 33.50; H, 5.19

General Procedure for Catalytic Hydrosilation Reactions. Hydrosilation catalytic runs were performed in Teflon capped J. Young NMR tubes. In a representative catalytic run, **1** (10 mg, 0.007 mmol, 1 mol%) was dissolved in 0.5 mL of bromobenzene-*d*$_5$, and the resulting solution was added to hexamethylbenzene (14.3 mg, 0.14 mmol) (as a standard) followed by alkene (0.14 mmol) and silane (0.14 mmol). The solution was transferred to a Teflon–capped J. Young NMR tube, and heated to 80 °C in an oil bath with a temperature-controlled hotplate for 1 – 18 h. The progress of the reaction was monitored via ^{1}H NMR spectroscopy and yields were obtained by integration against a standard. For kinetic runs, the sample was placed in an NMR probe preheated to 353.0 K. Single-scan spectra were obtained using an automated acquisition program that was started immediately after placing the sample in the probe, and the peaks were integrated relative to the internal standard.

X-ray Crystallography. The single-crystal X-ray analysis of compound **1** was carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker APEX II CCD area detector with micro-focus sealed source Mo Kα radiation (λ = 0.71069 Å). Data was integrated and analyzed for agreement using Bruker APEX2 v. 2009.1. Empirical absorption correction were made using SADABS. Structures were solved by direct methods using the SHELX program package.

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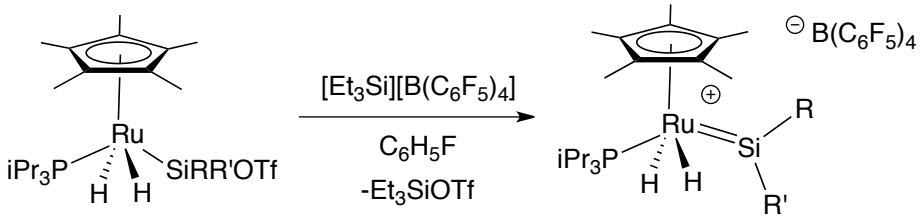
Chapter 3

Stoichiometric Reaction Chemistry of Cationic Ruthenium Silylene Complexes towards Polar and Non-polar Organic Substrates

Introduction

Transition metal silylene complexes, in which an :SiR_2 fragment is stabilized by coordination to a metal center, have been proposed as intermediates in industrially significant organosilicon transformations.[1] Since the isolation of the first base-free silylene complexes in the late 1980s, significant research has been undertaken to allow for access to a wider range of silylene species through different synthetic routes.[2] Concurrently, numerous reactivity studies with silylene complexes have been conducted.[2,3] Notably, two silylene-based systems that catalyze the hydrosilation of olefins have been discovered: $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh•Et_2O)][B(C_6F_5)_4]$[4] and $[PNPIrH(=SiHPh)][B(C_6F_5)_4]$.[5] These catalysts operate by a novel mechanism involving direct addition of the Si-H bond of the silylene ligand to an olefin, and give rise to unusually high selectivities to anti-Markovnikov, secondary silane products.[6]

A number of stoichiometric reactions of silylene complexes with organic substrates have been reported,[7,8] but at this stage it remains difficult to make generalizations about such reactivity in a predictive fashion. Such reactivity studies are expected to point the way toward applications of silylene complexes in new transformations and catalysis. The increasing number of convenient synthetic procedures that provide access to silylene complexes enables a broader examination of reactivity trends for these species. Along these lines, recent research from this laboratory has shown that the simple triflate complex $Cp^*(PiPr_3)RuOTf$ is useful as a starting material for the convenient syntheses of a broad range of cationic ruthenium silylene complexes that are related to known hydrosilation catalysts.[9] These synthetic procedures involve activation of secondary or primary silanes to form $Cp^*(PiPr_3)Ru(H)_2SiRR'OTf$ complexes, followed by triflate abstraction with $[Et_3Si•toluene][B(C_6F_5)_4]$ to give silylene complexes of the general type $[Cp^*(PiPr_3)Ru(H)_2(=SiRR')][B(C_6F_5)_4]$ (eq 1). The research described below details a number of stoichiometric reactions of two silylene complexes (**1** and **2**, eq 1) towards non-polar and polar organic substrates. Given the relation to known catalysts, the study of stoichiometric reaction chemistry of **1** and **2** may result in further understanding of known hydrosilation catalysis or the development of new catalytic transformations.



(1)

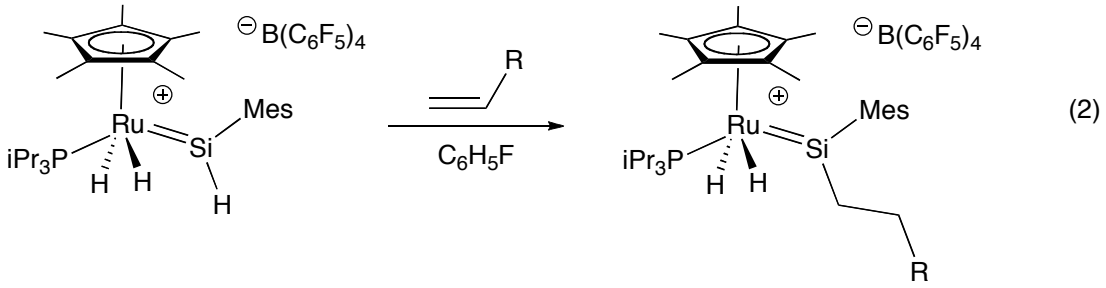
R = Mes, R' = H (**1**)
R = Si(SiMe$_3$), R' = H
R = R' = Ph (**2**)
R = Ph, R' = Me
R = R' = Flu

Results and Discussion

Reactions of $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F_5)_4]$ (1) with alkenes and alkynes. Several hydrogen-substituted silylene complexes have been shown to undergo olefin insertion into the Si–H bond of the silylene ligand,[4,5] and this is a key Si–C bond-forming step in catalytic alkene hydrosilations. For the direct addition of

$[Cp^*(PiPr_3)Ru(H)_2(=SiHPh\bullet Et_2O)][B(C_6F_5)_4]$ to 1-hexene, the product $[Cp^*(PiPr_3)Ru(H)_2(=SiPhHex)][B(C_6F_5)_4]$ can be observed in solution by NMR spectroscopy, but it has not proven to be amenable to isolation. Thus, it was of interest to explore the reactivity of **1** toward an array of unsaturated substrates, to gain further insight into the mechanism of hydrosilation by $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh)]^+$.

To a solution of complex **1** in C_6H_5F was added an excess of 1-hexene, resulting in an immediate color change from bright orange to bright yellow (eq 2). After stirring for 5 min, the reaction solution was reduced under vacuum to give a dark yellow oil. Subsequent washings with hexanes and further drying under vacuum resulted in $[Cp^*(PiPr_3)Ru(H)_2(=Si(Hex)Mes)][B(C_6F)_4]$ (**3**) as a bright yellow solid. Complex **3** decomposes in solution over 8 h but is stable as a solid for ca. 1 week at -30 °C.



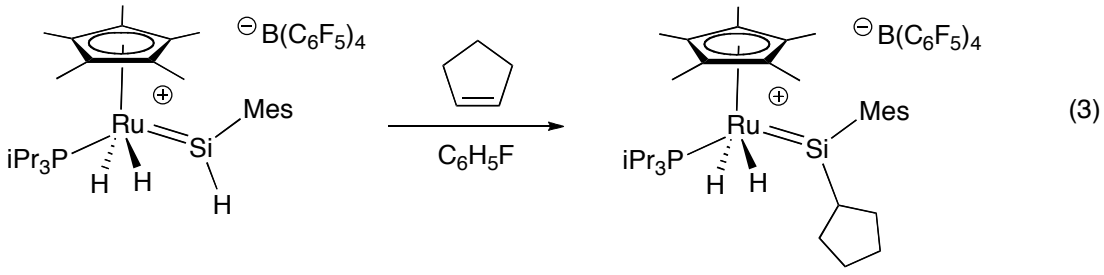
(2)

(**1**)

R = C_4H_9 (**3**)
R = tBu (**4**)
R = Ph (**5**)

Multinuclear NMR spectroscopy confirms the identity of **3**, and ^{1}H NMR spectroscopy reveals loss of the Si–H resonance for **1** (at 7.99 ppm). Additionally, new resonances between 1.44 ppm and 1.27 ppm confirm the presence of a hexyl substituent. The two equivalent hydride ligands appear at -11.65 ppm. Notably, while the hydride ligands of **1** exhibit a strong coupling to the silicon atom ($^2J_{SiH}$ = 58.2 ppm), complex **3** lacks such a strong interaction, as indicated by the small $^2J_{SiH}$ value of 10.9 ppm. The ^{29}Si NMR resonance at 240.7 ppm remains in the downfield region characteristic of a silylene ligand.[2]

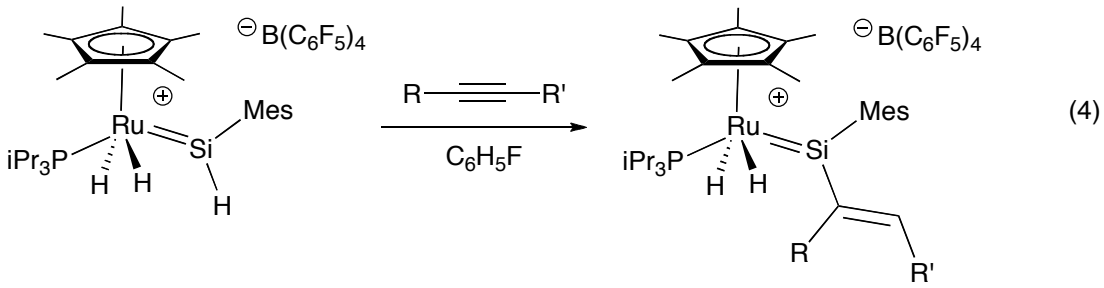
In addition to 1-hexene, **1** reacts cleanly with 3,3-dimethylbut-1-ene, styrene, and cyclopentene to yield the silylene complexes **4** – **6**, respectively (eqs 2 and 3). As observed for **3**, complexes **4** – **6** display resonances in the ^{29}Si NMR spectra in the characteristic region for silylene complexes. The hydride ligands for these complexes also exhibit small $^2J_{SiH}$ coupling constants (≤ 7 Hz), indicating a weak interaction between the hydride ligands and the silicon center. The NMR data for **1** and **3** – **6** are tabulated in Table 1. Complexes **3** – **6** complement the previously reported trend established for complexes of the type $[Cp^*(PiPr_3)Ru(H)_2(=SiRR')][B(C_6F)_4]$, that H-substituted silylene complexes have much stronger Ru–H···Si interactions in comparison to disubstituted silylene complexes, as indicated by $^2J_{SiH}$ coupling constants.[9] Presumably, H-substituted silylene complexes can readily adopt a conformation that maximizes donation of the two hydride ligands into the 3p orbital associated with the silicon center (silylene plane parallel to the Ru-Cp* centroid vector), whereas two substituents at silicon enforce a rotation about the Ru-Si bond and less favorable hydride-silicon interactions.[10]



(3)

(**1**) (**6**)

Especially in light of the unusual silylene-mediated catalysis reported for $[Cp^*(PiPr_3)Ru(H)_2(=SiHPh\bullet Et_2O)][B(C_6F_5)_4]$,[4] it is of interest to explore the propensity of other unsaturated substrates to undergo insertion into the Si–H bond of **1**. Despite their similarity to alkenes, the reactivity of silylene complexes toward alkynes has remained relatively unexplored. An excess of 2-butyne was added to a solution of **1** in C_6H_5F and the solution immediately became a golden yellow color (eq 4). The product, $[Cp^*(PiPr_3)Ru(H)_2(=Si(CMe=CHMe)Mes)][B(C_6F)_4]$ (**7**), was isolated as a yellow solid using a procedure analogous to that used for **3**–**6**. Similarly, $[Cp^*(PiPr_3)Ru(H)_2(=Si(CH=CHtBu)Mes)][B(C_6F)_4]$ (**8**) was prepared *via* reaction of **1** with 3,3-dimethylbut-1-yne. Complexes **7** and **8** represent the first examples of vinyl-substituted silylene complexes.



(4)

(**1**)

R = R' = Me (**7**)
R = H, R' = tBu (**8**)

The structure of **7** was confirmed through multinuclear and 2D NMR experiments. The ^{1}H NMR spectrum reveals a quartet at 6.42 ppm corresponding to the vinylic proton, a doublet (J = 6.6 Hz) at 1.76 ppm arising from the methyl group *trans* to Si, and a singlet at 1.68 due to the geminal methyl group. The methyl groups were determined to be in a *cis* conformation with respect to one other based on observed correlations in a 2D ^{1}H-^{1}H NOESY experiment. The hydride ligands remain equivalent (-11.02 ppm) and are associated with a $^2J_{SiH}$ coupling constant value of 14.1 Hz. This small coupling constant indicates that strong interactions between the hydride and silylene ligands are no longer present. The silylene ligand remains intact, as confirmed by ^{29}Si NMR spectroscopy (301.4 ppm).

By similar NMR experiments, the structure of **8** was determined. The two vinylic protons give rise to two doublets (J = 18.2 Hz) at 6.39 and 6.25 ppm in the ^{1}H NMR spectrum. The large H-H coupling constant indicates the presence of a *trans* alkene. The hydride ligands at -11.46 ppm display no observable $^2J_{SiH}$ to the silicon center ($\geq$ 7 Hz), and the ^{29}Si NMR spectrum contains a resonance for the silylene ligand at 282.3 ppm. Thus, the reaction of **1** with 3,3-

dimethylbut-1-yne is highly selective, and produces only the *trans* alkene, anti-Markovnikov addition product. This selectivity is likely due to steric interactions between **1** and the incoming alkyne, with the bulky *t*-butyl group enforcing the formation of only **8**. Notably, alkynes with two bulky substituents, such as diphenylacetylene, gave no reaction at room temperature in C_6D_5Br after 4 h. Prolonged reactions times and gentle heating resulted in decomposition of the parent silylene **1**.

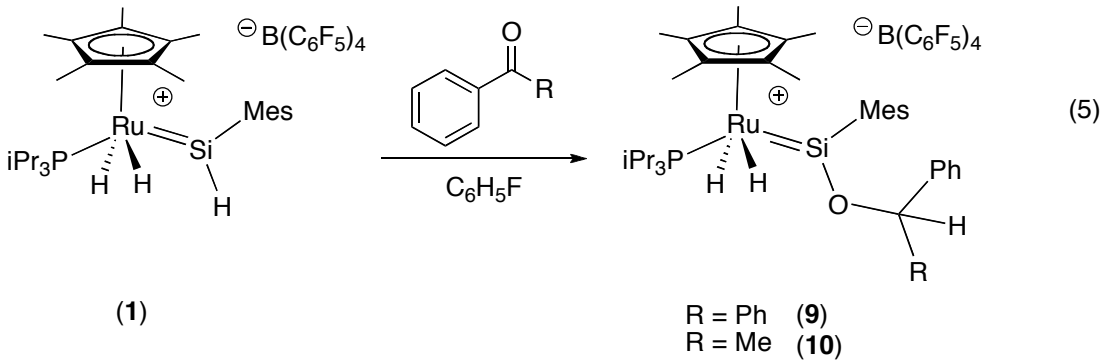
Table 1. NMR data for complexes **1** and **3** – **12**.

Complex	δ ^{1}H (RuH) ($^{2}J_{SiH}$)	δ ^{29}Si (RuSi)
$[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)]^+$ (**1**)	-11.46 (58.2)	226.5
$[Cp^*(PiPr_3)Ru(H)_2(=Si(Hexyl)Mes)]^+$ (**3**)	-11.65 (10.9)	240.7
$[Cp^*(PiPr_3)Ru(H)_2(=Si(CH_2CH_2tBu)Mes)]^+$ (**4**)	-11.64 (< 7)	278.9
$[Cp^*(PiPr_3)RuH_2(=Si(CH_2CH_2Ph)Mes)]^+$ (**5**)	-11.61 (< 7)	277.6
$[Cp^*(PiPr_3)RuH_2(=Si(C_5H_9)Mes)]^+$ (**6**)	-11.64 (< 7)	215.0
$[Cp^*(PiPr_3)Ru(H)_2(=Si(CMe=CHMe)Mes)]^+$ (**7**)	-11.02 (14.1)	301.4
$[Cp^*(PiPr_3)Ru(H)_2(=Si(CH=CHtBu)Mes)]^+$ (**8**)	-11.46 (< 7)	282.3
$[Cp^*(PiPr_3)Ru(H)_2(=Si(OCHPh_2)Mes)]^+$ (**9**)	-11.18 (38.3)	204.4
$[Cp^*(PiPr_3)Ru(H)_2(=Si(OCHPhMe)Mes)]^+$ (**10**)	-11.27, -11.49 (41.7)	199.7
$[Cp^*(PiPr_3)Ru(H)_2(SiMes\{\eta^2\text{-}O(CH)(NPh)\})^+$ (**11**)	-11.41, -11.59 (<7)	71.7
$[Cp^*(PiPr_3)Ru(H)_2(SiMes\{\eta^2\text{-}O(CH)(NPhCF_3)\})]^+$ (**12**)	-11.33, -11.48 (<7)	75.8

Reactions of 1 with ketones. Several H-substituted silylene complexes have been reported to react with carbonyl-containing organic substrates,[7f,8a,8g] with most of the products resulting from simple addition of the Si–H bond across the C=O bond of the carbonyl compound. For example, $[(PNP)(H)Ir{=}SiHMes][B(C_6F_5)_4]$ reacts with 1 equiv of benzophenone to give $[(PNP)(H)Ir{=}SiMes(OCHPh_2)][B(C_6F_5)_4]$.[7f] In constrast, reaction of

[(PNP)(H)Ir═SiHMes][$B(C_6F_5)_4$] with 1 equiv of acetophenone affords the enolate-substituted silyl complex [(PNPH)IrH($SiPh_2$(OC(═CH_2)Ph))][$B(C_6F_5)_4$]. Interestingly, all reports of reactions of a silylene complex with with an enolizable ketone describe similar enolate-based products.[7f,8g] The neutral complex Cp*(CO)(H)Ru=Si(H)[$C(SiMe_3)_3$] undergoes a net Si–H insertion reaction with ketones to give secondary silylene complexes of the type Cp*(CO)(H)Ru=Si(OCHRR')[$C(SiMe_3)_3$], and this reaction is proposed to proceed *via* coordination of the ketone to the electrophilic Si, followed by transfer of the metal hydride to the carbonyl carbon, and finally migration of the hydride from Si to Ru.[8f]

A solution of 1 equiv of benzophenone in C_6H_5F was added to an orange solution of **1** in C_6H_5F, giving an immediate color change to yellow. This color change is consistent with formation of a secondary silylene complex *via* insertion into the Si–H bond of **1**. Addition of hexanes to the solution resulted in precipitation of a dark yellow oil, and further hexane washes and drying under vacuum afforded a light brown solid identified as [Cp*($PiPr_3$)Ru($H)_2$(=Si(OCHPh_2)Mes)][$B(C_6F_4)$] (**9**, eq 5). The ^{1}H NMR spectrum of **9** contains a resonance at 5.85 ppm corresponding to the C*H*Ph_2 proton, which correlates to a $^{13}C\{^1H\}$ resonance at 83.9 ppm, observed with use of a 2D ^{1}H, $^{13}C\{^1H\}$ HMQC experiment. The equivalent ruthenium hydride ligands appear at -11.18 ppm. Interestingly, the hydride ligands in **9** retain strong interactions with the silicon center, as suggested by the relatively large $^2J_{SiH}$ value of 38.3 Hz. Additionally, while the ^{29}Si NMR resonance at 204.4 ppm remains in the region usually associated with silylene ligands, it has shifted somewhat upfield from the corresponding resonances for **1**-**9**.



(5)

(**1**)

R = Ph (**9**)
R = Me (**10**)

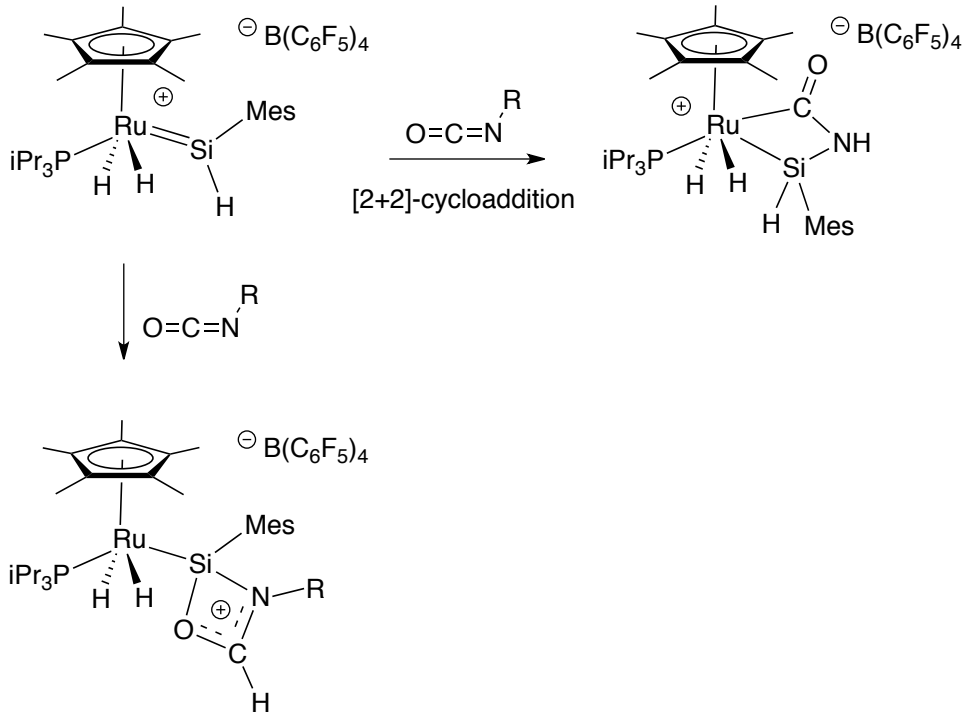
In complexes **2**–**8**, the presence of a strong, secondary Ru–H···Si interaction, as indicated by a large $^2J_{SiH}$ value, appears to require the presence of a hydrogen substituent at silicon. Complex **9** is the first disubstituted silylene complex in the Cp*($PiPr_3$)Ru($H)_2$(=SiRR')][$B(C_6F_4)$] family that maintains this interaction. The existence of a large $^2J_{SiH}$ for **9** indicates that inductive effects dominate the Si–O bonding, resulting in an electrophilic silicon center, and any π-donation from O to Si is negligible. Interestingly, other heteroatoms, such as sulfur, have been shown to donate electron density from lone pairs to the electropositive Si atom, stabilizing the silylene ligand. In fact, the first isolated, base-free silylene complexes featured heteroatoms on the silylene ligand.[11]

The reaction of **1** with acetophenone occurred under analogous conditions and gave a light green solid. Multinuclear and 2D NMR experiments allowed for this complex to be identified as {Cp*($PiPr_3$)Ru($H)_2$[=Si(OCHPhMe)Mes]}[$B(C_6F_4)$] (**10**), rather than an enolate product. The ^{1}H NMR spectrum is very similar to that of **9**. The resonance that arises from the

C*H*PhMe proton at 4.81 ppm is a quartet (J = 6.6 Hz) due to splitting by the CHPh*Me* methyl group, which appears at 1.46 ppm as a doublet. These two resonances unambiguously integrate in a 1:3 ratio, as expected. Additionally, a 2D ^{1}H, ^{13}C{^{1}H} HMQC experiment revealed that the C*H*PhMe proton correlates to a resonance in the ^{13}C{^{1}H} NMR spectrum at 78.4 ppm. The hydride ligands appear at -11.27 and -11.49 ppm and retain a strong coupling to the silicon atom ($^{2}J_{SiH}$ = 41.7 Hz). Interestingly, unlike complexes **1** – **9**, the hydride ligands are inequivalent, presumably due to the presence of three unique substituents on the silyl ether substituent (OCHPhMe). The ^{29}Si NMR resonance associated with the silicon center shifts upfield upon addition to the ketone, to 199.7 ppm.

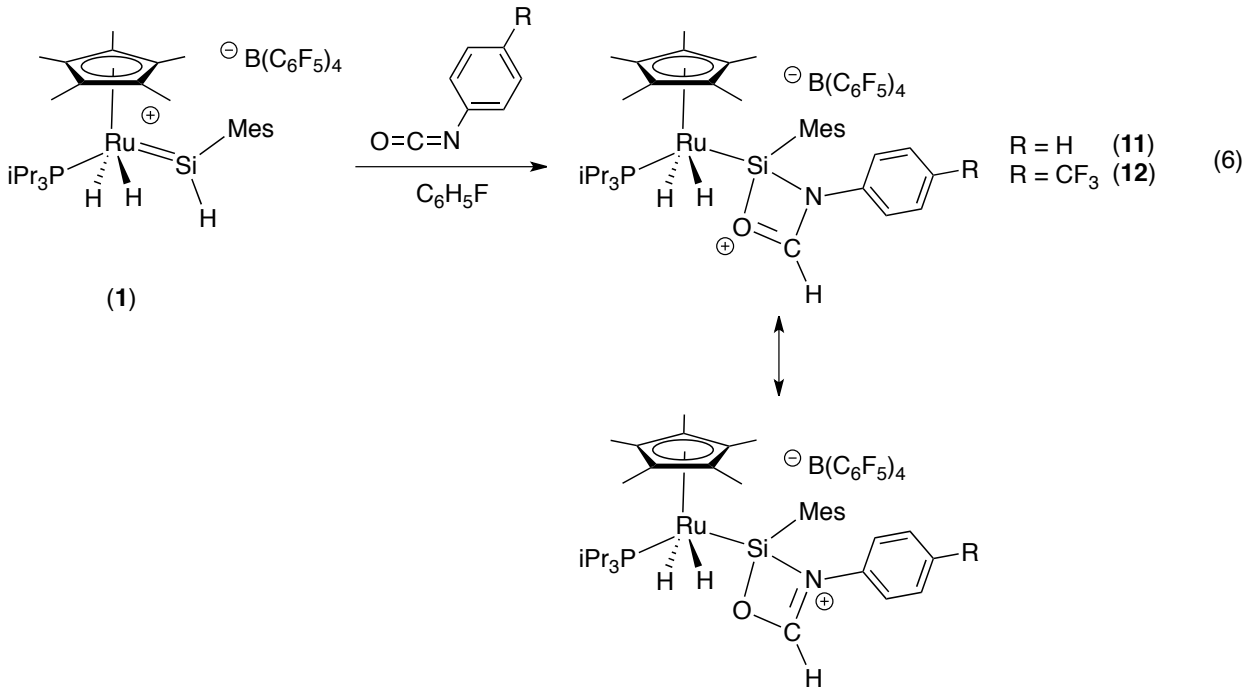
Reactions of 1 with isocyanates. Reactions of a silylene complex with an isocyanate substrate have been demonstrated to occur in one of two ways, as depicted in Scheme 1. The first possible reaction pathway involves a formal [2+2] cycloaddition, while the second involves insertion into an Si–R bond. The silylene system [Cp*(PMe$_3$)$_2$Ru=SiR$_2$][B(C$_6$F$_5$)$_4$] (R = Me, Ph, STol) has been reported to undergo both types of reactions with isocyanates.[7a] Additionally, reaction of the neutral silylene complex Cp*(CO)(H)Ru[=SiHC(SiMe$_3$)$_3$] with isocyanates results in reduction of the carbonyl group and formation of complexes featuring five-membered Ru–Si–O–CH–N(Ar) metallacyclic rings.[8i]

Scheme 1.



An excess of phenyl isocyanate was added to a solution of **1** in C$_6$H$_5$F, resulting in an immediate color change from bright orange to light yellow. The solution was allowed to stir at ambient temperature for 1 h before the volatile materials were removed *in vacuo*. The resulting dark yellow oil was washed with hexanes and further dried to give a light yellow solid, identified as [Cp*(PiPr$_3$)Ru(H)$_2$(Si(Mes)[κ^2-O(CH)(NPh)][B(C$_6$F$_5$)$_4$] (**11**) (eq 6). The new substituent at silicon is formulated as a κ^2-formamidate group, on the basis of multinuclear NMR

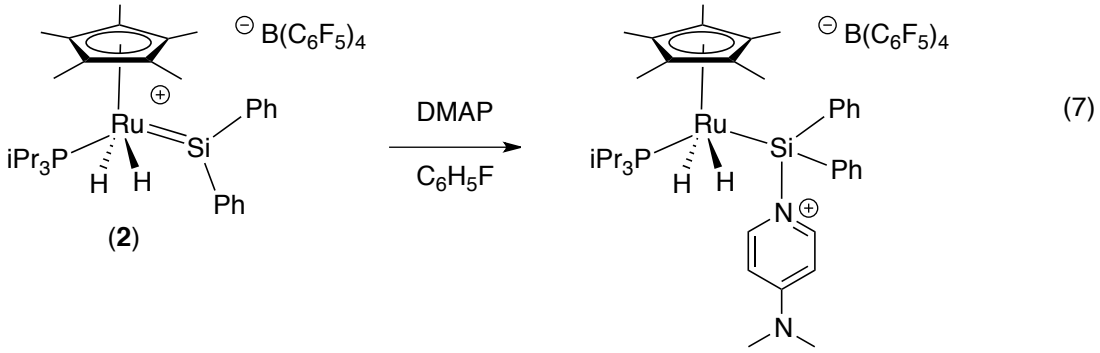
spectroscopy. The ^{1}H NMR spectrum of **11** contains a new signal at 8.14 ppm that correlates to a downfield resonance in the $^{13}C\{^{1}H\}$ NMR spectrum at 165.8 ppm (by a 2D ^{1}H, $^{13}C\{^{1}H\}$ HMQC experiment). This signal is attributed to a new C*H* moiety formed by insertion of the isocyanate into the Si–H bond, and corresponds closely to previously synthesized amide tautomers of (organosilyl)formanilides (O=C*H*-N(Ph)$SiR_1R_2R_3$: 8.33 – 8.78 ppm)[12] as well as the silacycle products observed for the reactions of $[Cp^*(PMe_3)_2Ru{=}SiR_2][B(C_6F_5)_4]$[7a] and $Cp^*(CO)(H)Ru[{=}SiHC(SiMe_3)_3]$[8i] with isocyanates. The ruthenium hydrides are diastereotopic due to the new chiral Si center (-11.41, -11.59 ppm) and display no observable coupling to silicon. The ^{29}Si NMR spectrum supports the formulation of **11**, as it contains an upfield-shifted resonance at 71.7 ppm, in the range for a metal-silyl or base-stabilized silylene complex.[13] Presumably, given the relatively low-field ^{29}Si NMR shift for this complex, the positive charge in the complex is delocalized significantly onto the κ^2-formamidate ligand, via the resonance structures depicted in eq 6. Additionally, IR spectroscopy reveals a stretch at 1608 cm^{-1} associated with a chelating amidate group.[14] This compares favorably to that observed for $[Cp^*(PMe_3)_2Ru][\kappa^2\text{-}O(CSTol)(NMe)][B(C_6F_5)_4]$[7a] (1625 cm^{-1}), which supports the formulation for **11** given in eq 6. Complex **12**, exhibiting a structure analogous to that of **11** (by NMR spectroscopy), was synthesized similarly (eq 6). The ^{29}Si NMR resonance for **12** appears at 75.8 ppm and the hydride ligands (-11.33, -11.48 ppm) exhibit no observable coupling to Si.



An intermediate in the formation of **11** and **12** was observed at short (5 min) reaction times after addition of the isocyanate to a solution of **1** in C_6D_5Br at room temperature. In both types of experiments, the reactions were observed to proceed initially to two species, one of which is the final product. Allowing the solution to stand at room temperature for 1 h results in complete conversion to the final product. In the case of phenyl isocyanate, one product can be identified as **11** and the other is speculated to be an isomer of the final product (**11a**). The ^{1}H NMR spectrum of the reaction mixture contains a new C*H* resonance at 7.85 ppm that displays weak coupling to Si ($^{2}J_{SiH} \leq 7$ Hz) that is associated with **11a**. Importantly, this C*H* resonance

correlates to the imidate tautomer of (organosilyl)formanilides (PhN=C*H*OSi$R_1R_2R_3$: 7.22 – 7.78 ppm),[12] which suggests that **11a** might be formulated as [Cp*($PiPr_3$)Ru$(H)_2$(Si(Mes)[κ^1-O(CH)(NPh)][$B(C_6F_5)_4$]. The ^{31}P NMR spectrum contains two resonances at 76.0 ppm for **11** and 74.1 ppm for **11a**. The most striking difference between **11** and **11a** is revealed by the ^{29}Si NMR spectrum with a new resonance at 116.3 ppm, indicating that **11a** retains more silylene character than the final product **11**. At room temperature, **11** and **11a** are initially present in a 1:2 ratio, with no **1** remaining. Interestingly, heating the solution to 40 ºC for 30 min increases the amount of **11a** to a maximum ratio of 1:6 (**11**/**11a**), indicating that **11** can be transformed to **11a**. It was not possible to observe or isolate pure **11a** due to its conversion to **11**, which precludes identification of this isomer. The reaction to form complex **12** behaves analogously, and gives rise to the intermediate/isomer **12a**, which displays a transient ^{29}Si resonance at 118.0 ppm. Given that both free tautomers of (organosilyl)formanilides can be observed by NMR spectroscopy, it seems reasonable to attribute similar structures to **11a** and **12a**.

Reactions of [Cp*($PiPr_3$)Ru$(H)_2$(=$SiPh_2$)][$B(C_6F_5)_4$] (2) with unsaturated Lewis bases. For comparative purposes, it was of interest to examine reactions of unsaturated organic substrates with the disubstituted silylene complex [Cp*($PiPr_3$)Ru$(H)_2$(=$SiPh_2$)][$B(C_6F_5)_4$] (**2**).[9] The diphenyl silylene complex was chosen because of its relative stability and ease of synthesis. One common mode of reactivity for silylene complexes is coordination of Lewis bases to the Lewis acidic silicon center.[15-16] Consistent with this, addition of one equiv of N,N-dimethylaminopyridine (DMAP) to a solution of complex **2** in fluorobenzene resulted in reaction to give a colorless solution. Drying under vacuum resulted in a white solid identified as the base-stabilized silylene complex [Cp*($PiPr_3$)Ru$(H)_2$($SiPh_2$•DMAP)][$B(C_6F)_4$] (**13**, eq 7). By ^{1}H NMR spectroscopy, the resonance for the hydride ligands (-11.92 ppm) appears upfield relative to the hydride resonance for **2** (-9.11 ppm). The DMAP significantly reduces the electron deficiency of the silylene ligand, as evidenced by a drastic upfield shift in the ^{29}Si NMR resonance to 68.5 ppm.

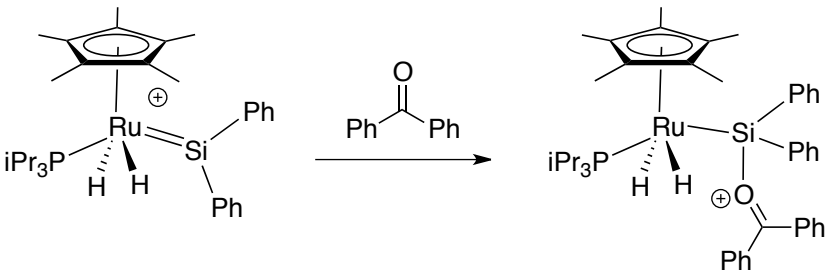


(**2**) (**13**) (7)

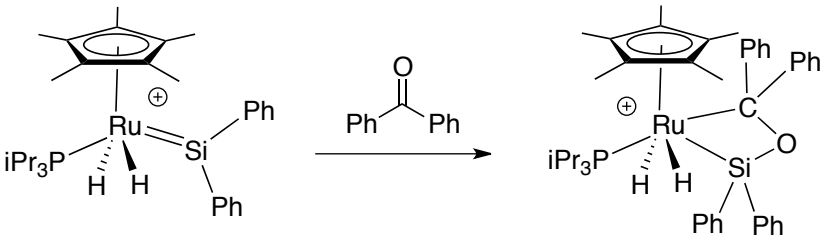
Having established that **2** interacts as expected with the simple Lewis base DMAP, a wider range of Lewis basic functionalities were explored. Benzophenone is an interesting case, as it can be envisioned to simply coordinate to the silylene ligand of **2**, engage in a cycloaddition to give a metallocyclic product,[7a] or undergo attack by a hydride ligand to produce a silyl ether linkage[7c] (Scheme 2).

Scheme 2.

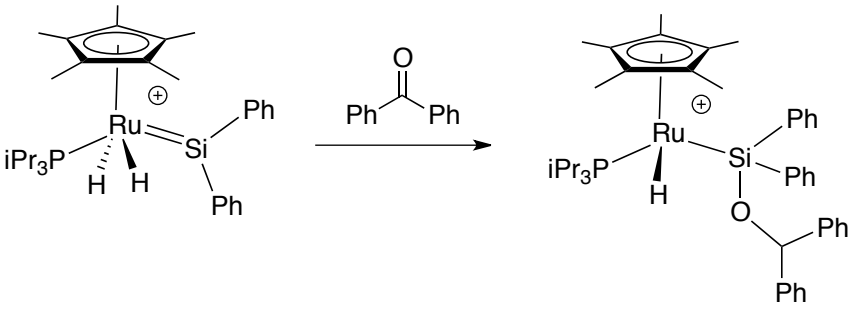
Reaction A



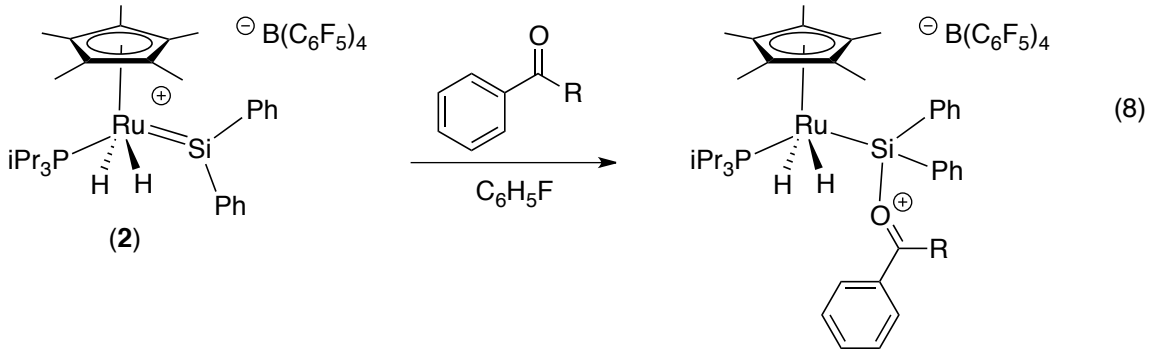
Reaction B



Reaction C



The reaction of one equiv of benzophenone with **2** in fluorobenzene gave a bright orange solution, from which the orange, base-stabilized silylene complex $[Cp^*(PiPr_3)Ru(H)_2(SiPh_2{\bullet}Ph_2CO)][B(C_6F)_4]$ (**14**, eq 8) was isolated. As observed for complex **13**, both the hydride ligands (-11.06 ppm) and silicon resonance (78.3 ppm) appear significantly upfield from the corresponding resonances for **2**. A silyl ether product, as proposed in Scheme 4c, may be ruled out by the integration of the hydride ligands and the lack of a new C*H* resonance. A metallocycle can also be eliminated as a possibility due to the observation of a downfield peak (201.9 ppm) in the ^{13}C NMR spectrum associated with O*C*Ph_2. This resonance has shifted very little from that of free benzophenone (ca. 197 ppm).



(8)

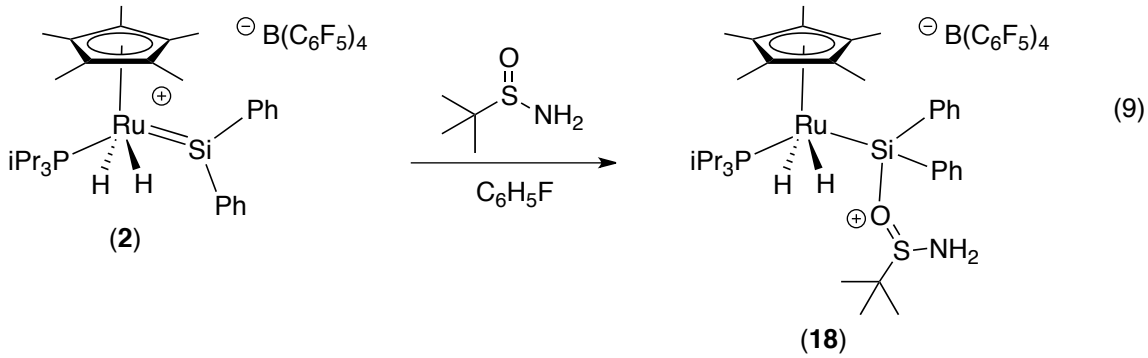
R = Ph (**14**)
R = NH_2 (**15**)

Another substrate that can be anticipated to have multiple modes of reactivity is benzamide. The C=O could bind to the silylene ligand to form a base-stabilized silylene complex, while the NH_2 group could add across the Ru=Si bond, as observed for the reaction of $[(PNP)(H)Ir{=}SiPh_2][B(C_6F_5)_4]$ with anilines.[7f] The reaction of **2** with benzamide yields a white solid ascertained to be the base-stabilized silylene complex $[Cp^*(PiPr_3)Ru(H)_2(SiPh_2{\bullet}PhCONH_2)][B(C_6F)_4]$ (**15**). Again, the ^{29}Si NMR spectrum reveals a resonance at 80.2 ppm, in the region associated with silyl and base-stabilized silylene ligands. The hydride ligands are shifted significantly upfield (-11.50 ppm) from those for **2** and only a small coupling to the silicon center is observed (J_{SiH} = 11.3 Hz). The N-*H* resonances are inequivalent and appear at 5.90 and 5.62 ppm. This inequivalency may be indicative of delocalization of the positive charge onto the N atom of benzamide (and C=N character). Gentle heating of **15** in C_6D_5Br results in decomposition of the complex rather than N-H activation.

To determine whether or not **2** has the ability to activate N–H bonds, complex **2** was treated with an excess of N-methyl aniline to afford the off-white compound $[Cp^*(PiPr_3)Ru(H)_2(SiPh_2{\bullet}NHMePh)][B(C_6F)_4]$ (**16**). The N*H* proton, observed as a broad singlet at 4.37 ppm in the ^{1}H NMR spectrum, indicates that activation of the N–H bond has not occurred. The hydride ligands appear at -11.14 ppm and do not exhibit observable $^2J_{SiH}$ coupling. The ^{29}Si NMR resonance of 55.7 ppm is in the range typical for base-stabilized silylene complexes. This result is somewhat surprising based on literature precedents for N–H and O–H bond activations by silylene complexes.[3,7f] For example, reaction of $[(PNP)(H)Ir{=}Ph_2][B(C_6F_5)_4]$ with aniline results in $[(PNPH)IrH(SiPh_2NHPh)][B(C_6F_5)_4]$,[7f] and $[Cp^*(PMe_3)_2Ru{=}SiPh_2(NCMe)][BPh_4]$ reacts with various alcohols (ROH) to give a silyl ether product, $Ph_2SiH(OR)$.[17] Interestingly, the same type of base-stabilized silylene complex is formed in the reaction of **1** with N-methylaniline, $[Cp^*(PiPr_3)Ru(H)_2(SiHMes{\bullet}NHMePh)][B(C_6F)_4]$ (**17**). The NMR spectroscopic data for complex **17** differ very little from **16**, with a broad N*H* peak at 5.17 ppm, upfield shifted hydride ligands at -12.16 ppm, and a ^{29}Si NMR resonance at 35.7 ppm. As observed for **15**, gentle heating of **16** and **17** in C_6D_5Br results in decomposition.

The reaction of **2** with the chiral substrate (*S*)-t-butylsulfinamide gave the base-stabilized silylene complex $[Cp^*(PiPr_3)Ru(H)_2(SiPh_2{\bullet}tBuSONH_2)][B(C_6F)_4]$ (**18**) as an off-white solid (eq 9). As with complexes **13**–**17**, the inequivalent hydride ligands (-11.04, -11.23) for complex **18** are shifted upfield relative to **2** and do not display observable coupling to the Si center. The hydride ligands are likely inequivalent due to coordination of a chiral Lewis base, as the hydride ligands of complexes **2** and **13**–**17** appear equivalent. The ^{29}Si NMR spectrum displays a

resonance at 89.6 ppm. To determine which functional group of the sulfinamide is bound to the silylene ligand, an infrared spectrum was taken. The IR bands at 3419 and 3327 cm^{-1} arising from the NH_2 group are similar to those of free t-butylsulfinamide (3324 and 3218 cm^{-1}).[18] A new band observed at 1018 cm^{-1} is attributed to the S=O group. The shift (from 1030 cm^{-1} in free t-butylsulfinamide) is associated with significant electron donation to the electon-deficient silylene ligand. This result is in agreement with the previously discussed complex **16**. The NMR data for complexes **13** – **18** are summarized in Table 2.



(9)

In addition to a variety of Lewis bases, solutions of complex **2** in C_6D_5Br were subjected to alkenes, alkynes, isocyanates, amines, and alcohols. In a typical experiment, no reaction was observed by multinuclear NMR spectroscopy at room temperature, and decomposition of **2** was observed upon gentle heating of the reaction mixture.

Table 2. NMR data for complexes **2** and **13** – **18**.

Complex	δ ^{1}H (RuH)	δ ^{29}Si (RuSi)
$[Cp^*(PiPr_3)RuH_2(=SiPh_2)]^+$ (**2**)	-9.11	339.0
$[Cp^*(PiPr_3)RuH_2(SiPh_2•DMAP)]^+$ (**13**)	-11.92	68.5
$[Cp^*(PiPr_3)RuH_2(SiPh_2•Ph_2CO)]^+$ (**14**)	-11.06	78.3
$[Cp^*(PiPr_3)RuH_2(SiPh_2•PhCONH_2)]^+$ (**15**)	-11.50	80.2
$[Cp^*(PiPr_3)RuH_2(SiPh_2•NHMePh)]^+$ (**16**)	-11.14	55.7
$[Cp^*(PiPr_3)RuH_2(SiPh_2•tBuSONH_2)]^+$ (**18**)	-11.04, -11.25	89.6

Conclusion

Silylene complexes of the type $[Cp^*(PiPr_3)Ru(H)_2(=SiRR')][B(C_6F_5)_4]$ have been observed to display two main types of reactivity. Complex **1**, a hydrogen-substituted silylene complex, favors insertion chemistry involving the Si-H bond. Both polar and non-polar

substrates have been demonstrated to activate the Si–H bond of the silylene ligand, resulting in secondary silylene complexes, and these reactions are typically instantaneous at room temperature. The conversions to complexes **3**–**10** allow further insight into the mechanism of silylene-mediated hydrosilations, and suggest new possibilities for catalytic reactions. Complex **1** is currently being evaluated for its ability to perform catalytic hydrosilations of olefin, alkyne, and ketone substrates.

Reactions of the secondary silylene complex **2** are dominated by its behavior as a strong Lewis acid, even with protic substrates. This is in contrast to $[(PNP)(H)Ir{=}Ph_2][B(C_6F_5)_4]$, which stoichiometrically and catalytically activates N–H and O–H bonds. Interestingly, the PNP pincer ligand plays a significant, non-innocent role in the observed reactivity of the iridium complex, as the amide is protonated during these reactions. Thus, the modes of reactivity available for a secondary silylene ligand appear to be highly dependent on additional ligands present in the complex. Note that reactions of secondary silylene complexes in hydrosilation catalysis are important in defining selectivity and the key transformation to products.[2,4,5,19]

Importantly, key differences in reactivity trends also exist for the comparison between neutral and cationic silylene complexes. While neutral hydrogen-substituted silylene complexes have been demonstrated to undergo novel stoichiometric reactions with a number of polar organic substrates,[8] they have not yet been observed to react with non-polar substrates (alkenes and alkynes), and thus do not catalyze the hydrosilation of olefins.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and then $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene and toluene were then dried over $CaCl_2$ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Fluorobenzene was dried over P_2O_5, degassed and distilled under N_2. Methylene chloride-d_2 was dried by vacuum distillation from CaH_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Bromobenzene-d_5 was refluxed over CaH_2 for 20 h and then distilled under nitrogen. The complexes $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes)][B(C_6F)_4]$ (**1**) and $[Cp^*(PiPr_3)Ru(H)_2(=SiPh_2)][B(C_6F)_4]$ (**2**) were prepared according to literature methods.[9] All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{19}F\{^1H\}$ spectra were referenced relative to a C_6F_6 external standard. $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^1H ^{29}Si HMBC unless specified otherwise. The following abbreviations have been used to describe peak multiplicities in the reported NMR spectroscopic data: “m” for

complex multiplet, and "br" for broadened resonances. In $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Si(Hex)Mes)][B(C$_6$F)$_4$] (3). An excess of 1-hexene (*ca*. 0.1 mL) was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a bright yellow solution. After 5 min, the reaction mixture was evaporated to dryness under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a bright yellow solid in 87% yield (0.046 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 6.95 (2H, s, Ar*H*), 2.45 (6H, s, ArC*H*$_3$), 2.37 (3H, s, ArC*H*$_3$), 2.09 (3H, br s, C*H*(CH$_3$)$_2$), 1.55 (15H, s, C$_5$*Me*$_5$), 1.44 (2H, m, C*H*$_2$), 1.39 (2H, m, C*H*$_2$), 1.34 (2H, m, C*H*$_2$), 1.27 (4H, m, C*H*$_2$), 1.16 (18H, dd, J = 6.3 Hz, J_{PH} = 13.6 Hz, CH(C*H*$_3$)$_2$), -11.65 (2H, d, $^2J_{PH}$ = 15.4 Hz, $^2J_{SiH}$ = 10.9 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 149.7 (Ar*C*), 148.0 (Ar*C*), 142.2 (Ar*C*), 139.5 (Ar*C*), 138.7 (Ar*C*), 138.3 (Ar*C*), 137.6 (Ar*C*), 135.9 (Ar*C*), 134.9 (Ar*C*), 128.9 (Ar*C*), 98.2 (*C*$_5$Me$_5$), 34.9 (Hexyl), 32.6 (Hexyl), 31.9 (Hexyl), 31.3 (Hexyl), 27.5 (*C*H(CH$_3$)$_2$), 27.3 (*C*H(CH$_3$)$_2$), 25.6 (Hexyl), 23.9 (Hexyl), 23.0 (Ar*Me*), 22.9 (Ar*Me*), 19.5 (CH(*C*H$_3$)$_2$), 10.7 (C$_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 68.9. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 240.7. $^{19}F\{^1H\}$ NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.9, -166.6. Anal. Calcd for $C_{58}H_{62}BF_{20}PRuSi$•2/3(C_6H_5F): C, 54.19; H, 4.79. Found: C, 54.34; H, 4.78.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Si(CH$_2$CH$_2$tBu)Mes)][B(C$_6$F)$_4$] (4). By a procedure analogous to that for **3**, complex **4** was obtained as a bright orange solid in 94% yield (0.050 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 6.91 (2H, s, Ar*H*), 2.43 (6H, s, ArC*H*$_3$), 2.31 (3H, s, ArC*H*$_3$), 2.09 (3H, br s, C*H*(CH$_3$)$_2$), 1.53 (15H, s, C$_5$*Me*$_5$), 1.47 (2H, m, $^2J_{SiH}$ = 6.36 Hz, C*H*$_2$), 1.21 (2H, m, $^2J_{SiH}$ = 15.5 Hz, SiC*H*$_2$), 1.15 (18H, dd, J = 6.2 Hz, J_{PH} = 12.5 Hz, CH(C*H*$_3$)$_2$), -11.64 (2H, d, $^2J_{PH}$ = 16.1 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 149.6 (Ar*C*), 148.0 (Ar*C*), 142.3 (Ar*C*), 139.4 (Ar*C*), 138.6 (Ar*C*), 137.5 (Ar*C*), 135.9 (Ar*C*), 98.3 (*C*$_5$Me$_5$), 37.2 (*C*H$_2$), 30.9 (*C*H$_2$), 28.9 (tBu), 28.3 (tBu), 27.5 (*C*H(CH$_3$)$_2$), 27.3 (*C*H(CH$_3$)$_2$), 22.9 (Ar*Me*), 21.3 (Ar*Me*), 19.5 (CH(*C*H$_3$)$_2$), 10.6 (C$_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 68.9. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 278.9. $^{19}F\{^1H\}$ NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.9, -166.6. Anal. Calcd for $C_{58}H_{62}BF_{20}PRuSi$: C, 53.18; H, 4.77. Found: C, 53.33; H, 4.77.

Cp*(PiPr$_3$)Ru(H)$_2$(=Si(CH$_2$CH$_2$Ph)Mes)][B(C$_6$F)$_4$] (5). By a procedure analogous to that for **3**, complex **5** was obtained as a bright yellow solid in 89% yield (0.048 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 7.30 (2H, m, Ph*H*), 7.07 (2H, m, Ph*H*), 6.96 (2H, s, Ar*H*), 6.95 (1H, m, Ph*H*), 2.63 (2H, m, C*H*$_2$), 2.41 (3H, s, ArC*H*$_3$), 2.36 (6H, s, ArC*H*$_3$), 2.05 (3H, br s, C*H*(CH$_3$)$_2$), 1.87 (2H, m, C*H*$_2$), 1.54 (15H, s, C$_5$*Me*$_5$), 1.12 (18H, dd, J = 6.9 Hz, J_{PH} = 15.0 Hz, CH(C*H*$_3$)$_2$), -11.61 (2H, d, $^2J_{PH}$ = 15.7 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 149.6 (Ar*C*), 148.1 (Ar*C*), 142.5 (Ar*C*), 141.4 (Ar*C*), 139.4 (Ar*C*), 138.9 (Ar*C*), 137.7 (Ar*C*), 137.2 (Ar*C*), 135.9 (Ar*C*), 128.7 (Ar*C*), 128.0 (Ar*C*), 127.7 (Ar*C*), 98.4 (*C*$_5$Me$_5$), 34.9 (*C*H$_2$), 31.9 (*C*H$_2$), 27.5 (*C*H(CH$_3$)$_2$), 27.4 (*C*H(CH$_3$)$_2$), 23.0 (Ar*Me*), 22.8 (Ar*Me*), 21.5 (Ar*Me*), 19.4 (CH(*C*H$_3$)$_2$), 10.7 (C$_5$*Me*$_5$). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 69.1. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 277.6. $^{19}F\{^1H\}$ NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for $C_{60}H_{58}BF_{20}PRuSi$•1/2(C_6H_5F): C, 54.91; H, 4.43. Found: C, 55.16; H, 4.59.

Cp*(PiPr$_3$)Ru(H)$_2$(=Si(C$_5$H$_9$)Mes)][B(C$_6$F)$_4$] (6). By a procedure analogous to that for **3**, complex **5** was obtained as a bright yellow solid in 85% yield (0.045 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 6.95 (2H, s, Ar*H*), 2.43 (6H, s, ArC*H$_3$*), 2.37 (3H, s, ArC*H$_3$*), 2.11 (3H, br s, C*H*(CH$_3$)$_2$), 1.88 (4H, m, C$_5$*H$_9$*), 1.52 (15H, s, C$_5$*Me$_5$*), 1.47 (2H, m, C$_5$*H$_9$*), 1.28 (3H, m, C$_5$*H$_9$*), 1.14 (18H, dd, J = 6.9 Hz, J_{PH} = 13.7 Hz, CH(C*H$_3$*)$_2$), -11.64 (2H, d, $^2J_{PH}$ = 14.7 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.6 (Ar*C*), 148.0 (Ar*C*), 142.1 (Ar*C*), 139.6 (Ar*C*), 139.4 (Ar*C*), 137.6 (Ar*C*), 136.0 (Ar*C*), 129.0 (Ar*C*), 97.7 (*C$_5$*Me$_5$), 29.1 (*C$_5$*H$_9$), 27.6 (*C*H(CH$_3$)$_2$), 27.4 (*C*H(CH$_3$)$_2$), 25.9 (*C$_5$*H$_9$), 23.7 (Ar*Me*), 23.0 (Ar*Me*), 21.4 (*C$_5$*H$_9$), 19.6 (CH(*C*H$_3$)$_2$), 10.6 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 68.1. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 215.0. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.2, -162.8, -166.6. Anal. Calcd for $C_{57}H_{58}BF_{20}PRuSi$: C, 52.91; H, 4.52. Found: C, 53.30; H, 4.62.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Si(CMe=CHMe)Mes)][B(C$_6$F)$_4$] (7). By a procedure analogous to that for **3**, complex **7** was obtained as a golden yellow solid in 90% yield (0.047 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 6.91 (2H, s, Ar*H*), 6.47 (1H, quartet, C*H*Me), 2.39 (6H, s, ArC*H$_3$*), 2.36 (3H, s, ArC*H$_3$*), 1.92 (3H, quartet, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 1.76 (3H, d, J = 6.6 Hz, CH*Me*), 1.68 (3H, s, SiC*Me*), 1.64 (15H, s, C$_5$*Me$_5$*), 1.06 (18H, dd, J = 6.7 Hz, J_{PH} = 14.2 Hz, CH(C*H$_3$*)$_2$), -11.02 (2H, d, $^2J_{PH}$ = 20.3 Hz, $^2J_{SiH}$ = 14.1 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.7 (Ar*C*), 148.0 (Ar*C*), 146.3 (*C*Me), 145.3 (*C*Me), 142.4 (Ar*C*), 139.3 (Ar*C*), 137.6 (Ar*C*), 136.8 (Ar*C*), 136.6 (Ar*C*), 99.4 (*C$_5$*Me$_5$), 27.7 (*C*H(CH$_3$)$_2$), 27.5 (*C*H(CH$_3$)$_2$), 23.9 (Ar*Me*), 21.4 (Ar*Me*), 19.3 (CH(*C*H$_3$)$_2$), 14.8 (C*Me*), 14.4 (C*Me*), 10.9 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 71.1. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 301.4. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.9, -166.6. Anal. Calcd for $C_{56}H_{56}BF_{20}PRuSi$: C, 52.55; H, 4.41. Found: C, 52.25; H, 4.51.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Si(CH=CHtBu)Mes)][B(C$_6$F)$_4$] (8). By a procedure analogous to that for **3**, complex **8** was obtained as a bright yellow solid in 85% yield (0.045 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 6.97 (2H, s, Ar*H*), 6.39 (1H, d, J = 18.2 Hz, SiC*H*), 6.25 (1H, d, J = 18.2 Hz, C*H*tBu), 2.43 (6H, s, ArC*H$_3$*), 2.36 (3H, s, ArC*H$_3$*), 2.10 (3H, m, C*H*(CH$_3$)$_2$), 1.62 (15H, s, C$_5$*Me$_5$*), 1.16 (18H, dd, J = 6.9 Hz, J_{PH} = 13.8 Hz, CH(C*H$_3$*)$_2$), -11.46 (2H, d, $^2J_{PH}$ = 17.4 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 170.9 (*C*HSi), 149.4 (Ar*C*), 147.7 (Ar*C*), 142.3 (Ar*C*), 139.6 (Ar*C*), 139.1 (Ar*C*), 137.4 (Ar*C*), 135.7 (Ar*C*), 98.5 (*C$_5$*Me$_5$), 27.6 (tBu), 27.2 (*C*H(CH$_3$)$_2$), 27.0 (*C*H(CH$_3$)$_2$), 22.9 (Ar*Me*), 21.1 (Ar*Me*), 19.0 (CH(*C*H$_3$)$_2$), 10.4 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 70.6. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 282.3. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.6, -163.2, -166.9. Anal. Calcd for $C_{58}H_{60}BF_{20}PRuSi$: C, 53.26; H, 4.62. Found: C, 53.13; H, 4.35.

Cp*(PiPr$_3$)Ru(H)$_2$(=Si(OCHPh$_2$)Mes)][B(C$_6$F)$_4$] (9). A solution of benzophenone (0.008 g, 0.04 mmol) in C_6H_5F was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a yellow solution. After 5 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a light brown solid in 96% yield (0.055 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.36 (5H, m, Ph*H*), 7.22 (5H, m, Ph*H*), 6.92 (2H, s, Ar*H*), 5.85 (1H, s, OC*H*), 2.38 (3H, s, ArC*H$_3$*), 2.35 (6H, s, ArC*H$_3$*), 2.09 (3H, br s, C*H*(CH$_3$)$_2$), 1.60 (15H, s, C$_5$*Me$_5$*), 1.04 (18H, m, CH(C*H$_3$*)$_2$), -11.18 (2H, d, $^2J_{PH}$ = 19.6 Hz, $^2J_{SiH}$ = 38.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.6 (Ar*C*), 148.1 (Ar*C*), 143.4 (Ar*C*), 140.8 (Ar*C*), 139.9 (Ar*C*), 139.5 (Ar*C*), 137.9 (Ar*C*), 137.6

(Ar*C*), 135.9 (Ar*C*), 132.3 (Ar*C*), 128.9 (Ar*C*), 128.4 (Ar*C*), 99.6 (C_5Me_5), 83.9 (O*C*H), 26.9 ($CH(CH_3)_2$), 26.8 ($CH(CH_3)_2$), 22.8 (Ar*Me*), 22.7 (Ar*Me*), 21.5 (Ar*Me*), 19.1 ($CH(CH_3)_2$), 10.6 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 70.7. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 204.4. $^{19}F\{^1H\}$ NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.9, -166.6. Anal. Calcd for $C_{65}H_{60}BF_{20}OPRuSi \cdot 3(C_6H_5F)$: C, 58.82; H, 4.46. Found: C, 58.77; H, 4.46.

Cp*(PiPr$_3$)Ru(H)$_2$(=Si(OCHPhMe)Mes)][B(C$_6$F)$_4$] (10). By a procedure analogous to that for **3**, complex **4** was obtained as a pale yellow-green solid in 78% yield (0.043 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 7.37 (3H, m, Ph*H*), 6.99 (1H, s, Ar*H*), 6.96 (2H, m, Ph*H*), 6.91 (1H, s, Ar*H*), 4.81 (1H, q, *J* = 6.6 Hz, O*CH*), 2.61 (3H, s, ArC*H*$_3$), 2.40 (3H, s, ArC*H*$_3$), 2.17 (3H, br s, C*H*$(CH_3)_2$), 2.11 (3H, s, ArC*H*$_3$), 1.59 (15H, s, C_5Me_5), 1.46 (3H, d, *J* = 6.6 Hz, OCH*Me*) 1.14 (9H, m, CH(C*H*$_3$)$_2$), 1.05 (9H, m, CH(C*H*$_3$)$_2$), -11.27 (1H, d, $^2J_{PH}$ = 18.9 Hz, $^2J_{SiH}$ = 41.7 Hz, Ru*H*), -11.49 (1H, d, $^2J_{PH}$ = 18.7 Hz, $^2J_{SiH}$ = 41.7 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 149.3 (Ar*C*), 147.7 (Ar*C*), 143.0 (Ar*C*), 141.2 (Ar*C*), 139.7 (Ar*C*), 139.1 (Ar*C*), 138.8 (Ar*C*), 137.3 (Ar*C*), 135.6 (Ar*C*), 98.9 (C_5Me_5), 78.4 (O*C*H), 31.5 (OCH*Me*), 26.6 ($CH(CH_3)_2$), 26.5 ($CH(CH_3)_2$), 24.0 (Ar*Me*), 22.7 (Ar*Me*), 21.2 (Ar*Me*), 18.8 ($CH(CH_3)_2$), 10.3 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 70.3. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 199.7. $^{19}F\{^1H\}$ NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.9, -166.6. Anal. Calcd for $C_{60}H_{58}BF_{20}OPRuSi$: C, 53.54; H, 4.34. Found: C, 53.30; H, 4.04.

[Cp*(PiPr$_3$)Ru(H)$_2$(Si(Mes){κ^2-O(CH)(NPh)}][B(C$_6$F$_5$)$_4$] (11). An excess of phenylisocyanate (3 drops) was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a bright yellow solution. After 1 h, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a light yellow solid in 85% yield (0.047 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 8.14 (1H, s, O*CH*), 7.41 (2H, t, *J* = 7.1 Hz, NPh*H*), 7.34 (1H, t, *J* = 7.1 Hz, NPh*H*), 7.02 (2H, d, *J* = 7.1 Hz, NPh*H*), 6.87 (2H, s, Ar*H*), 2.48 (6H, br s, ArC*H*$_3$), 2.31 (3H, s, ArC*H*$_3$), 1.93 (15H, s, C_5Me_5), 1.73 (3H, m, C*H*$(CH_3)_2$), 1.04 (18H, m, CH(C*H*$_3$)$_2$), -11.41 (1H, d, $^2J_{PH}$ = 24.4 Hz, Ru*H*), -11.59 (1H, d, $^2J_{PH}$ = 22.6 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 165.8 (O*C*HN), 149.7 (Ar*C*), 148.1 (Ar*C*), 142.6 (Ar*C*), 142.4 (Ar*C*), 141.0 (Ar*C*), 139.5 (Ar*C*), 138.6 (Ar*C*), 137.6 (Ar*C*), 135.9 (Ar*C*), 135.0 (Ar*C*), 98.2 (C_5Me_5), 28.1 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 23.0 (Ar*Me*), 21.1 (Ar*Me*), 19.5 ($CH(CH_3)_2$), 19.2 ($CH(CH_3)_2$), 11.4 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 76.0. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 71.7. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for $C_{59}H_{55}BF_{20}NOPRuSi$: C, 52.69; H, 4.12; N, 1.04. Found: C, 52.48; H, 3.76; N, 1.02.

[Cp*(PiPr$_3$)Ru(H)$_2$(Si(Mes){κ^2-O(CH)(NPhCF$_3$)})][B(C$_6$F$_5$)$_4$] (12). By a procedure analogous to that for **11**, complex **12** was obtained as a light brown solid in 88% yield (0.051 g). ^1H NMR (C_6D_5Br, 600 MHz): δ 8.31 (1H, s, O*CH*), 7.40 (2H, d, *J* = 7.9 Hz, NPh*H*), 6.93 (2H, s, Ar*H*), 6.87 (2H, d, *J* = 7.9 Hz, NPh*H*), 2.48 (6H, br s, ArC*H*$_3$), 2.36 (3H, s, ArC*H*$_3$), 1.92 (18H, s, C_5Me_5 + C*H*$(CH_3)_2$), 1.01 (18H, m, CH(C*H*$_3$)$_2$), -11.33 (1H, d, $^2J_{PH}$ = 23.3 Hz, Ru*H*), -11.48 (1H, br s, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 166.2 (O*C*HN), 149.5 (Ar*C*), 147.9 (Ar*C*), 142.3 (Ar*C*), 139.4 (Ar*C*), 137.5 (Ar*C*), 136.9 (Ar*C*), 135.8 (Ar*C*), 127.1 (Ar*C*), 98.4 (C_5Me_5), 27.8 ($CH(CH_3)_2$), 23.8 (Ar*Me*),22.9 (Ar*Me*), 21.0 (Ar*Me*), 19.3 ($CH(CH_3)_2$), 19.0 ($CH(CH_3)_2$), 11.3 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 75.8. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 75.8. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -62.4, -62.5, -63.5, -132.4, -162.8, -166.7.

Anal. Calcd for $C_{60}H_{54}BF_{23}NOPRuSi$: C, 51.00; H, 3.85; N, 0.99. Found: C, 50.63; H, 3.91; N, 1.33.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$•DMAP)][B(C$_6$F)$_4$] (13). A solution of DMAP (0.005 g, 0.04 mmol) in C_6H_5F was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a colorless solution. Immediately, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give an off-white solid in 82% yield (0.045 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 8.32 (2H, m, Ar*H*), 7.64 (4H, m, Ph*H*), 7.40 (6H, m, Ph*H*), 6.31 (2H, m, Ar*H*), 2.70 (3H, s, N*Me*), 2.66 (3H, s, N*Me*), 1.59 (18H, s, C_5Me_5 + PC*H*$(CH_3)_2$), 1.05 (18H, dd, J = 6.9 Hz, J_{PH} = 13.0 Hz, CH(C*H*$_3$)$_2$), -11.92 (2H, d, $^2J_{PH}$ = 27.0 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 156.1 (Ar*C*), 149.6 (Ar*C*), 148.0 (Ar*C*), 141.9 (Ar*C*), 139.4 (Ar*C*), 137.7 (Ar*C*), 135.9 (Ar*C*), 134.9 (Ar*C*), 127.9 (Ar*C*), 105.8 (Ar*C*), 97.1 (*C*$_5$Me$_5$), 39.0 (N*Me*), 38.8 (N*Me*), 27.6 (*C*H(CH$_3$)$_2$), 19.8 (CH(*C*H$_3$)$_2$), 10.9 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 77.4. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 68.5. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.8, -166.5. Anal. Calcd for $C_{62}H_{58}BF_{20}N_2PRuSi$: C, 53.88; H, 4.23; N, 2.03. Found: C, 54.27; H, 4.07; N, 1.94.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$•Ph$_2$CO)][B(C$_6$F)$_4$] (14). A solution of benzophenone (0.008 g, 0.04 mmol) in C_6H_5F was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give an orange solution. After 15 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give an orange solid in 87% yield (0.050 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.92 (8H, d, J = 7.3 Hz, Ph*H*), 7.56 (4H, t, J = 7.3 Hz, Ph*H*), 7.36 (8H, d, J = 7.3 Hz, Ph*H*), 1.68 (18H, s, C_5Me_5 + PC*H*$(CH_3)_2$), 1.08 (18H, dd, J = 6.9 Hz, J_{PH} = 13.4 Hz, CH(C*H*$_3$)$_2$), -11.06 (2H, d, $^2J_{PH}$ = 25.1 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 201.9 (O*C*Ph$_2$), 149.6 (Ar*C*), 148.0 (Ar*C*), 137.6 (Ar*C*), 135.9 (Ar*C*), 135.8 (Ar*C*), 135.2 (Ar*C*), 132.2 (Ar*C*), 128.6 (Ar*C*), 128.5 (Ar*C*), 127.8 (Ar*C*), 97.5 (*C*$_5$Me$_5$), 28.0 (*C*H(CH$_3$)$_2$), 27.9 (*C*H(CH$_3$)$_2$), 19.7 (CH(*C*H$_3$)$_{22}$), 11.1 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 78.1. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 78.3. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for $C_{68}H_{58}BF_{20}PRuSi$: C, 56.63; H, 4.05. Found: C, 56.88; H, 4.01.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$•PhCONH$_2$)][B(C$_6$F)$_4$] (15). A solution of benzamide (0.005 g, 0.04 mmol) in C_6H_5F was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a colorless solution. Immediately, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give an off-white solid in 93% yield (0.051 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.97 (4H, d, J = 7.1 Hz, Ph*H*), 7.84 (1H, d, J = 7.6 Hz, Ar*H*), 7.66 (2H, d, J = 7.6 Hz, Ar*H*), 7.51 (4H, t, J = 7.1 Hz, Ph*H*), 7.45 (2H, d, J = 7.1 Hz, Ph*H*), 7.34 (4H, t, J = 7.6 Hz, Ar*H*), 5.90 (1H, br s, N*H*), 5.62 (1H, s, N*H*), 1.64 (15H, s, C_5Me_5), 1.41 (3H, sept, J = 7.1 Hz, PC*H*$(CH_3)_2$), 1.07 (18H, dd, J = 7.1 Hz, J_{PH} = 13.3 Hz, CH(C*H*$_3$)$_2$), -11.50 (2H, d, $^2J_{PH}$ = 26.5 Hz, $^2J_{SiH}$ = 11.3 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 172.9 (*C*ONH$_2$), 149.6 (Ar*C*), 148.1 (Ar*C*), 141.2 (Ar*C*), 139.5 (Ar*C*), 137.6 (Ar*C*), 136.0 (Ar*C*), 134.9 (Ar*C*), 132.2 (Ar*C*), 128.7 (Ar*C*), 128.6 (Ar*C*), 128.5 (Ar*C*), 127.3 (Ar*C*), 124.2 (Ar*C*), 115.5 (Ar*C*), 115.3 (Ar*C*), 97.0 (*C*$_5$Me$_5$), 27.6 (*C*H(CH$_3$)$_2$), 19.5 (CH(*C*H$_3$)$_{22}$), 11.0 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 78.0. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 80.2. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.4, -162.7, -

166.5. Anal. Calcd for $C_{62}H_{55}BF_{20}NOPRuSi$: C, 53.92; H, 4.01; N, 1.01. Found: C, 53.36; H, 3.94; 1.02.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$•NHMePh)][B(C$_6$F)$_4$] (16). An excess of N-methylaniline (3 drops) was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a yellow solution. After 10 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a white solid in 87% yield (0.047 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.71 (4H, m, Ph*H*), 7.45 (2H, m, Ph*H*), 7.40 (4H, m, Ph*H*), 7.22 (2H, m, Ar*H*), 7.06 (1H, m, Ar*H*), 6.58 (2H, m, Ar*H*), 4.37 (1H, s, N*H*), 2.94 (3H, s, N*Me*), 1.77 (15H, s, C_5Me_5), 1.66 (3H, m, PC*H*$(CH_3)_2$), 1.05 (18H, m, CH(C*H*$_3)_2$), -11.14 (2H, d, $^2J_{PH}$ = 24.2 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.7 (Ar*C*), 148.1 (Ar*C*), 139.5 (Ar*C*), 137.6 (Ar*C*), 136.9 (Ar*C*), 135.9 (Ar*C*), 127.8 (Ar*C*), 97.7 (C_5Me_5), 35.0 (N*Me*), 27.3 (*C*H$(CH_3)_2$), 27.2 (*C*H$(CH_3)_2$), 19.5 (CH(*C*H$_3)_2$), 11.4 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 76.7. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 55.7. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for $C_{62}H_{57}BF_{20}NPRuSi$: C, 54.47; H, 4.20; N, 1.02. Found: C, 54.38; H, 4.20; N, 1.35.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiHMes•NHMePh)][B(C$_6$F)$_4$] (17). By a procedure analogous to that for **3**, complex **17** was obtained as an off-white solid in 91% yield (0.049 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.29 (2H, t, *J* = 7.8 Hz, Ph*H*), 6.89 (3H, s, Ph*H*), 6.87 (2H, s, Ar*H*), 6.16 (1H, br s, Si*H*), 5.17 (1H, br s, N*H*), 3.12 (3H, s, NC*H*$_3$), 2.50 (6H, s, ArC*H*$_3$), 2.34 (3H, s, ArC*H*$_3$), 1.68 (18H, br s, C_5Me_5 + C*H*$(CH_3)_2$), 0.95 (18H, br m, CH(C*H*$_3)_2$), -12.16 (2H, br s, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.3 (Ar*C*), 147.6 (Ar*C*), 144.5 (Ar*C*), 142.0 (Ar*C*), 139.0 (Ar*C*), 137.3 (Ar*C*), 135.6 (Ar*C*), 97.0 (C_5Me_5), 34.7 (N*Me*), 27.6 (*C*H$(CH_3)_2$), 22.7 (Ar*Me*), 20.8 (Ar*Me*), 19.0 (CH(*C*H$_3)_2$), 10.7 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 76.6. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 35.7. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.7, -163.1, -166.9. Anal. Calcd for $C_{59}H_{59}BF_{20}NPRuSi$: C, 53.16; H, 4.46; N, 1.05. Found: C, 53.38; H, 4.25; N, 1.35.

[Cp*(PiPr$_3$)Ru(H)$_2$(SiPh$_2$•tBuSONH$_2$)][B(C$_6$F)$_4$] (18). A solution of 2-methylpropane-2-sulfinamide (0.006 g, 0.04 mmol) in C_6H_5F was added to a solution of **1** (0.050 g, 0.04 mmol) in 1 mL of C_6H_5F to give a pale yellow solution. After 10 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give an off-white solid in 89% yield (0.049 g). ^{1}H NMR (C_6D_5Br, 600 MHz): δ 8.18 (4H, t, *J* = 7.4 Hz, Ph*H*), 7.64 (4H, m, Ph*H*), 7.57 (2H, m, Ph*H*), 4.38 (2H, s, N*H*$_2$), 2.05 (3H, m, PC*H*$(CH_3)_2$), 1.56 (15H, s, C_5Me_5), 1.27 (9H, dd, *J* = 6.5 Hz, J_{PH} = 13.1 Hz, CH(C*H*$_3)_2$), 1.22 (9H, dd, *J* = 7.1 Hz, J_{PH} = 13.0 Hz, CH(C*H*$_3)_2$), -11.04 (1H, d, $^2J_{PH}$ = 27.6 Hz, Ru*H*), -11.23 (1H, d, $^2J_{PH}$ = 26.5 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): 149.7 (Ar*C*), 148.0 (Ar*C*), 141.5 (Ar*C*), 140.3 (Ar*C*), 139.5 (Ar*C*), 137.6 (Ar*C*), 136.6 (Ar*C*), 136.3 (Ar*C*), 136.0 (Ar*C*), 128.5 (Ar*C*), 128.2 (Ar*C*), 96.5 (C_5Me_5), 59.9 (*C*$(CH_3)_3$), 27.9 (*C*H$(CH_3)_2$), 22.1 (C(*C*H$_3)_3$), 19.7 (CH(*C*H$_3)_2$), 19.4 (CH(*C*H$_3)_2$), 10.7 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 79.3. ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 89.6. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ -132.3, -162.7, -166.5. Anal. Calcd for $C_{59}H_{59}BF_{20}PRuSi$: C, 51.31; H, 4.31; N, 1.01. Found: C, 51.19; H, 4.67; N, 1.39.

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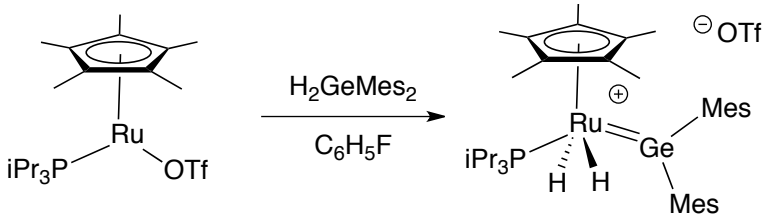
Chapter 4

Synthesis and Reactivity of Cationic Ruthenium Germylene Complexes $[Cp^*(PiPr_3)RuH_2(=GeRR')]^+$

Recent years have seen rapid progress in the development of transition metal silylene chemistry, and silylene complexes are now thought to be involved in a number of new stoichiometric and catalytic transformations.[1] Of particular interest are cationic silylene complexes that are implicated by experimental and computational studies as key intermediates in the Si-C bond-forming step of catalytic hydrosilations that are highly selective toward anti-Markovnikov products.[2]

Given the novel chemical behavior of silylene complexes, analogous transition metal germylene complexes, $L_nM{=}GeR_2$, might also be expected to exhibit interesting chemistry. Indeed, germylene complexes are hypothesized to be key intermediates in dehydrogenative couplings of arylgermanes[3] and in the demethanative coupling of $HGeMe_3$.[4] While transition metal germylene complexes were first reported in 1971, the reactivity of such complexes remains relatively unexplored.[5] Tobita and co-workers have studied the neutral germylene complex $Cp^*(CO)_2(H)W{=}Ge(H)[C(SiMe_3)_3]$ and its reactions with polar substrates.[6] This laboratory, using methods developed to access silylene complexes, recently discovered synthetic routes to $Cp^*(iPr_2MeP)(H)Ru{=}GeH(Trip)$[7] (Trip = 2,4,6-triisopropylphenyl) and $Cp^*(dmpe)Mo(H){=}GePh_2$.[8] In light of the exceptional properties associated with cationic silylene complexes, it is of interest to explore related cationic germylene complexes. Here we describe convenient synthetic routes to such compounds and their chemical properties.

Synthesis of the cationic germylene complex $[Cp^*(PiPr_3)Ru(H)_2(=GeMes_2)][OTf]$ (**1**) was achieved by reaction of 1.5 equiv of H_2GeMes_2 with $Cp^*(PiPr_3)RuOTf$[9] in C_6H_5F (eq 1). The addition of pentane resulted in separation of the product as a yellow oil. Removal of the supernatant and drying *in vacuo* gave pure 1 as a light yellow solid in excellent yield.

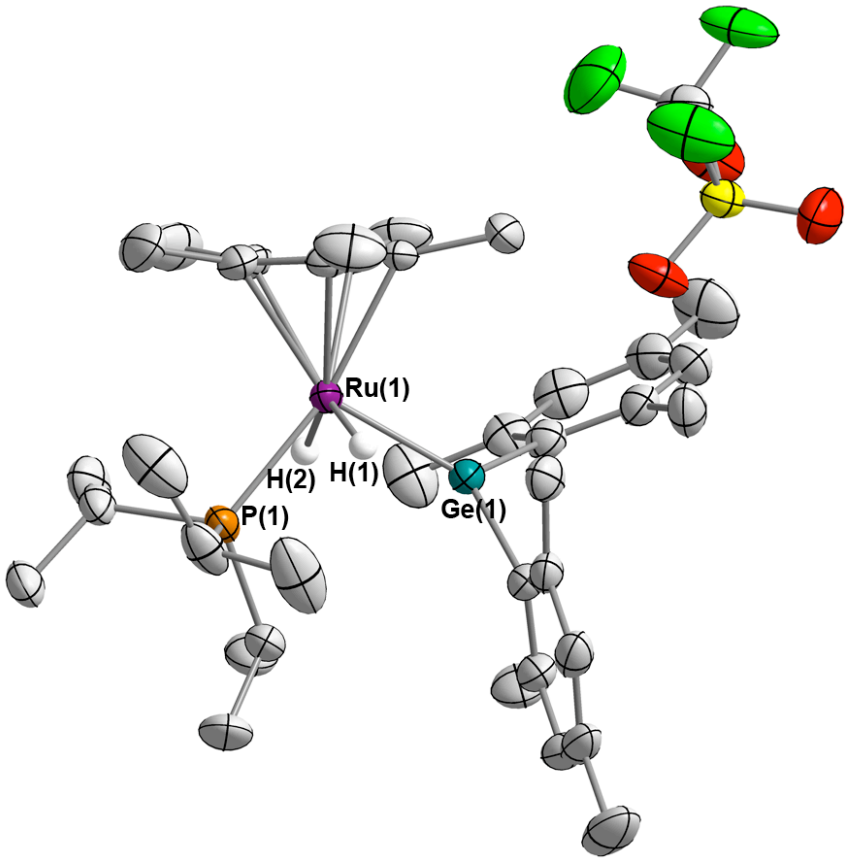


(1)

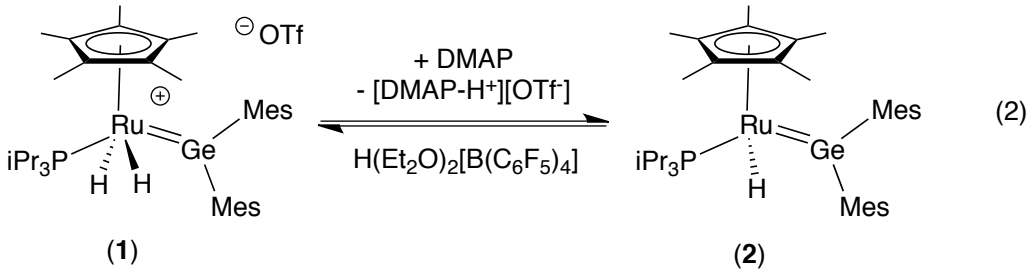
(**1**)

Single crystals of **1** were grown by slow evaporation of a concentrated C_6H_5F solution over two days. The X-ray structure determination reveals a four-legged piano stool geometry about the Ru center with a short Ru – Ge bond distance of 2.3318(5) Å and an outer- sphere triflate anion (Figure 1). This Ru – Ge distance is significantly shorter than that observed for $Cp^*(CO)_2(H)W{=}Ge(H)[C(SiMe_3)_3]$[6] (2.4289(8) Å). Both hydride ligands were located in the Fourier map. Based on the Ge···H distances of 2.3 Å (average), it is reasonable to assume that the Ge – H bonds have undergone complete oxidative addition and retain little to no Ge···H interactions. The H – Ru – Ge – C dihedral angles (19.45°, 156.52°, 72.72°, 111.31°) indicate that the hydride ligands are not geometrically disposed to interact favorably with the germanium center.[8] Additionally, the sum of angles around Ge is 359.89° (C – Ge – C 111.46(13)°; Ru – Ge – C 124.82(9)°,123.61(9)°), indicating sp^2 hybridization at Ge. The ^1H NMR spectrum reveals the presence of inequivalent mesityl groups and equivalent hydride ligands at -8.82 ppm, and a single resonance is observed at 77.8 ppm by $^{31}P\{^1H\}$ NMR spectroscopy.

Figure 1. Molecular structure of **1** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms and the triflate counterion are omitted for clarity. Selected bond lengths (Å): Ru(1) – Ge(1) 2.3318(5), Ru(1) – P(1) 2.3501(8), Ru(1) – H(1) .44(4), Ru(1) – H(2) 1.51(4).



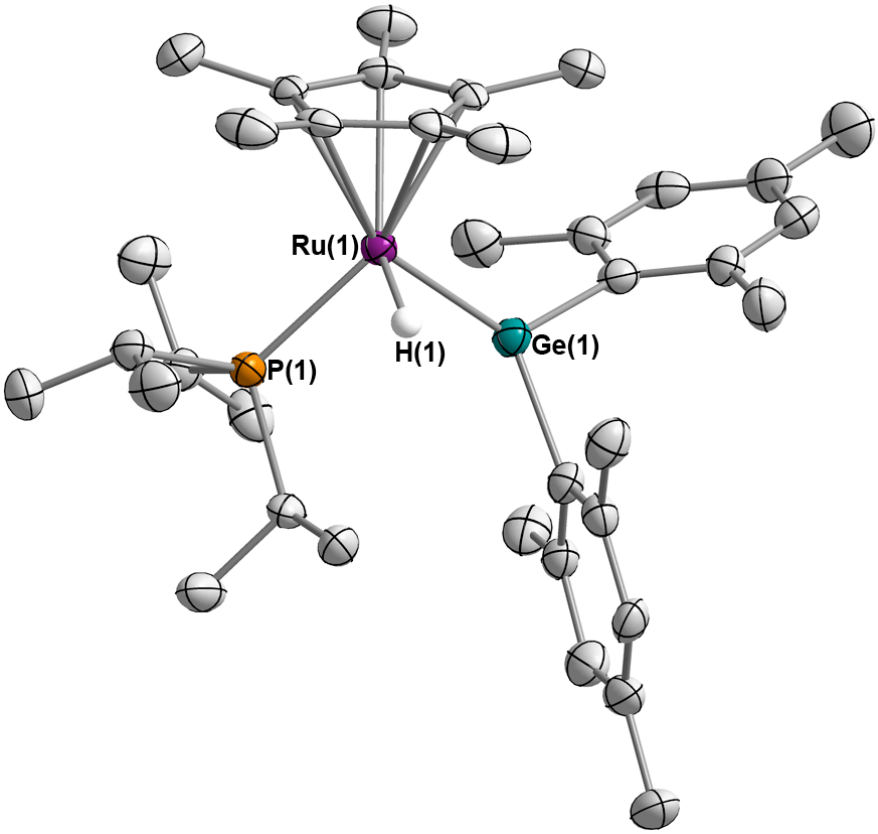
Silylene complexes typically display distinctive electrophilic, Lewis acidic character. Thus, they usually combine with a Lewis base such as *N*,*N*-*p*-dimethylaminopyridine (DMAP) to afford a base-stabilized silylene ligand.[10] This reactivity toward DMAP has also been observed for the stannylene complex Cp*(PiPr$_3$)Os(H)(=SnHTrip).[11] To investigate the electrophilic character of **1**, this complex was added to one equivalent of DMAP in C_6H_5F solution to give a rapid color change from pale yellow to bright pink. The reaction mixture was evaporated to dryness, and the resulting pink complex **2** was extracted into pentane and crystallized in excellent yield (92 %). Surprisingly, this product is not a DMAP adduct, but is instead the neutral germylene complex Cp*(PiPr$_3$)RuH(=GeMes$_2$), resulting from deprotonation of **1** by DMAP (eq 2).



(2)

Single crystals of **2** suitable for X-ray analysis were grown by slow evaporation from a pentane solution at -30 °C. The coordination geometry of **2** is very similar to that of 1 (Figure 2). The hydride ligand, located in the Fourier map, was found to be 2.44 Å from the Ge atom, indicating the lack of a Ge···H interaction, and the H – Ru – Ge – C dihedral angles (20.86, 146.86) further support this conclusion. The summation of angles about Ge is 359.1° (C – Ge – C 102.7(2)°; Ru – Ge – C 127.48(17)°, 128.88(17)°), as expected for the germylene ligand. Notably, the Ru – Ge bond distance of 2.2978(9) Å is shorter than that observed in **1**, presumably due to greater double-bond character in **2**.

Figure 2. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1) – Ge(1) 2.2978(9), Ru(1) – P(1) 2.3036(17), Ru(1) – H(1) 1.46(6).



The ^{1}H NMR spectrum for **2** displays an upfield resonance at -12.47 ppm (J_{PH} = 36.0 Hz) attributed to a single hydride ligand. A singlet resonance at 84.5 ppm in the ^{31}P{^{1}H} NMR spectrum is shifted downfield relative to that observed for **1**. No resonances are detected by ^{19}F NMR spectroscopy, confirming the absence of the triflate anion.

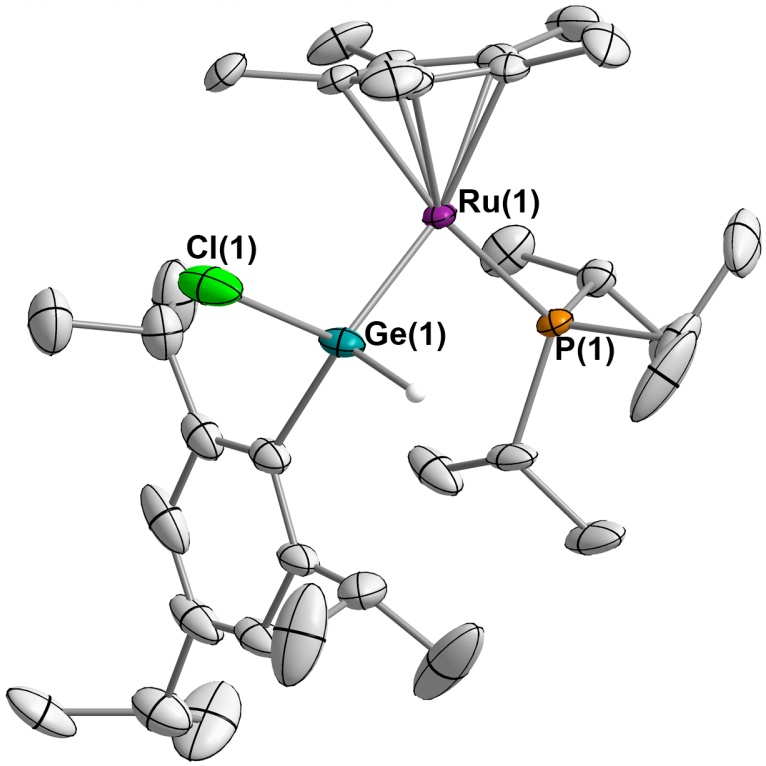
Complex **2** can be protonated to reform **1** (eq 2). A solution of 1 equiv of $H(Et_2O)_2[B(C_6F_5)_4]$ in C_6D_5Br was added to **2**, resulting in a color change from bright pink to pale yellow over 24 h with heating at 60 °C. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the product are identical to those observed for **1**, and the reaction is quantitative.

Complex **1** is rather unusual in that the germylene ligand does not appear to interact with OTf^- and DMAP. Both of these Lewis bases might have been expected to bind directly to the Ge

center, as observed for the complexes $CpRe(NO)(PPh_3)(GePh_2OTf)$[12] and $[Cp^*(CO)_2FeGeMe_2DMAP]BPh_4$[13]. The observed reactivity of **1** can be attributed to steric congestion due to the presence of bulky mesityl substituents on Ge. Indeed, the only known example of an isolable silylene complex with an outer-sphere triflate counterion is $[Cp^*(PMe_3)Ir(SiMes_2)(H)][OTf]$.[14]

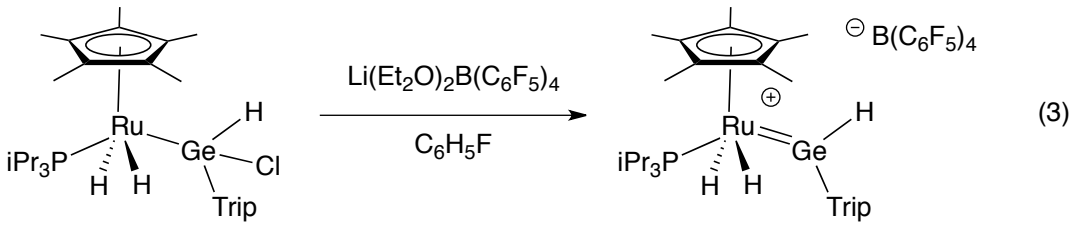
To explore a possible route to less sterically hindered and more reactive germylene complexes, the reaction of $Cp^*(PiPr_3)RuCl$ with a primary germane was examined. Analogous reactions utilizing $Cp^*(PiPr_3)RuOTf$ gave intractable mixtures of products. The reaction of $TripGeH_3$ with $Cp^*(PiPr_3)RuCl$ in diethyl ether resulted in clean conversion to $Cp^*(PiPr_3)Ru(H)_2(GeHTripCl)$ (**3**), isolated as a dark orange solid. The ^1H NMR spectrum of **3** contains a resonance at 7.17 ppm for the Ge – H hydrogen and two upfield resonances at -9.89 and -10.62 ppm for the hydride ligands. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a pentane solution at -35 °C, and the crystal structure confirmed the identity of **3** (Figure 3).

Figure 3. Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms are omitted for clarity. Selected bond lengths (Å): Ru(1) – Ge(1) 2.4376(10), Ru(1) – P(1) 2.3180(8), Ge(1) – Cl(1) 2.2883(17).



Complex **3** proved to be an excellent precursor to a cationic germylene complex, via addition of $Li(Et_2O)_2[B(C_6F_5)_4]$ in C_6H_5F. After the reaction mixture was stirred at room temperature for 5 min, 15 mL of pentane was added and the solution was allowed to stand at -35 °C for 45 min, after which the supernatant was decanted to leave a dark orange oil. Washing with additional pentane and drying under vacuum gave $[Cp^*(PiPr_3)Ru(H)_2(=GeHTrip)][B(C_6F_5)_4]$ (**4**) as an orange solid (eq 3). Multinuclear NMR spectroscopy confirms the identity of **4** as a hydrogen-substituted ruthenium germylene complex. The ^1H NMR spectrum contains a Ge – H resonance at 12.73 ppm, significantly downfield-

shifted relative to that of the germyl complex **3**. The two hydride ligands at -10.09 ppm are equivalent. The $^{31}P\{^{1}H\}$ NMR spectrum displays a single peak at 77.9 ppm, shifted upfield compared to that for **3**. The ^{19}F NMR spectrum reveals three resonances at -132.2, -162.8, and -166.6 ppm that are characteristic of the $[B(C_6F_5)_4]^-$ counterion. The reaction of **4** with one equiv of DMAP in C_6D_5Br did not cleanly give one product. However, no deprotonation products were observed in the reaction mixture.

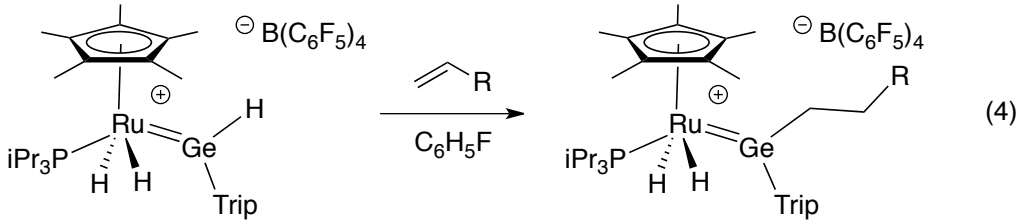


(3)

(**3**) (**4**)

Notably, while metal silylene complexes typically form base-stabilized silylene complexes in the presence of ethereal solvents, complex **4** does not bind Et_2O and no precautions to exclude ethereal solvents need to be taken. For example, under analogous conditions the reaction of $Cp^*(PiPr_3)Ru(H)_2(SiHMesOTf)$ with 1 equiv of $Li(Et_2O)_2[B(C_6F_5)_4]$ affords $[Cp^*(PiPr_3)Ru(H)_2(=SiHMes{\bullet}Et_2O][B(C_6F)_4]$ and the coordinated Et_2O cannot be removed under vacuum.[9] In contrast, **4** was not isolated as a diethyl ether adduct.

Direct addition of the Si – H bond of a cationic, H-substituted silylene complex to an alkene has now been observed in several cases, and this reaction appears to represent a key step in catalytic, silylene-mediated hydrosilations.[1] Additionally, neutral Ge(II) hydride compounds supported by bulky β-diketimido ligands have been shown to react with a number of small molecules via activation of the Ge – H bond.[15] Thus, it was of interest to explore the potential for related H-substituted germylene compounds to engage in similar chemistry, and for these reasons interactions of **4** with various alkenes were examined. A solution of complex **4** was observed to react with 1-hexene in C_6H_5F solution, to result in an immediate color change from bright yellow-orange to bright yellow (eq 4). After 5 min, the solution was concentrated under vacuum to give a dark yellow oil. Subsequent washings with pentane and further drying under vacuum provided $[Cp^*(PiPr_3)Ru(H)_2(=Ge(Hexyl)Trip)][B(C_6F)_4]$ (**5**) as a bright yellow solid. Additionally, **4** cleanly transforms to the corresponding secondary germylene complexes upon reaction with styrene, 3,3-dimethylbut-1-ene, and allyl chloride (eq 4).



(4)

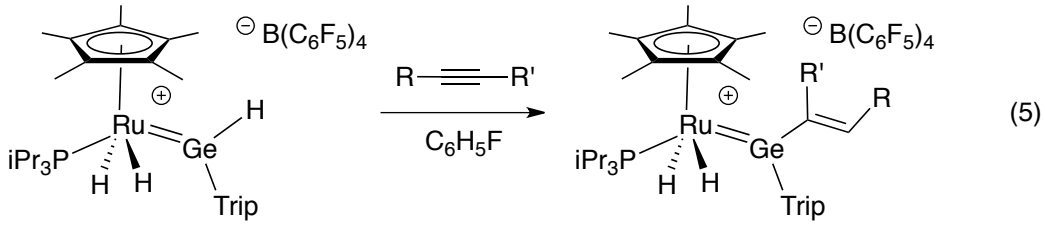
(**4**)

R = C_4H_9 (**5**)
R = Ph (**6**)
R = tBu (**7**)
R = CH_2Cl (**8**)

Multinuclear NMR spectroscopy confirms the identities of **5** – **8**. For all complexes, the ^{1}H NMR spectra contain no evidence for a Ge – H resonance at *ca.* 12 – 13 ppm. In addition,

new resonances confirm the presence of the expected new substituent at germanium; for example, complex **5** displays resonances between 1.44 ppm and 1.27 ppm corresponding to a hexyl group. The two hydride ligands for all complexes are chemically equivalent and appear between -9.07 and -9.27 ppm. The $^{31}P\{^{1}H\}$ NMR resonances for **5** – **8** range from 77.4 – 77.9.

Complex **4** also engages in stoichiometric hydrogermylation reactions in the presence of alkynes. An excess of t-butylacetylene was added to a solution of **4** in C_6H_5F at room temperature to give a bright yellow solution (eq 5), from which complex **9** was isolated as an orange solid. Additionally, reaction of **4** with 2-butyne yields complex **10** as a yellow solid.



(5)

(**4**)

R = tBu, R' = H (**9**)
R = R' = Me (**10**)

The ^{1}H NMR spectrum for **9** reveals a doublet at 7.24 ppm arising from the vinylic C-H group geminal to Ge. The terminal vinylic proton appears as a doublet at 6.42 ppm, and the t-butyl group is at 1.48 ppm. The large J_{HH} coupling constant (17.9 Hz) associated with the doublets indicates that the vinylic hydrogens are in a *trans* arrangement, which implies that the t-butyl group is *trans* to Ge. Additionally, the hydride ligands have shifted slightly downfield to -9.31 ppm, and the $^{31}P\{^{1}H\}$ NMR reveals a single resonance at 78.1 ppm. Complex **10** displays a ^{1}H NMR resonance for a terminal vinylic proton which is a multiplet at 6.32 ppm, and the terminal methyl group appears as a doublet (J_{HH} = 6.4 Hz) at 1.26 ppm. The methyl group geminal to Ge arises as a singlet at 1.98 ppm. Again, there is a downfield shift of the hydride ligands to -8.70 ppm, and a single peak at 78.7 ppm is revealed by $^{31}P\{^{1}H\}$ spectroscopy.

In summary, two new cationic ruthenium germylene complexes have been synthesized and preliminary reactivity studies show that a hydrogen-substituted, cationic germylene complex exhibits electrophilic character related to that observed previously for silylene analogs. Thus, compound **4** is the first reported germylene complex that undergoes hydrogermylation reactions with unsaturated non-polar organic compounds. This indicates that compounds such as **4** may catalyze germane additions to unsaturated substrates, and this possibility is currently being explored.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene and pentane were dried over Na and distilled under N_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Bromobenzene-d_5 was refluxed over CaH_2 for 20 h and then distilled under nitrogen.

Fluorobenzene was dried over P_2O_5, degassed, and distilled under N_2. $Cp^*(PiPr_3)RuCl$,[16] $Cp^*(PiPr_3)RuOTf$,[9] Mes_2GeH_2,[17] and $TripGeH_3$[18] were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley or Atlantic Microlab, Inc.

$[Cp^*(PiPr_3)Ru(H)_2(GeMes_2)][OTf]$ (1). A solution of Mes_2GeH_2 (0.050 g, 0.16 mmol) in 1 mL of C_6H_5F was added to a solution of $Cp^*(PiPr_3)RuOTf$ (0.050 g, 0.092 mmol) in 1 mL of C_6H_5F. The reaction solution was stirred for 1 h. To the resulting C_6H_5F solution was added 10 mL of cold pentane, and the solution was placed in the -30 °C freezer. After 1 h, the yellow oil was isolated by carefully decanting off the solution. The oil was washed with pentane and dried to give a yellow solid (0.037 g, 48% yield). ^1H NMR (C_6D_5Br, 600 MHz): δ 6.89 (2H, s, Ar*H*), 6.82 (2H, s, Ar*H*), 2.45 (6H, s, ArCH_3), 2.38 (6H, s, ArCH_3), 2.33 (3H, s, ArCH_3), 2.28 (3H, s, ArCH_3), 1.79 (15H, s, C_5Me_5), 1.74 (3H, septet, J = 7.0 Hz, PC*H*$(CH_3)_2$), 1.02 (9H, dd, J = 7.0 Hz, 14.5 Hz, PCH(CH_3)$_2$), -8.82 (2H, d, $^2J_{PH}$ = 26.2 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 150.9 MHz): 139.1 (Ar*C*), 138.9 (Ar*C*), 128.8 (Ar*C*), 115.5 (Ar*C*), 115.4 (Ar*C*), 100.1 (C_5Me_5), 29.2 (br, P*C*H$(CH_3)_2$), 23.2 (Mes*C*H$_3$), 22.8 (Mes*C*H$_3$), 21.4 (Mes*C*H$_3$), 21.3 (Mes*C*H$_3$), 19.1 (PCH(*C*H$_3$)$_2$), 19.3 (PCH(*C*H$_3$)$_2$), 11.4 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 163.0 MHz): δ 77.8. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -76.3. Anal. Calcd for $C_{38}H_{60}F_3GeO_3PRuS$: C, 53.16; H, 7.04. Found: C, 53.41; H, 7.15.

$Cp^*(PiPr_3)Ru(H)(=GeMes_2)$ (2). A solution of DMAP (0.004 g, 0.035 mmol) in 1 mL of C_6H_5F was added to a solution of $[Cp^*(PiPr_3)Ru(H)_2(GeMes_2)][OTf]$ (0.030 g, 0.035 mmol) in 1 mL of C_6H_5F. The reaction solution was stirred for 1 h to give a magenta solution, and then the solution was stripped to dryness. The dark pink oil was dissolved in pentane, filtered through Celite, and dried to give a pink solid. Recrystallization from pentane at -30 °C gave **2** as dark pink crystals (0.023 g, 92% yield). ^1H NMR (C_6D_6, 600 MHz): δ 6.92 (1H, s, Ar*H*), 6.83 (1H, s, Ar*H*), 6.66 (1H, s, Ar*H*), 6.57 (1H, s, Ar*H*), 3.17 (3H, s, ArCH_3), 2.99 (3H, s, ArCH_3), 2.28 (3H, s, ArCH_3), 2.18 (3H, s, ArCH_3), 2.14 (3H, s, ArCH_3), 2.11 (3H, s, ArCH_3), 1.86 (3H, septet, J = 7.2 Hz, PC*H*$(CH_3)_2$), 1.79 (15H, s, C_5Me_5), 1.08 (18H, m, PCH(CH_3)$_2$), -12.47 (1H, d, $^2J_{PH}$ = 36.0 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 156.5 (Ar*C*), 154.7 (Ar*C*), 141.8 (Ar*C*), 141.5 (Ar*C*), 138.7 (Ar*C*), 138.0 (Ar*C*), 136.7 (Ar*C*), 136.3 (Ar*C*), 128.7 (Ar*C*), 128.4 (Ar*C*), 128.3 (Ar*C*), 128.1 (Ar*C*), 92.0 (C_5Me_5), 29.3 (br, P*C*H$(CH_3)_2$), 23.2 (Mes*C*H$_3$), 23.1 (Mes*C*H$_3$), 22.9 (Mes*C*H$_3$), 22.6 (Mes*C*H$_3$), 20.8 (Mes*C*H$_3$), 20.7 (Mes*C*H$_3$), 20.1 (PCH(*C*H$_3$)$_2$), 19.6 (PCH(*C*H$_3$)$_2$), 11.8 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 84.5. Anal. Calcd for $C_{37}H_{59}GePRu \bullet 1/2(C_6H_5F)$: C, 63.50; H, 8.19. Found: C, 63.48; H, 8.23.

$Cp^*(PiPr_3)Ru(H)_2(GeHTripCl)$ (3). A solution of $TripGeH_3$ (0.070 g, 0.25 mmol) in 1 mL of diethyl ether was added to a solution of $Cp^*(PiPr_3)RuCl$ (0.10 g, 0.23 mmol) in 2 mL of diethyl

ether. The reaction solution was stirred for 20 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a dark orange solid (0.095 g, 79% yield). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.20 (2H, s, Ar*H*), 7.17 (1H, s, Ge*H*), 2.67 (2H, septet, *J* = 6.5 Hz, TripC*H*), 2.11 (1H, septet, *J* = 6.9 Hz, TripC*H*), 1.84 (15H, s, C_5Me_5), 1.77 (3H, septet, *J* = 7.1 Hz, PC*H*$(CH_3)_2$), 1.59 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.48 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.32 (6H, dd, *J* = 2.1 Hz, 6.9 Hz, TripCH_3), 1.06 (9H, dd, *J* = 7.1 Hz, J_{PH} = 13.4 Hz, PCH(C$H_3)_2$), 0.88 (9H, dd, *J* = 7.1 Hz, J_{PH} = 13.3 Hz, PCH(C$H_3)_2$), -9.89 (1H, d, $^{2}J_{PH}$ = 30.0 Hz, Ru*H*), -10.62 (1H, d, $^{2}J_{PH}$ = 28.2 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 153.4 (Ar*C*), 148.5 (Ar*C*), 141.5 (Ar*C*), 121.0 (Ar*C*), 95.6 (C_5Me$_5$), 34.3 (Trip*C*H), 32.0 (Trip*C*H), 27.8 (br, P*C*H$(CH_3)_2$), 25.1 (Trip*C*H_3), 24.0 (Trip*C*H_3), 22.6 (Trip*C*H_3), 19.1 (PCH(*C*$H_3)_2$), 18.7 (PCH(*C*$H_3)_2$), 10.6 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 82.9. Anal. Calcd for $C_{34}H_{62}ClPRuGe$: C, 57.44; H, 8.79. Found: C, 57.60; H, 8.46.

[Cp*(PiPr$_3$)Ru(H)$_2$(=GeHTrip)][B(C$_6$F$_5$)$_4$] (4). A solution of $Li(Et_2O)_2B(C_6F_5)_4$ (0.058 g, 0.07 mmol) in 0.5 mL of C_6H_5F was added to a solution of **3** (0.050 g, 0.07 mmol) in 1 mL of C_6H_5F. After stirring for 5 min at room temperature, 15 mL of pentane was added to the bright orange solution and the reaction vessel was placed in the −30 °C freezer. After 1 h, an orange oil settled to the bottom of the vial. The solution was carefully decanted and the resulting orange oil was dried under vacuum for 1 h to afford **4** as an orange solid in 60% yield (0.057 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 12.73 (1H, s, Ge*H*), 7.22 (2H, s, Ar*H*), 3.43 (1H, br s, TripC*H*), 3.03 (1H, br s, TripC*H*), 2.47 (1H, br s, TripC*H*), 1.97 (3H, br s, PC*H*$(CH_3)_2$), 1.78 (15H, s, C_5Me_5), 1.42 (36H, br s, TripCH_3), 1.59 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.48 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.07 (18H, dd, *J* = 6.0 Hz, J_{PH} = 14.4 Hz, PCH(C$H_3)_2$), -10.09 (1H, d, $^{2}J_{PH}$ = 24.1 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 150.7 (Ar*C*), 149.7 (Ar*C*), 148.1 (Ar*C*), 140.9 (Ar*C*), 139.5 (Ar*C*), 137.6 (Ar*C*), 135.9 (Ar*C*), 133.3 (Ar*C*), 100.0 (C_5Me$_5$), 35.0 (Trip*C*H), 34.8 (Trip*C*H), 31.9 (Trip*C*H), 27.6 (P*C*H$(CH_3)_2$), 27.4 (P*C*H$(CH_3)_2$), 24.5 (Trip*C*H_3), 24.1 (Trip*C*H_3), 23.0 (Trip*C*H_3), 18.9 (PCH(*C*$H_3)_2$), 10.9 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 77.9. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for $C_{58}H_{62}BF_{20}GePRu$•1/2(C_6H_5F): C, 52.23; H, 4.64. Found: C, 52.21; H, 4.94.

[Cp*(PiPr$_3$)Ru(H)$_2$(=GeHexylTrip)][B(C$_6$F$_5$)$_4$] (5). An excess of 1-hexene (*ca*. 0.1 mL) was added to a solution of **4** (0.020 g, 0.015 mmol) in 1 mL of C_6H_5F to give a bright yellow solution. After 5 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a bright yellow solid in 95% yield (0.020 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.20 (2H, s, Ar*H*), 2.99 (1H, septet, *J* = 6.6 Hz, TripC*H*), 2.20 (4H, ov m, TripC*H* + Hexyl), 1.87 (15H, s, C_5Me_5), 1.69 (3H, m, PC*H*$(CH_3)_2$), 1.49 – 1.30 (26H, ov m, TripCH_3 + Hexyl), 1.00 (18H, m, PCH(C$H_3)_2$), -9.21 (2H, br d, $^{2}J_{PH}$ = 24.9 Hz, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 153.0 (Ar*C*), 145.8 (Ar*C*), 99.3 (C_5Me$_5$), 36.1 (Hexyl), 35.9 (Trip*C*H), 33.5 (Trip*C*H), 26.1 (Hexyl), 23.8 (br, P*C*H$(CH_3)_2$), 22.7 (br, Trip*C*H_3), 17.2 (PCH(*C*$H_3)_2$), 9.8 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 77.8. ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ -132.6, -163.2, -166.9. Anal. Calcd for $C_{64}H_{74}BF_{20}GePRu$: C, 53.43; H, 5.18. Found: C, 53.24; H, 5.00.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Ge(CH$_2$CH$_2$Ph)Trip)][B(C$_6$F$_5$)$_4$] (6). By a procedure analogous to that for **5**, complex **6** was obtained as a bright yellow solid in 88% yield (0.019 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.42 (2H, t, *J* = 7.3 Hz, Ar*H*), 7.35 (1H, t, *J* = 7.3 Hz, Ar*H*), 7.24 (2H, s, Ar*H*), 7.22

(2H, s, Ar*H*), 3.02 (1H, septet, *J* = 6.9 Hz, TripC*H*), 2.93 (2H, m, CH_2), 2.48 (2H, m, CH_2), 2.23 (2H, septet, *J* = 6.5 Hz, TripC*H*), 1.87 (15H, s, C_5Me_5), 1.73 (3H, m, PC*H*$(CH_3)_2$), 1.47 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.42 (6H, d, *J* = 6.9 Hz, TripCH_3), 1.36 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.01 (18H, dd, *J* = 7.1, J_{PH} = 14.6 Hz, PCH(CH_3)$_2$), -9.07 (2H, d, $^2J_{PH}$ = 25.3 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 153.3 (Ar*C*), 149.8 (Ar*C*), 149.6 (Ar*C*), 147.6 (Ar*C*), 146.1 (Ar*C*), 141.2 (Ar*C*), 139.3 (Ar*C*), 137.5 (Ar*C*), 135.5 (Ar*C*), 99.5 (C_5Me_5), 47.7 (*C*H_2), 37.6 (Trip*C*H), 34.4 (Trip*C*H), 31.0 (*C*H_2), 29.1 (P*C*H$(CH_3)_2$), 25.4 (Trip*C*H_3), 23.8 (Trip*C*H_3), 22.8 (Trip*C*H_3), 18.6 (PCH(*C*H_3)$_2$), 11.2 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 77.9. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -130.4, -160.9, -164.8.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Ge(CH$_2$CH$_2$tBu)Trip)][B(C$_6$F$_5$)$_4$] (7). By a procedure analogous to that for **5**, complex **7** was obtained as a bright yellow solid in 95% yield (0.020 g). ^1H NMR (C_6D_6, 600 MHz): δ 7.23 (2H, s, Ar*H*), 3.69 (1H, septet, *J* = 6.9 Hz, TripC*H*), 3.00 (2H, m, CH_2), 2.25 (2H, m, CH_2), 2.23 (2H, septet, *J* = 6.5 Hz, TripC*H*), 1.87 (15H, s, C_5Me_5), 1.76 (3H, m, PC*H*$(CH_3)_2$), 1.39 (18H, m, TripCH_3), 1.03 (18H, dd, *J* = 6.8, J_{PH} = 14.0 Hz, PCH(CH_3)$_2$), 0.95 (9H, s, tBu), -9.27 (2H, d, $^2J_{PH}$ = 24.4 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 149.8 (Ar*C*), 149.2 (Ar*C*), 147.6 (Ar*C*), 145.3 (Ar*C*), 139.0 (Ar*C*), 137.3 (Ar*C*), 135.6 (Ar*C*), 99.5 (C_5Me_5), 42.3 (*C*H_2), 37.6 (Trip*C*H), 34.2 (Trip*C*H), 31.4 (*C*H_2), 30.6 (P*C*H$(CH_3)_2$), 28.3 (tBu), 26.2 (Trip*C*H_3), 24.1 (Trip*C*H_3), 22.8 (Trip*C*H_3), 18.6 (PCH(*C*H_3)$_2$), 11.2 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 77.4. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -132.9, -162.9, -166.9. Anal. Calcd for $C_{64}H_{74}BF_{20}GePRu$: C, 53.43; H, 5.18. Found: C, 53.16; H, 4.96.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Ge(CH$_2$CH$_2$CH$_2$Cl)Trip)][B(C$_6$F$_5$)$_4$] (8). By a procedure analogous to that for **5**, complex **8** was obtained as a golden yellow solid in 81% yield (0.017 g). ^1H NMR (C_6D_6, 600 MHz): δ 7.24 (2H, s, Ar*H*), 4.00 (2H, m, CH_2), 3.51 (4H, m, CH_2), 3.01 (3H, ov m, TripC*H*), 2.04 (15H, s, C_5Me_5), 1.97 (3H, m, PC*H*$(CH_3)_2$), 1.55 (6H, d, *J* = 6.9 Hz, TripCH_3), 1.37 (12H, d, *J* = 6.9 Hz, TripCH_3), 1.08 (18H, dd, *J* = 7.2, J_{PH} = 14.7 Hz, PCH(CH_3)$_2$), -11.03 (2H, br s, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 149.6 (Ar*C*), 148.0 (Ar*C*), 140.3 (Ar*C*), 139.4 (Ar*C*), 137.8 (Ar*C*), 137.6 (Ar*C*), 136.0 (Ar*C*), 133.9 (Ar*C*), 100.6 (C_5Me_5), 65.9 (*C*H_2), 45.2 (*C*H_2), 34.8 (Trip*C*H), 34.1 (Trip*C*H), 29.1 (P*C*H$(CH_3)_2$), 24.6 (Trip*C*H_3), 23.8 (Trip*C*H_3), 18.6 (PCH(*C*H_3)$_2$), 11.7 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 74.5. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -132.4, -162.6, -166.6. Anal. Calcd for $C_{61}H_{67}BClF_{20}GePRu \bullet 1/2(C_6H_5F)$: C, 52.80; H, 4.87. Found: C, 52.69; H, 4.75.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Ge(CH=CHtBu)Trip)][B(C$_6$F$_5$)$_4$] (9). By a procedure analogous to that for **5**, complex **9** was obtained as a bright yellow solid in 95% yield (0.020 g). ^1H NMR (C_6D_6, 600 MHz): δ 7.24 (1H, d, *J* = 17.9 Hz, Ge-C*H*), 7.22 (2H, s, Ar*H*), 6.42 (1H, d, *J* = 17.9 Hz, CH=C*H*), 3.00 (1H, septet, *J* = 6.5 Hz, TripC*H*), 2.33 (2H, septet, *J* = 6.5 Hz, TripC*H*), 1.87 (15H, s, C_5Me_5), 1.78 (3H, m, PC*H*$(CH_3)_2$), 1.46 (6H, d, *J* = 6.5 Hz, TripCH_3), 1.48 (12H, ov d, TripCH_3 + tBu), 1.29 (6H, dd, *J* = 6.5 Hz, TripCH_3), 1.05 (9H, s, tBu), 1.03 (18H, dd, *J* = 7.3, J_{PH} = 14.4 Hz, PCH(CH_3)$_2$), -9.31 (2H, d, $^2J_{PH}$ = 25.1 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 164.6 (CH=*C*HtBu), 153.3 (Ar*C*), 152.6 (Ar*C*), 150.9 (Ar*C*), 149.5 (Ar*C*), 147.6 (Ar*C*), 142.7 (*C*H=*C*HtBu), 142.1 (*C*Me$_3$), 140.8 (Ar*C*), 139.7 (Ar*C*), 139.2 (Ar*C*), 137.4 (Ar*C*), 135.5 (Ar*C*), 99.2 (C_5Me_5), 37.0 (Trip*C*H), 35.5 (Trip*C*H), 34.4 (Trip*C*H), 28.0 (tBu), 25.5 (Trip*C*H_3), 23.8 (P*C*H$(CH_3)_2$), 22.9 (Trip*C*H_3), 22.7 (Trip*C*H_3), 18.6 (PCH(*C*H_3)$_2$), 11.2 (C_5Me_5). $^{31}P\{^1H\}$

NMR (C_6D_6, 163.0 MHz): δ 78.1. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -130.8, -161.3, -165.2. Anal. Calcd for $C_{64}H_{72}BF_{20}GePRu$: C, 53.50; H, 5.05. Found: C, 53.30; H, 5.24.

[Cp*(PiPr$_3$)Ru(H)$_2$(=Ge(CMe=CHMe)Trip)][B(C$_6$F$_5$)$_4$] (10). By a procedure analogous to that for **5**, complex **10** was obtained as a bright yellow solid in 86% yield (0.018 g). ^1H NMR (C_6D_6, 600 MHz): δ 7.23 (2H, s, Ar*H*), 6.32 (1H, m, CMe=C*H*Me), 3.70 (1H, septet, *J* = 6.9 Hz, TripC*H*), 2.99 (2H, septet, *J* = 6.9 Hz, TripC*H*), 1.98 (3H, s, C*Me*=CHMe), 1.79 (15H, s, C_5Me_5), 1.66 (3H, br m, PC*H*$(CH_3)_2$), 1.38 (18H, m, TripCH_3), 1.26 (3H, d, *J* = 6.4 Hz, CMe=CH*Me*), 1.01 (18H, dd, *J* = 6.9, 14.3 Hz, PCH(CH_3)$_2$), -8.70 (2H, br d, $^2J_{PH}$ = 21.4 Hz, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): 158.9 (CMe=*C*HMe), 153.5 (Ar*C*), 150.8 (Ar*C*), 149.6 (Ar*C*), 148.0 (Ar*C*), 145.7 (Ar*C*), 140.4 (Ar*C*), 139.5 (Ar*C*), 137.7 (Ar*C*), 135.9 (Ar*C*), 99.3 (C_5Me_5), 37.4 (Trip*C*H), 34.6 (Trip*C*H), 34.6 (Trip*C*H), 30.9 (CMe=CH*Me*), 25.5 (Trip*C*H_3), 24.4 (P*C*H$(CH_3)_2$), 24.0 (Trip*C*H_3), 23.2 (Trip*C*H_3), 18.6 (PCH(*C*H_3)$_2$), 11.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ 78.7. $^{19}F\{^1H\}$ NMR (C_6D_6, 376.5 MHz): δ -132.5, -162.7, -166.6. Anal. Calcd for $C_{62}H_{68}BF_{20}GePRu$: C, 52.86; H, 4.87. Found: C, 52.80; H, 4.65.

X-ray Crystallography. The single-crystal X-ray analysis of compounds **1**, **2**, and **3** were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data was integrated and analyzed for agreement using Bruker APEX2 v. 2009.1. Empirical absorption correction were made using SADABS. Structures were solved by direct methods using the SHELX program package.

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Chapter 5

Multiple Si–H Bond Activations by $^{t}Bu_2PCH_2CH_2P^{t}Bu_2$ and $^{t}Bu_2PCH_2P^{t}Bu_2$ Di(phosphine) Complexes of Rhodium and Iridium

Introduction

Catalytic transformations involving organosilanes, such as hydrosilation, are commercially quite significant[1] and much of this catalysis involves the activation of a silane at a transition metal center.[2] Within this context, a thorough understanding of the fundamental steps in such reactions, such as Si – H bond activation and Si – C bond formation,[3] can be extremely valuable in the design of new catalysts.[4]

Complexes of rhodium and iridium supported by pincer ligands display rich chemistry with regard to silane activation and catalysis.[5] However, while related di(phosphine) rhodium complexes have been implicated as catalysts for a number of reactions, such as the dehydrocoupling of phosphines,[6] CO_2 hydrogenation,[7] and the hydroboration of alkenes,[8] their silicon chemistry has not been as extensively explored. Promisingly, complexes supported by the di(isopropylphosphino)ethane ligand (dippe) have demonstrated both stoichiometric and catalytic reactivity toward silanes.[9] The dinuclear complex $[(dippe)Rh(\mu\text{-}H)]_2$ undergoes reactions with primary and secondary silanes to give complexes such as $[(dippe)Rh]_2(\mu\text{-}SiPh_2)_2$ and $[(dippe)Rh]_2(\mu\text{-}\eta^2\text{-}SiHMe_2)_2$.[9] A number of these dinuclear complexes also display various Si–H bond activations, resulting in terminal hydrides, hydrides that bridge two rhodium atoms, and hydrides that bridge between rhodium and silicon. Additionally, transformations catalyzed by this family of complexes include olefin hydrosilation, redistribution of substituents at silicon, dehydrocoupling of silanes, and deuterium exchange.[9]

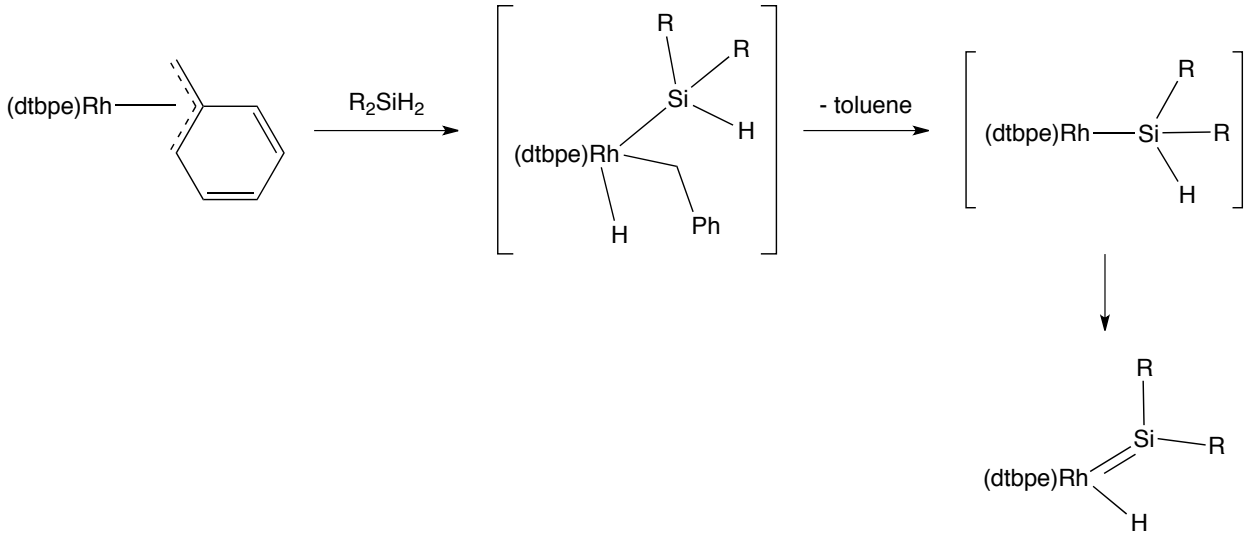
Although (dippe)Rh complexes display interesting reactivity toward primary and secondary silanes, the resulting metal-silicon products are consistently dinuclear, and feature bridging silyl or silylene ligands.[9] Given the interesting possibility of observing and/or isolating related, mononuclear silylene species, it is reasonable to explore silane activations by more sterically hindered diphosphine complexes. Rhodium complexes supported by the di(t-butylphosphino)methane ligand (dtbpm), such as $[(dtbpm)RhCl]_2$ and $(dtbpm)RhCl(PPh_3)$, have previously been reported to be active catalysts for the hydrosilation of alkynes, and synthesis of the silyl complex $(dtbpm)Rh[Si(OEt)_3](PMe_3)$ has been described.[10] Despite these interesting results, the silicon chemistry of such complexes remains relatively unexplored. Herein we report investigations that target (dtbpe)Rh and (dtbpm)Rh complexes, and associated activations of silanes and germanes.

Results and Discussion

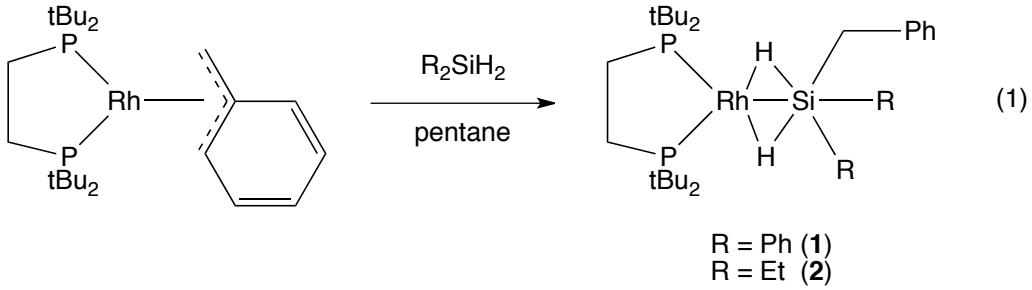
Reaction of (dtbpe)Rh(CH_2Ph) with secondary silanes. The mononuclear complex $(dtbpe)Rh(CH_2Ph)$[11] was envisioned as a potentially useful starting material and precursor to hydrido silylene complexes, as outlined in Scheme 1. Oxidative addition of an Si-H bond to this complex would give a (dtbpe)Rh(III) benzyl silyl hydride, which could then undergo reductive elimination of toluene. This would result in a reactive three-coordinate (dtbpe)Rh(I) silyl species, and α-hydrogen migration from the silicon to the rhodium center could provide a pathway to a (dtbpe)Rh silylene complex.[12]

Reactions of $(dtbpe)Rh(CH_2Ph)$ with secondary silanes were found to result in conversion to new, isolable products. For example, a pentane solution of one equiv of Ph_2SiH_2 was added to a pentane solution of $(dtbpe)Rh(CH_2Ph)$ at room temperature, and after 24 h the resulting orange-red solution was cooled to –35° C to give $(dtbpe)Rh(H)_2(SiBnPh_2)$ (**1**, Bn = CH_2Ph) as orange crystals in 69% yield (eq 1). The ^1H NMR spectrum of **1** displays peaks in the aromatic region corresponding to two phenyl groups and one benzyl group, and the methylene

Scheme 1.



group of the benzyl substituent appears as a singlet at 3.28 ppm. Two equivalent hydrides appear as a multiplet at -5.35 ppm (J_{PH} = 19.6 Hz, J_{RhH} = 33.8 Hz) and exhibit a large J_{SiH} value of 44.4 Hz, indicating a strong interaction with Si. The $^{31}P\{^{1}H\}$ NMR spectrum exhibits a single resonance as a doublet at 111.3 ppm (J_{PRh} = 114 Hz), and the single ^{29}Si NMR peak at -5.6 is consistent with a silyl group.[13] Complex **1** can be stored at room temperature for 4 weeks before significant decomposition is observed.



(1)

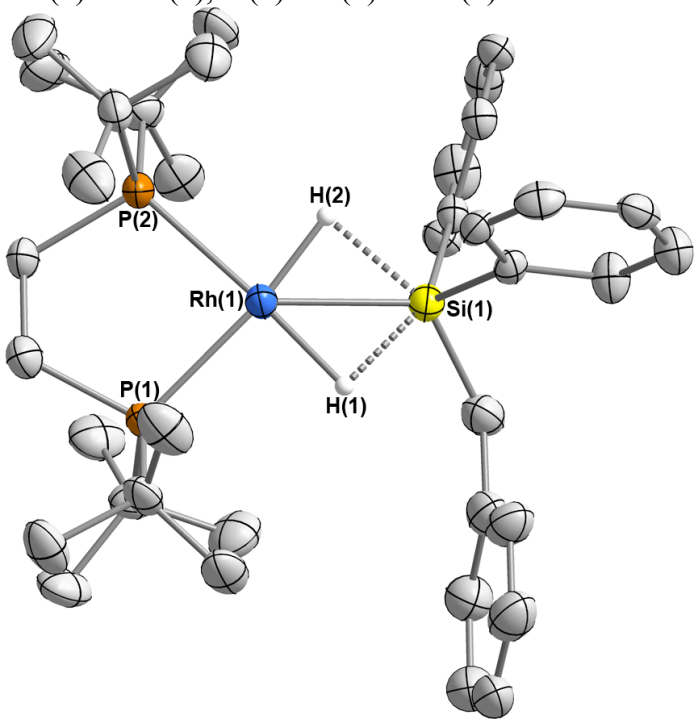
R = Ph (**1**)
R = Et (**2**)

The identity of **1** was confirmed by X-ray crystallography (Figure 1). The Rh(1), P(1), P(2), H(1), and H(2) atoms are coplanar (±0.04 Å), and the Rh–Si bond forms an angle of 22.1° with this plane. The Rh–Si bond length of 2.354(2) Å is typical for Rh–Si single bonds,[13] and the Rh–P bond lengths are nearly identical (2.327(2) and 2.323(2) Å). The rhodium hydride ligands, H(1) and H(2), were located in the Fourier map. The Rh(1)–H(1) bond distance of 1.67(4) is longer than the Rh(1)–H(2) bond distance of 1.49(4). However, the Si–H bond lengths are essentially the same (1.84(4) and 1.88(4) Å). The geometry about Si(1) is approximately square pyramidal (ignoring the Rh atom), with a phenyl group in the apical position. This type of structure strongly resembles that of related σ-complexes such as $[RuH_2\{(\eta^2\text{-}HSiMe_2)_2C_6H_4\}(PCy_3)_2]$[14a] and $Cp(PiPr_2Me)Fe(H_2SiR_3)$,[14b] in which the silicon ligand is best described as a $[\eta^3\text{-}H_2SiR_3^-]$ hydrosilicate anion.

The analogous complex $(dtbpe)Rh(H)_2(SiBnEt_2)$ (**2**) was obtained similarly, by reaction of one equiv of Et_2SiH_2 with $(dtbpe)Rh(CH_2Ph)$ in pentane, followed by cooling to –35° C to give yellow crystals in 70% yield. The ^{1}H NMR spectrum of **2** is similar to that of **1**, and most

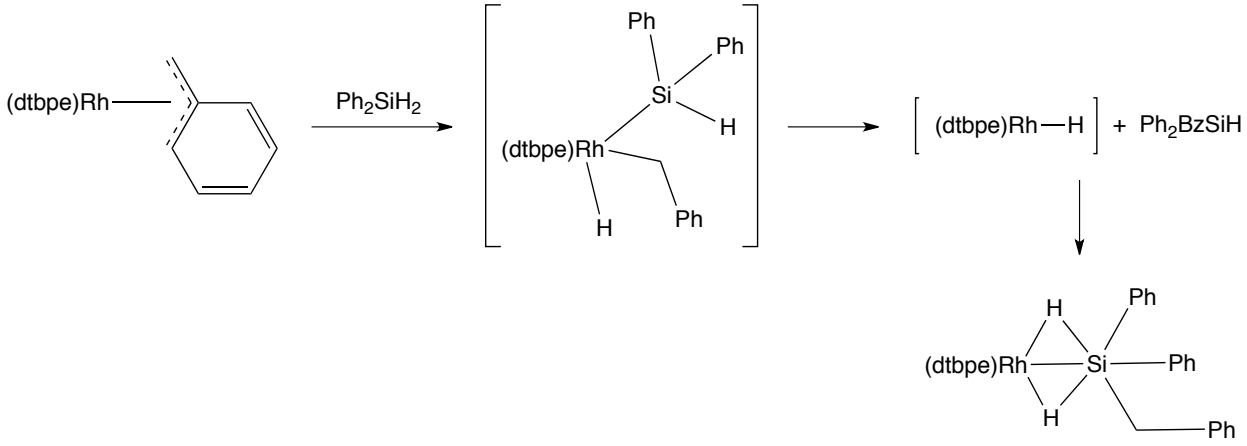
notably the hydride ligands appear as one multiplet (-5.63 ppm, J_{PH} = 19.1 Hz, J_{RhH} = 27.3 Hz) and retain a large coupling to Si with a J_{SiH} value of 52.1 Hz. The $^{31}P\{^{1}H\}$ NMR spectrum displays a doublet at 114.7 ppm (J_{PRh} = 136 Hz), and the silicon resonance appears at 0.8 ppm in the ^{29}Si NMR spectrum. Complex **2** is much more thermally sensitive than **1** and decomposes in solution over 2 h.

Figure 1. Molecular structure of **1** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1) – Si(1) = 2.3536(19); Rh(1) – P(1) = 2.327(2), Rh(1) – P(2) 2.323(2), Rh(1) – H(1) = 1.67(4), Rh(1) – H(2) = 1.49(4), Si(1) – H(1) =1.84(4), Si(1) – H(2) =1.88(4).

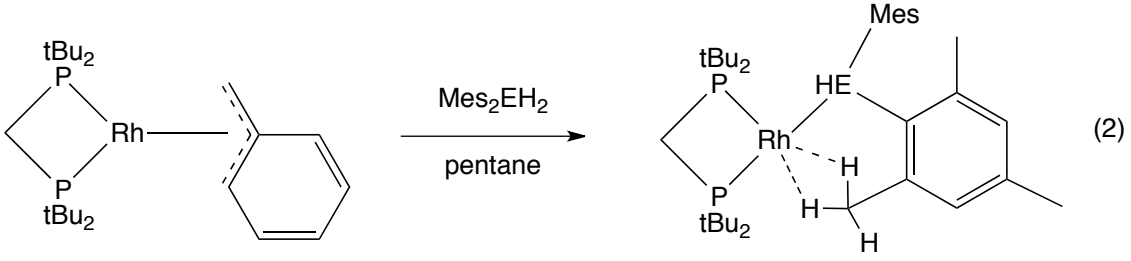


Complexes **1** and **2** may form *via* a series of oxidation addition and reductive elimination steps (Scheme 2). Initial oxidative addition of an Si–H bond to (dtbpe)Rh(CH_2Ph) may give (dtbpe)RhH(CH_2Ph)($SiHPh_2$), which would rapidly undergo Si–C bond reductive elimination to produce $Ph_2(CH_2Ph)SiH$ and a rhodium hydride species. Finally, $Ph_2(CH_2Ph)SiH$ would add to [(dtbpe)RhH] to give the final product. This mechanism is supported by several observations. A solution of (dtbpe)Rh(CH_2Ph) with 1 equiv of Ph_2SiH_2 in C_6D_6 was monitored over the course of the reaction and was found to contain $Ph_2(PhCH_2)SiH$, as compared to an independently synthesized sample. After 15 min, ca. 0.25 equiv of $Ph_2(PhCH_2)SiH$ was present, and this amount remained constant throughout most of the course of the reaction, until it is finally consumed in formation of the final product. Additionally, the reaction of (dtbpe)Rh(CH_2Ph) with 0.5 equiv of Ph_2SiH_2 and 0.5 equiv of Ph_2SiD_2 in C_6D_6 resulted in 3 isotopomers - (dtbpe)Rh$(H)_2(SiBnPh_2)$, (dtbpe)Rh$(D)_2(SiBnPh_2)$, and (dtbpe)Rh(H)(D)[$SiBnPh_2$)], as determined by ^{1}H and ^{2}H NMR spectroscopy. This H/D scrambling suggests a mechanism in which $Ph_2(CH_2Ph)Si(H/D)$ leaves the coordination sphere of a [(dtbpe)Rh(H/D)] species.

Scheme 2.



Reactions of (dtbpm)Rh(CH_2Ph) with Mes_2EH_2 (E = Si, Ge). Silane and germane activations by the related benzyl derivative (dtbpm)Rh(CH_2Ph)[10] were also examined. In screening the reactivity of (dtbpm)Rh(CH_2Ph) with a number of primary and secondary silanes, it was found that certain sterically hindered secondary silanes provided isolable reaction products. Thus, reaction of one equiv of Mes_2SiH_2 with (dtbpm)Rh(CH_2Ph) gave orange crystals of **3** from pentane, isolated in 81% yield (eq 2). The $^{31}P\{^1H\}$ NMR spectrum of **3** reveals two resonances, a doublet of doublets at 45.9 ppm ($^2J_{PP}$ = 17.9 Hz, $^1J_{PRh}$ = 226.6 Hz) and a doublet of doublets at 10.6 ppm ($^2J_{PP}$ = 17.9 Hz, $^1J_{PRh}$ = 89.7 Hz), indicating that each P atom of the dtbpm ligand is in a unique environment. The large difference in Rh-P couplings has previously been observed for (dtbpm)Rh complexes,[15] and decreased coupling is attributed to the presence of an additional ligand that displays a strong *trans*-influence.[16] The ^{29}Si NMR spectrum displays a single peak at -12.4 ppm, in the region expected for silyl ligands.[13] However, the ^1H NMR spectrum of **3** at room temperature is difficult to interpret, since it contains no observable Si–H resonance but two broad peaks at 2.56 and 2.24 ppm for the methyl groups of the mesityl substituents, which together integrate to only 15 H. In addition, a singlet at 6.81 ppm integrates for 4 H and arises from the aromatic protons of the mesityl substituents on Si.



(2)

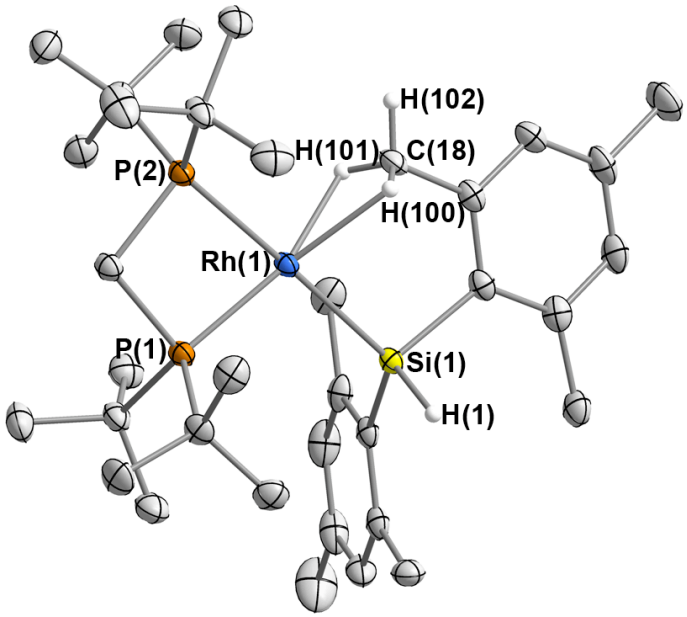
E = Si (**3**)
E = Ge (**4**)

The NMR spectrum of **3** in toluene-d_8 solution at -80 °C is more informative, as it contains four aromatic resonances (7.06–6.74 ppm) and a broad singlet at 6.21 ppm attributed to the Si–H group. Additionally, there are five singlets in the methyl region, four that integrate for

3 H each and one that integrates for 6 H. No Rh–H coupling is observed for these methyl resonances. The t-butyl groups of the dtbpm ligand have split into four sets of doublets, each integrating to 9 H. This NMR data indicates that complex **3** may be formulated as (dtbpm)Rh(SiHMes$_2$), possessing a geometry that renders the P atoms and the mesityl groups inequivalent.

Single crystals of **3** suitable for X-ray crystallography were grown by slow evaporation from a pentane solution at -35 °C (Figure 2). Surprisingly, the structure of **3** was found to involve agostic interactions, such that two C–H bonds of one mesityl methyl group interact with the Rh center. The coordination geometry about Rh is square planar, with C(18) constituting one corner of the square. The Rh–Si bond length of 2.3777(7) Å is typical for a Rh–Si single bond.[13] The Rh–P(1) bond length (2.2181(7) Å) is shorter than that of Rh–P(2) (2.3462(7) Å), due to the *trans* influence of Si. The hydrogen atoms H(1), H(100), H(101), and H(102) were located in the Fourier map, and the Rh–H(100) and Rh–H(101) bond distances are both 2.01(3) Å. The third C–H bond does not interact with Rh, and the Si–H bond is not in a position to interact with Rh. For comparison, the alkyl complexes (dtbpm)RhNp[17] and (dtbpe)NiNp[18] display very similar geometries but feature a single γ-CH agostic interaction. The Rh–C(18) distance of 2.377(3) Å is significantly shorter than that observed for (dtbpm)RhNp (2.491(4) Å), which is likely due to presence of an additional agostic interaction for **3**.

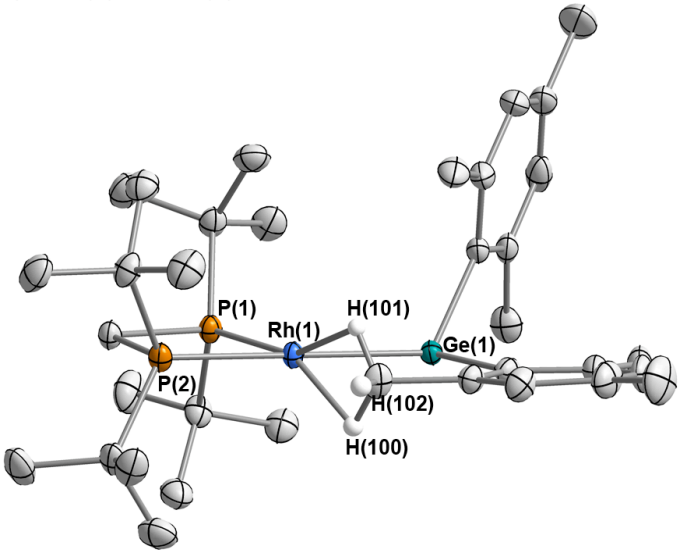
Figure 2. Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1) – Si(1) = 2.3777(7); Rh(1) – P(1) = 2.2181(7), Rh(1) – P(2) 2.3462(7), Rh(1) – H(100) = 2.01(3), Rh(1) – H(101) = 2.01(3), Si(1) – H(1) =1.38(3).



The analogous germyl complex **4** was prepared by reaction of (dtbpm)Rh(CH$_2$Ph) with Mes$_2$GeH$_2$, and dark red crystals were isolated in 71% yield from pentane (eq 2). Unlike **3**, the ^{1}H NMR spectrum of **4** displays all expected resonances at room temperature. A singlet at 6.89 ppm is assigned to the aromatic protons of the mesityl substituents, a doublet at 5.98 ppm (J_{RhH} = 14.0 Hz) arises from the Ge–H, and three singlets at 2.71, 2.32, and 2.25 ppm each integrate for

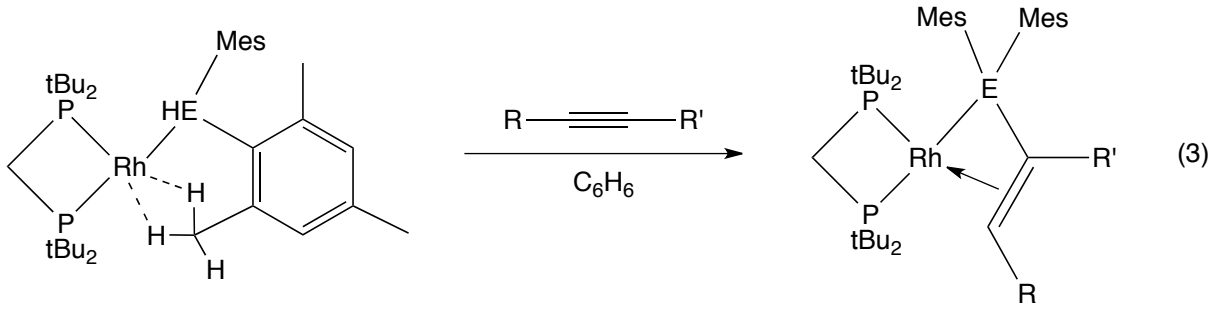
6 H, accounting for all methyl groups of the mesityl substituents. The peaks associated with the dtbpm ligand appear as a triplet at 2.97 (J_{PH} = 7.5 Hz) for the methylene protons and as two doublets at 1.21 (J_{PH} = 13.4 Hz) and 1.17 ppm (J_{PH} = 12.3 Hz). The methyl(mesityl) resonances for this complex are quite broad at room temperature, but at –80 °C in toluene-d_8 they are resolved into five sharp singlets, four that integrate as 3 H and one that integrates as 6 H. In addition, two singlets at 7.01 and 6.69 ppm for the aromatic mesityl protons are observed. The Ge–H resonance changes very little, remaining as a doublet at 5.94 ppm (J = 14.2 Hz). At room temperature, the $^{31}P\{^1H\}$ NMR spectrum reveals two doublets at 42.6 ($^2J_{PP}$ = 20.9 Hz, $^1J_{PRh}$ = 218.6 Hz) ppm and 9.6 ppm ($^2J_{PP}$ = 20.9 Hz, $^1J_{PRh}$ = 109.1 Hz). The structure of **4** obtained by X-ray crystallography differs very little from that of **3** (Figure 3).

Figure 3. Molecular structure of **4** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1) – Ge(1) = 2.4433(6); Rh(1) – P(1) = 2.2098(7), Rh(1) – P(2) 2.3079(8), Rh(1) – H(100) = 1.99(2), Rh(1) – H(101) = 2.05(2), Ge(1) – H(1) =1.41(2).



Reactions of (dtbpm)Rh(EHMes$_2$) with alkynes. Reactions with complexes **3** and **4** with alkynes were examined, given the literature precedent for alkyne hydrosilation by (dtbpm)Rh complexes.[10] A solution of one equiv of diphenylacetylene in C_6H_6 was added to **3** in C_6H_6 at room temperature to afford (dtbpm)Rh[Si(CPh=CHPh)Mes$_2$] (**5**) in high yield (eq 3). The identity of **5** was determined by multinuclear NMR spectroscopy. At room temperature, four peaks in the aromatic region are associated with two phenyl groups and two mesityl groups (one peak is comprised of overlapping resonances correlating to both a phenyl group and mesityl group). Five resonances attributed to methyl protons reflect the presence of inequivalent mesityl groups, and the t-butyl resonances for the dtbpm ligandare present as three broad singlets (18 H: 9 H: 9 H). A new singlet at 5.36 ppm is attributed to a vinylic C*H*Ph proton, determined by a 2D $^1H,^1H$ NOESY experiment to be in the *cis* position relative to the Si atom. No Si–H resonance appears in this spectrum, or in a spectrum of the sample cooled to -60 °C in toluene-d_8. However, at -60 °C the vinylic resonance at 5.36 ppm appears as a multiplet, likely due to coupling to Rh and P, indicating coordination of the vinyl group. Thus, complex **5** may be viewed as the product of net insertion of the alkyne into the Si–H bond. An absorption at 1550 cm^{-1} in the

infrared spectrum may reflect weak coordination of the vinyl group (cf. free cis-stilbene 1628 cm^{-1}).[19]



(3)

E = Si (**3**)
E = Ge (**4**)

E = Si, R = R' = Ph (**5**)
E = Ge, R = R' = Ph (**6**)
E = Si, R = Ph, R' = H (**7**)
E = Si, R = R' = Me (**8**)
E = Ge, R = R' = Me (**9**)

In an analogous manner, the reaction of diphenylacetylene with **4** gave (dtbpm)Rh[Ge(CPh=CHPh)Mes_2] (**6**) as a dark orange solid. The ^{1}H NMR spectrum at room temperature contains a new resonance at 5.62 ppm, corresponding to the C*H*Ph proton. A resonance associated with a Ge–H bond is not observed at room temperature or at -60 °C. The resonance at 5.62 ppm broadens significantly (FWHH = 34 Hz) upon cooling but does not display a clear splitting from coupling to Rh or P. The ^{31}P NMR spectrum displays two doublets of doublets at 31.4 ($^2J_{PP}$ = 8.2 Hz, $^1J_{PRh}$ = 136.7 Hz) and 7.8 ppm ($^2J_{PP}$ = 8.2 Hz, $^1J_{PRh}$ = 88.0 Hz). In general, the spectroscopic properties for complexes **5** and **6** are very similar.

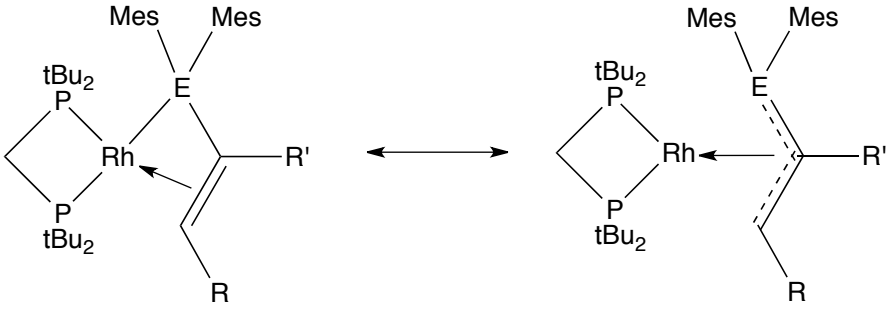
Complex **3** reacted with phenylacetylene under analogous conditions to yield (dtbpm)Rh[Si(CH=CHPh)Mes_2] (**7**) as a bright orange solid. The arrangement of substituents on the allyl group was determined by J_{HH} coupling constants. In the ^{1}H NMR spectrum, a doublet at 5.23 and a doublet of doublets at 4.16 ppm for the vinylic protons are associated with a relatively large J_{HH} coupling constant (J = 16.2 Hz) consistent with a *trans* arrangement.[20] The additional splitting of the resonance at 4.16 ppm (J_{RhH} = 6.7 Hz) arises from an interaction with Rh. This *trans* arrangement of vinylic protons indicates that Si-H addition to the alkyne has occurred in an anti-Markovnikov way. Like **5** and **6**, the phosphine ligand of **7** appears as two doublets of doublets at 37.4 ($^2J_{PP}$ = 15.9 Hz, $^1J_{PRh}$ = 187.5 Hz) and 6.8 ppm ($^2J_{PP}$ = 15.9 Hz, $^1J_{PRh}$ = 127.4 Hz) in the ^{31}P{^{1}H} NMR spectrum, and the silyl group is observed at 0.6 ppm by ^{29}Si NMR spectroscopy. The reaction of complex **4** with phenylacetylene resulted in an intractable mixture of products.

Reactions of complexes **3** and **4** with 2-butyne in benzene resulted in color changes from orange to dark red. However, attempts to isolate products from the reaction solutions resulted only in quantitative recovery of the starting materials, **3** and **4**. The products of these reactions were therefore characterized *in situ* by NMR spectroscopy as the E–H insertion products (dtbpm)Rh[Si(CMe=CHMe)Mes_2] (**8**) and (dtbpm)Rh[Si(CMe=CHMe)Mes_2] (**9**). Complex **8** displays new ^{1}H NMR resonances at 3.91 (C*H*Me), 2.14, and 2.12 ppm (inequivalent methyl groups on the silaallyl moiety) and all appear as broad singlets at room temperature. At -60 °C, the C*H*Me proton shifts to 3.47 ppm and appears as a multiplet due to H-H and Rh coupling. The dtbpm ligand appears as two doublets of doublets in the ^{31}P{^{1}H} NMR spectrum (30.2 ppm, $^2J_{PP}$ = 7.5 Hz, $^1J_{PRh}$ = 154.9 Hz; 13.95 ppm, $^2J_{PP}$ = 7.5 Hz, $^1J_{PRh}$ = 99.4 Hz), and the ^{29}Si NMR

spectrum contains a single peak at 5.2 ppm. The ^{1}H NMR spectrum for complex **9** exhibits a broad multiplet at 4.39 ppm for the C*H*Me proton, a multiplet at 2.15 ppm for one CH_3 group due to coupling to the terminal C*H* proton, P and Rh, and a singlet at 2.13 ppm for the other CH_3 group. The ^{31}P{^{1}H} NMR spectrum contains two doublets of doublets at 32.6 ($^{2}J_{PP}$ = 9.8 Hz, $^{1}J_{PRh}$ = 117.4 Hz) and 13.7 ppm ($^{2}J_{PP}$ = 9.8 Hz, $^{1}J_{PRh}$ = 92.9 Hz). When complexes **8** and **9** are exposed to vacuum in the solid state, **3** and **4** are regenerated and 2-butyne is removed (by ^{1}H NMR spectroscopy).

Silaallyl complexes are quite rare,[21] and **5**, **7**, and **8** appear to represent the first family of such complexes with rhodium. The terminal vinyl proton of these complexes display coupling to Rh, which provides evidence for coordination of the allyl group. This type of complex has been targeted for a number of years due to the similarity to the well-known η^3-allyl complexes (Scheme 3).[22] Synthesis of silaallyl species has typically relied on reaction of a suitable metal precursor with a vinyl silane, such as (dimethylvinyl)dimethylsilane. Thus, the formation of silaallyl complexes from the addition of alkynes to a metal silyl species is unprecedented. Additionally, complexes **6** and **9** represent the first reported germaallyl complexes. Unfortunately, further structural data could not be obtained because all efforts to grow X-ray quality crystals of **5** – **9** were unsuccessful.

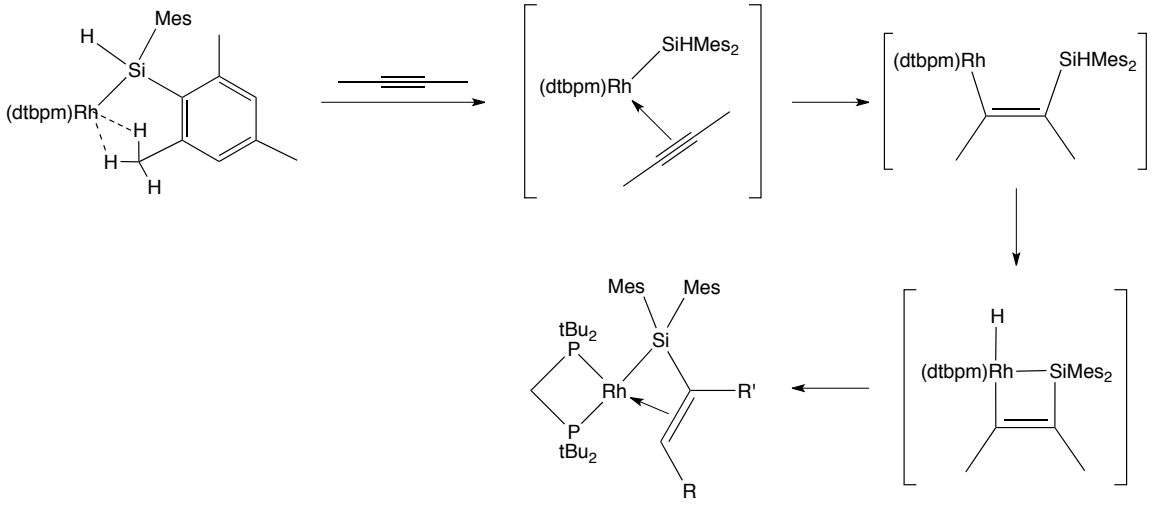
Scheme 3.



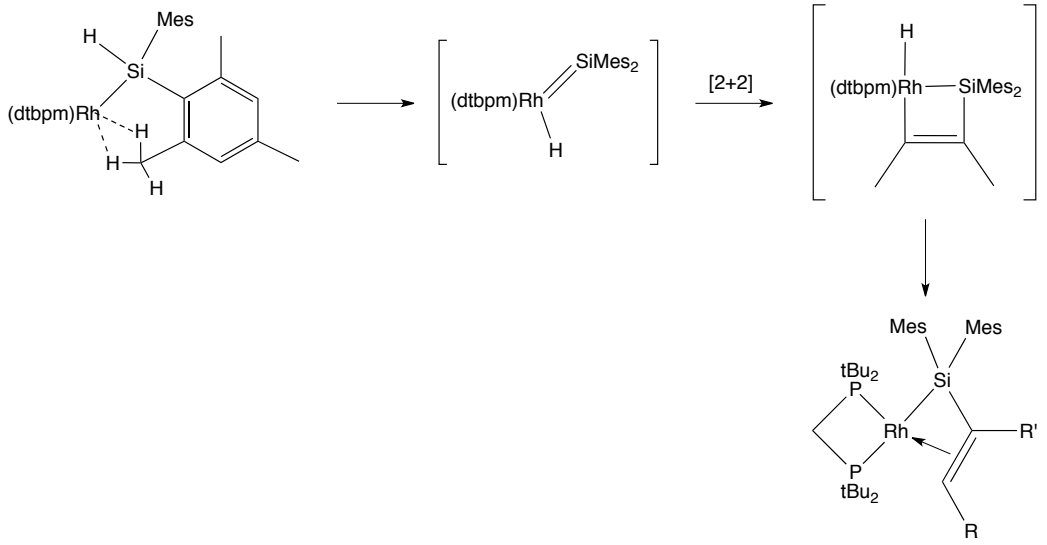
Two possible routes to complexes **5** – **9** are outlined in Scheme 4. In route A, complex **3** first binds the alkyne, and then the coordinated alkyne inserts into the Rh–Si bond. The Si–H bond could then add to the rhodium center to produce a metallocycle, and reductive elimination of the C–H bond would generate the observed product. Alternatively, as indicated by route B, α-hydrogen migration to a Rh silylene complex could be followed by a [2+2] cycloaddition with the alkyne to form the same metallocycle proposed in route A. Again, reductive elimination would give the silaallyl complex. Interestingly, the process by which these reactions occur must be reversible (at least in the case of 2-butyne).

Scheme 4.

Route A

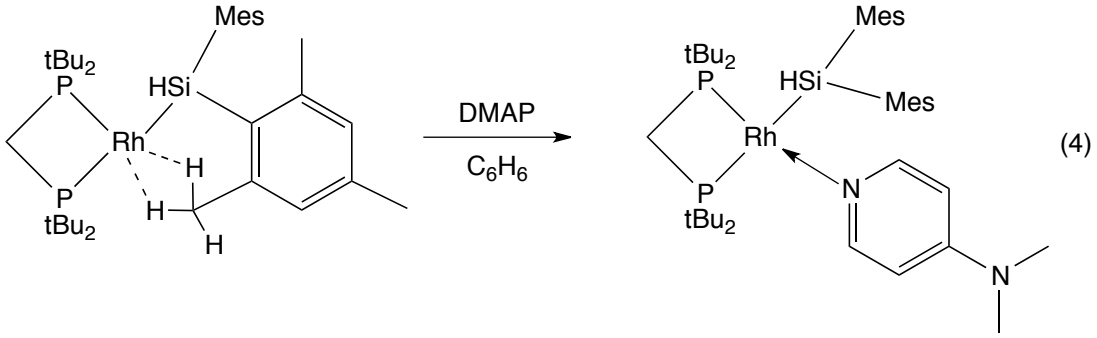


Route B



To probe which of these possible reaction pathways might be operative, the reaction between complex **3** and the Lewis base DMAP (*para*-dimethylaminopyridine) was examined. This Lewis base has been observed to interact with a number of silylene complexes *via* coordination to silicon,[23] and it was hypothesized that DMAP may act as a trap for a transient silylene complex. A solution of DMAP in pentane was added to a solution of **3** in C_6H_6 and the reaction mixture was cooled to -35 ºC to afford (dtbpm)Rh(SiHMes$_2$)(DMAP) (**10**) as yellow crystals (eq 4). The ^{1}H NMR spectrum at room temperature contains resonances for DMAP and the dtbpm ligand but none for the silyl group. However, upon cooling to -60 °C, peaks corresponding to two mesityl groups and an Si–H group (6.06 ppm) appear. No hydride ligands are observed. The dtbpm ligand displays two doublets of doublets in the ^{31}P{^{1}H} NMR

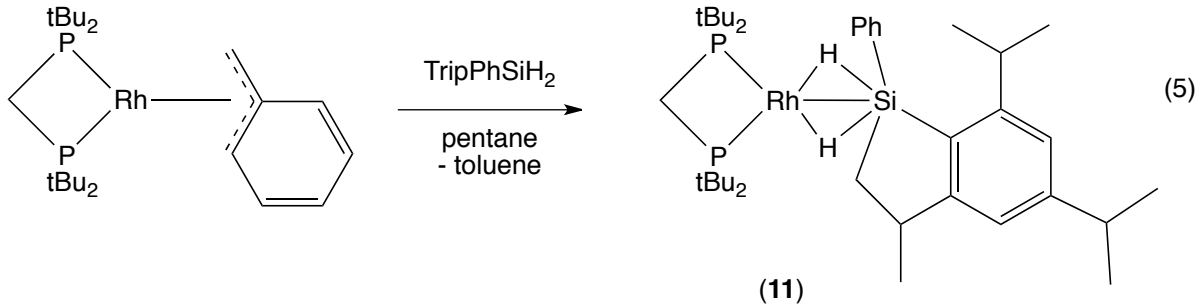
spectrum at 39.14 ($^2J_{PP}$ = 9.0, J_{PRh} = 169.5 Hz) and 3.63 ppm ($^2J_{PP}$ = 8.9, J_{PRh} = 97.8 Hz). The ^{29}Si NMR resonance at -33.8 ppm confirms the presence of a silyl group.[13] Given this result, the precedence for alkyne insertions into metal-silicon bonds,[24] and the lack of a precedent for 2+2 cycloadditions involving alkynes and silylene complexes,[12a,25] we currently favor the mechanism of route A.



(4)

(**3**) (**10**)

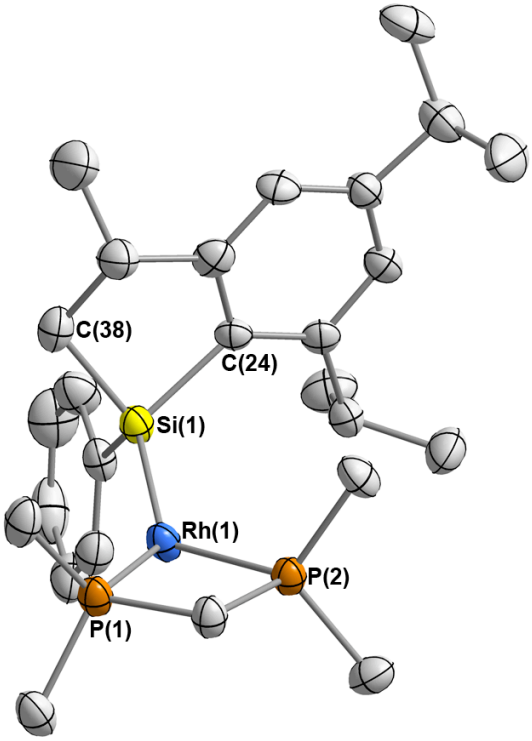
Reaction of (dtbpm)Rh(CH$_2$Ph) with TripPhSiH$_2$. The benzyl complex (dtbpm)Rh(CH$_2$Ph) was also found to undergo a clean reaction with TripPhSiH$_2$ (Trip = 2,4,6-triisopropylphenyl). A pentane solution of one equiv of TripPhSiH$_2$ was added to a pentane solution of (dtbpm)Rh(CH$_2$Ph), and cooling the reaction solution to -35 ºC afforded (dtbpm)Rh(H)$_2$[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindenyl-κSi] (**11**) as orange crystals in 65% isolated yield (eq 5). Because complex **11** is not stable at room temperature in solution, multinuclear NMR experiments were performed on solutions of **11** cooled to 0 °C in toluene-d_8. The ^{1}H NMR spectrum displays typical resonances for the dtbpm ligand, a triplet at 3.14 ppm (J_{PH} = 6.9 Hz) for the methylene protons and two doublets at 1.23 (J_{PH} = 12.6 Hz) and 1.10 ppm (J_{PH} = 12.8 Hz) for the inequivalent t-butyl groups. Three peaks in the aromatic region correspond to the phenyl substituent on Si and one peak corresponds to the aryl protons of the Trip group. Only five CH$_3$ groups from the Trip substituent are apparent, indicating C–H activation at one of the methyl groups. Two resonances at 1.99 and 1.61 ppm correlate to diastereotopic protons for the new methylene group. No Si–H group is observed, and two hydrides are present at -7.04 ppm as a complex multiplet, which displays a strong coupling to Si (J_{SiH} = 51.8 Hz). The multiplet arises from the presence of inequivalent hydrides (due to the chiral silicon center) and coupling to the Rh and inequivalent P atoms. Unlike complexes **3**–**10**, the ^{31}P{^{1}H} NMR spectrum displays only one doublet at 19.8 (J_{PRh} = 113.9 Hz). Additionally, the ^{29}Si NMR resonance of 0.89 is typical for a silyl ligand. Taken together, the NMR data indicate that activation of one Trip methyl group has occurred to create a new Si–C bond. The two new rhodium hydride ligands originate from the activation of Si–H and C–H bonds. Like complexes **1** and **2**, **11** appears to best be represented as a (dtbpm)Rh(I) complex with an [η^3-H$_2$SiR$_3^-$] ligand (eq 5). Interestingly, the decomposition of **11** in C$_6$D over 24 h at room temperature gives an unidentified Rh complex and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole.



(**11**)

Single crystal X-ray diffraction confirms the identity of **11** (Figure 4). The Rh–Si distance of 2.3163(15) Å is quite a bit shorter than that observed for **3**, and the Rh–P bond lengths are very similar (2.3249(13) and 2.3381(16) Å). Unlike complexes **3** and **4**, the dtbpm phosphorous atoms and Si are not co-planar. The Si–C bonds of the 5-membered ring are nearly identical, with Si(1)–C(24) at 1.901(5) Å and Si(1)–C(38) at 1.906(5) Å. Although the rhodium hydride ligands were not located, the strong coupling to Si observed by NMR spectroscopy indicates that the hydrides likely occupy positions similar to those located for complex **1**. The coordination geometry of **11** is therefore similar to that of **1**.

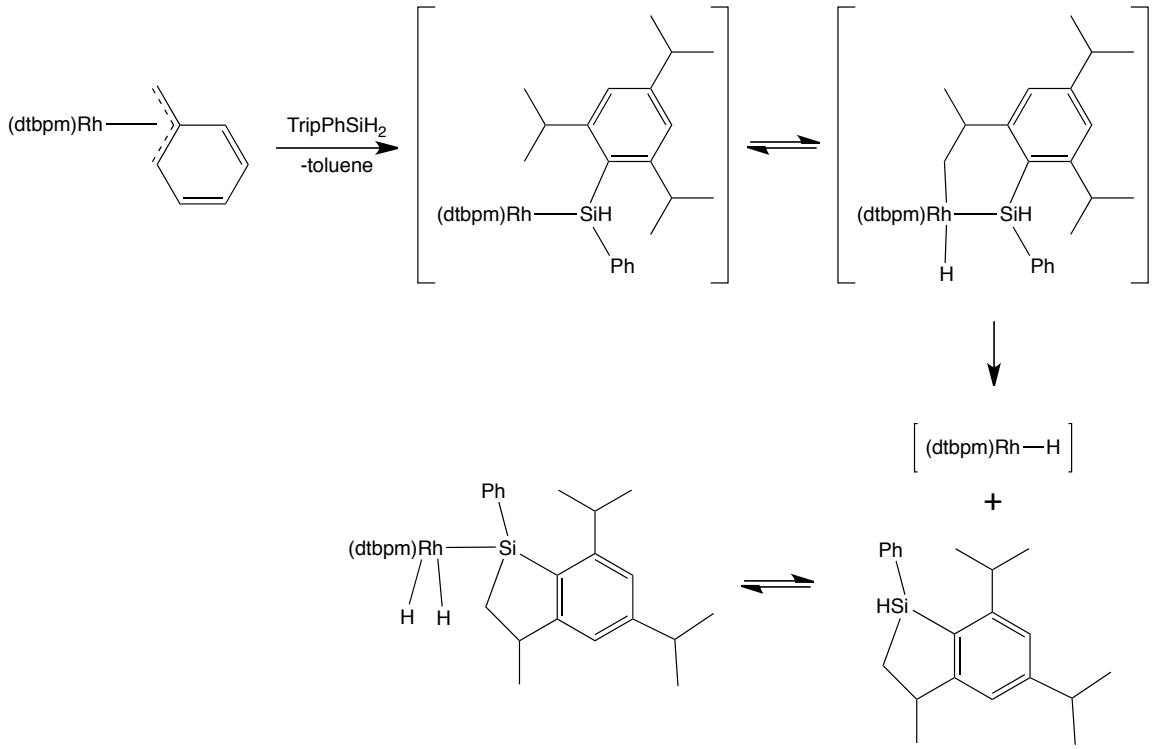
Figure 4. Molecular structure of **11** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Rh(1) – Si(1) = 2.3163(15); Rh(1) – P(1) = 2.3249(13), Rh(1) – P(2) 2.3381(16), Si(1) – C(24) = 1.901(5), Si(1) – C(38) = 1.906(5).



The proposed formation of **11** is outlined in Scheme 5. Oxidative addition of $TripPhSiH_2$ followed by reductive elimination of toluene can result in a (dtbpm)Rh(SiHTripPh) complex, which can then undergo C–H activation of a methyl group to give a cyclometallated species. Reductive elimination from this species would result in a (dtbpm)RhH species and 5,7-

diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. Finally, 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole would add *via* Si–H oxidative addition to give **11**. The related complex (dippe)Rh(CH_2Ph) (dippe = bis(diisopropylphosphino)ethane) undergoes a similar reaction with [2,4,6-tri(tert-butyl)phenyl]phosphine to afford (dippe)Rh(H)[5,7-Di(tert-butyl)-2,3-dihydro-3,3-dimethyl-1H-phosphindole-κP].[6b]

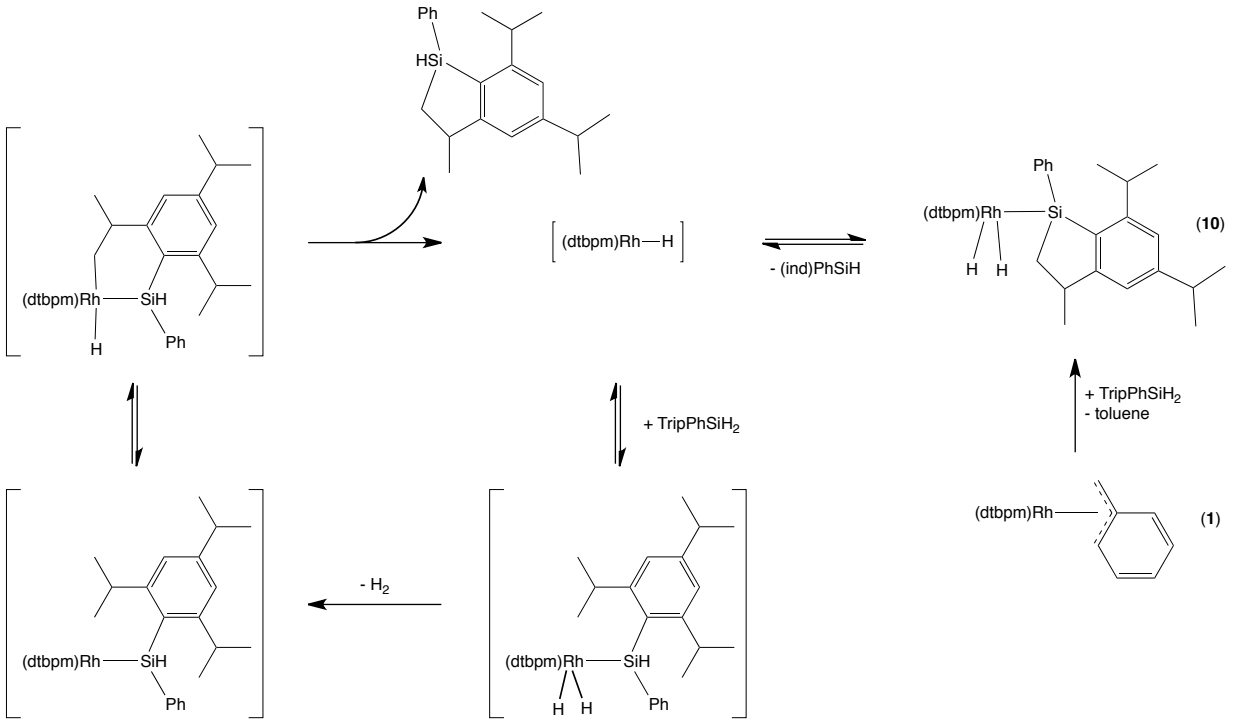
Scheme 5.



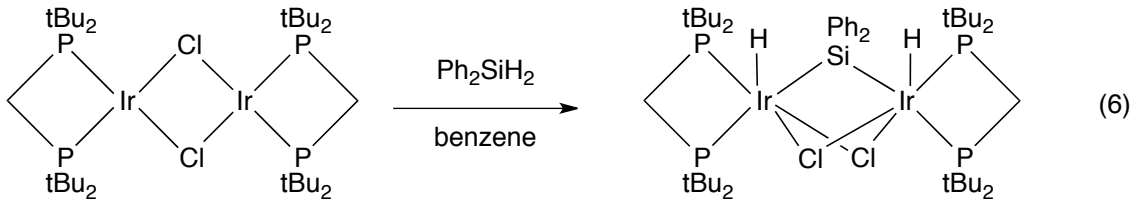
The observation of 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole in 15% yield from the decomposition of **11** led to investigations on the catalytic production of this species. A solution of $TripPhSiH_2$ in benzene-d_6 with a 10% loading of (dtbpm)Rh(CH_2Ph) was monitored at room temperature. Over 48 h, a yield of 90% of 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole was observed, along with the concurrent release of hydrogen (by ^1H NMR spectroscopy). Longer reaction times did not increase the product yield. Complex **11** also acts as a competent catalyst for this transformation. After 20 h at room temperature with 10% of **11**, 49% conversion was observed. For comparison, after 20 h with (dtbpm)Rh(CH_2Ph), 55% conversion was observed. This result suggests that (dtbpm)Rh(CH_2Ph) and **11** function as pre-catalysts to the same active species. However, further catalytic studies were hindered by decomposition of the rhodium complexes in this system. A proposed mechanism is outlined in Scheme 6. When (dtbpm)Rh(CH_2Ph) is used as the pre-catalyst, the reaction of (dtbpm)Rh(CH_2Ph) and $TripPhSiH_2$ can give **11** and enter into the catalytic cycle by reductive elimination to form [(dtbpm)RhH] and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. Similarly, **11** would function as a precatalyst by reductive elimination to form [(dtbpm)RhH] and 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. The [(dtbpm)RhH] species could then oxidatively add $TripPhSiH_2$ to give a (dtbpm)Rh(H)$_2$(SiHTripPh) complex, which could then lose an equiv of H_2 via reductive elimination. The

resulting (dtbpm)Rh(SiHTripPh) could then activate a methyl C–H bond to form a cyclometallated species. Reductive elimination of the Si and C groups would release 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole and reform [(dtbpm)RhH].

Scheme 6.



Reactions of [(dtbpm)IrCl]$_2$ with silanes. Silane activations related to those above were investigated for the (dtbpm)Ir fragment, using [(dtbpm)IrCl]$_2$[26] as a starting material. The complex [(dtbpm)IrCl]$_2$ reacted with two equiv of H_2SiPh_2 in benzene at room temperature over 40 min to give the bridging silylene complex [(dtbpm)IrH](μ-$SiPh_2$)(μ-Cl)$_2$[(dtbpm)IrH] (**12**) as a yellow-orange solid in 89% yield (eq 6). The identity of **12** was determined by X-ray crystallography (Figure 5), with single crystals grown from a toluene solution at -35 °C. The Ir–Si bond distances of 2.425(2) and 2.427(2) Å are quite long compared to most Ir–Si single bonds.[13] The hydride ligands were not located in the Fourier map. Neglecting the hydride ligands, the coordination environment for Ir(1) can be described as an approximate square pyramid, with P(3), P(4), Si(1), and Cl(1) forming the square plane. The empty coordination site *trans* to Cl(2) is presumed to contain a hydride ligand (see below). In a similar manner, Ir(2) adopts an octahedral geometry with P(1), P(2), Si(1), and Cl(2) defining a coordination plane, and the coordination site *trans* to Cl(1) being occupied by a hydride ligand. The strong *trans* influence of Si is manifested in different Ir–P bond lengths; the Ir(1)–P(4) bond length is 2.233(2) Å while the Ir(1)–P(3) bond length is significantly longer at 2.406(2) Å. The same trend is observed for the Ir(2)–P(1) (2.237(2) Å) and Ir(2)–P(2) (2.412(2) Å) bonds.

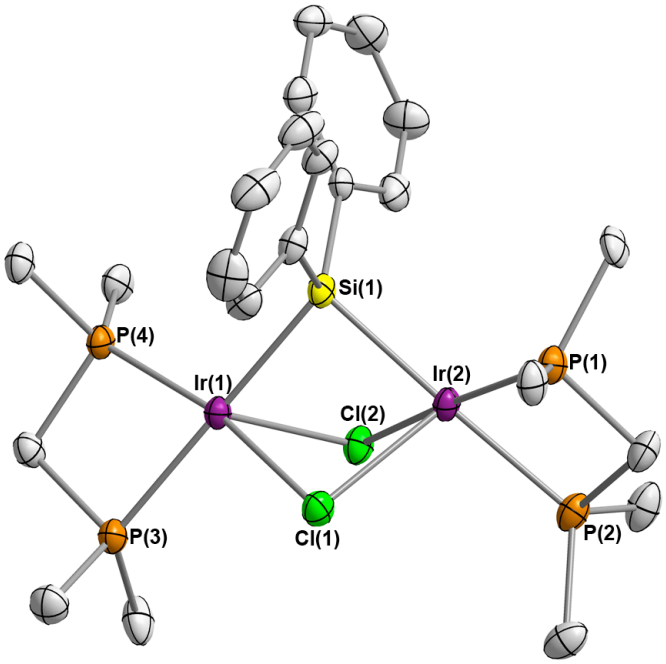


(6)

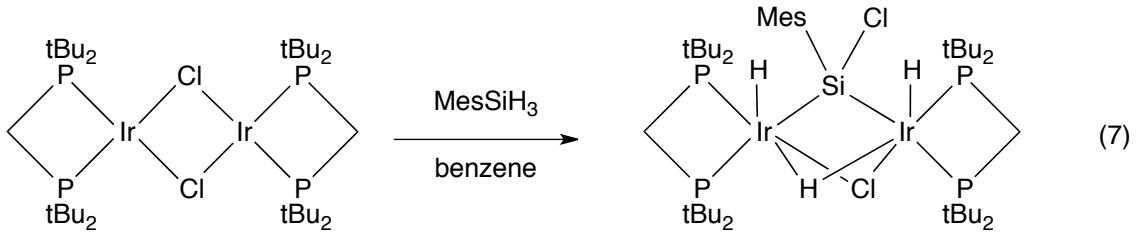
(**12**)

The NMR spectroscopic data for **12** are consistent with the observed X-ray structure. By ^{1}H NMR spectroscopy, two sets of tBu resonances are observed, as well as resonances associated with equivalent phenyl groups. Two equivalent hydride ligands give rise to a doublet at -23.3, due to splitting by ^{31}P (J_{PH} = 24.8 Hz). Coupling to the second ^{31}P nucleus is likely too small to be observed, which is supported by an analogous small coupling in **14** (*vida infra*). As discussed above, the terminal Ir–H ligands are in coordination sites *trans* to a Cl atom, and the small coupling to ^{31}P supports a *cis* arrangement of the phosphine and hydride ligands. The ^{31}P{^{1}H} spectrum displays two doublets at 8.9 and -3.7 ppm (J_{PP} = 6.1 Hz). Additionally, a single resonance at -34.4 ppm in the ^{29}Si NMR spectrum is in a region consistent with a bridging silylene complex of iridium.[13,27] Additionally, two terminal hydride stretches are observed by infrared spectroscopy (2328, 2288 cm^{-1}). Overall, complex **12** can be considered to be the product of two Si–H oxidative additions across the two Ir centers of [(dtbpm)IrCl]$_2$.

Figure 5. Molecular structure of **12** displaying thermal ellipsoids at the 50% probability level. H-atoms and t-butyl groups have been omitted for clarity. Selected bond lengths (Å): Ir(1) – Si(1) = 2.427(2), Ir(1) – P(3) = 2.406(2), Ir(1) – P(4) = 2.233(2), Ir(1) – Cl(1) = 2.503(2), Ir(1) – Cl(2) = 2.551(2), Ir(2) – Si(1) = 2.425(2), Ir(2) – P(1) = 2.237(2), Ir(2) – P(2) = 2.412(2), Ir(2) – Cl(1) = 2.555(2), Ir(2) – Cl(2) = 2.502(2).



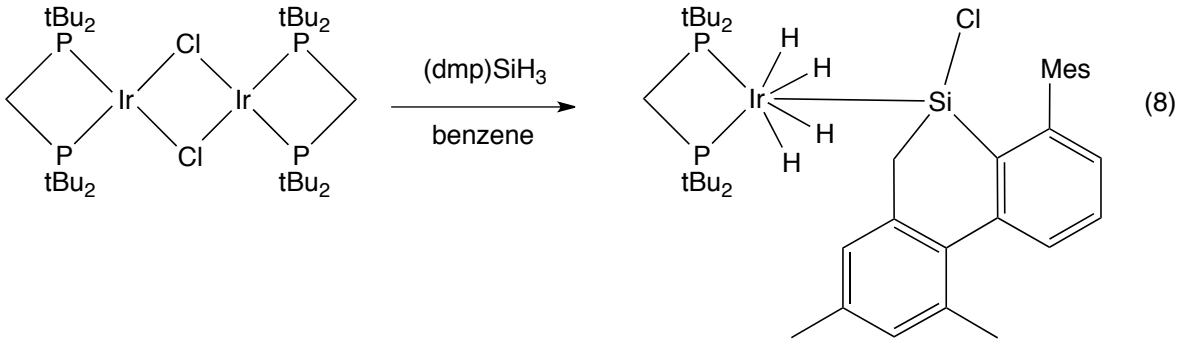
Under analogous conditions, $[(dtbpm)IrCl]_2$ undergoes clean conversion to a new product with two equiv of $MesSiH_3$ (eq 7). The yellow-orange solid, isolated in 90% yield, was characterized as [(dtbpm)IrH](μ-SiMesCl)(μ-Cl)(μ-H)[(dtbpm)IrH] (**13**) via multi-nuclear NMR experiments. The ^1H NMR spectrum of complex **13** contains resonances corresponding to one mesityl group and two dtbpm ligands. There is no resonance ca. 5 ppm, indicating that the Si–H bond is not present in the molecule. A triplet of triplets at -12.59 ppm (J_{PH} = 5.3, 63.3 Hz) arises from a bridging hydride ligand due to coupling to each dtbpm ligand, and a doublet of doublets integrating to 2H at -24.66 ppm (J_{PH} = 2.4, 18.0 Hz) results from the two terminal Ir–H ligands. No J_{SiH} was observed for these hydride ligands. The presence of terminal hydrides is further supported by infrared spectroscopy (2391, 2327 cm^{-1}). Contrary to the common trend, by ^1H NMR spectroscopy the terminal hydride ligands appear far upfield from the bridging hydride ligand,[28] but this is consistent with the hydride ligands observed for **12**. The $^{31}P\{^1H\}$ NMR spectrum contains doublets at 18.50 and 3.28 ppm (J_{PP} = 14.5 Hz). By ^{29}Si NMR spectroscopy, a pseudo-triplet at 75.0 ppm (J_{SiP} ~ 150 Hz) is observed for the bridging silylene ligand. Based on previous reports, this resonance is much further downfield than one would expect for a bridging SiMesCl moiety.[13,27] However, the connectivity of **13** was confirmed by a low quality X-ray structure.



(7)

(**13**)

In an effort to synthesize a mononuclear (dtbpm)Ir silyl complex, an extremely bulky primary silane was utilized. The reaction of $[(dtbpm)IrCl]_2$ with two equiv of $H_3Si(dmp)$ (dmp = 2,6-dimesitylphenyl) in benzene at 55 °C for 18 h afforded $(dtbpm)Ir(H)_4$(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydrosilaphenanthrene-κSi) (**14**) as a yellow solid in moderate (72%) isolated yield (eq 8).



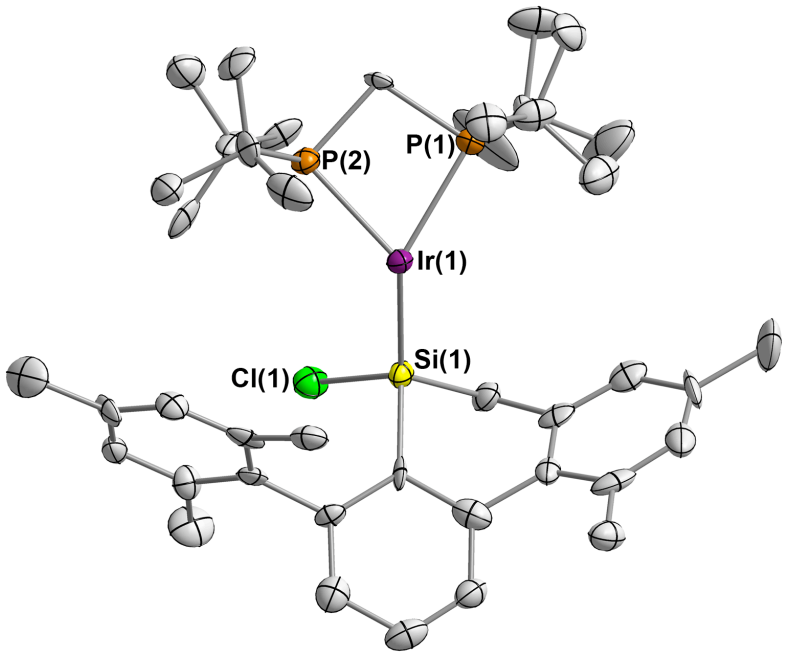
(8)

(**14**)

The identity of **14** was determined by a combination of X-ray crystallography (Figure 6) and multinuclear NMR spectroscopy. Single crystals of **14** were grown from a concentrated toluene solution at -35 °C. The Ir–Si bond length of 2.323(4) Å is in the region expected for Ir silyl

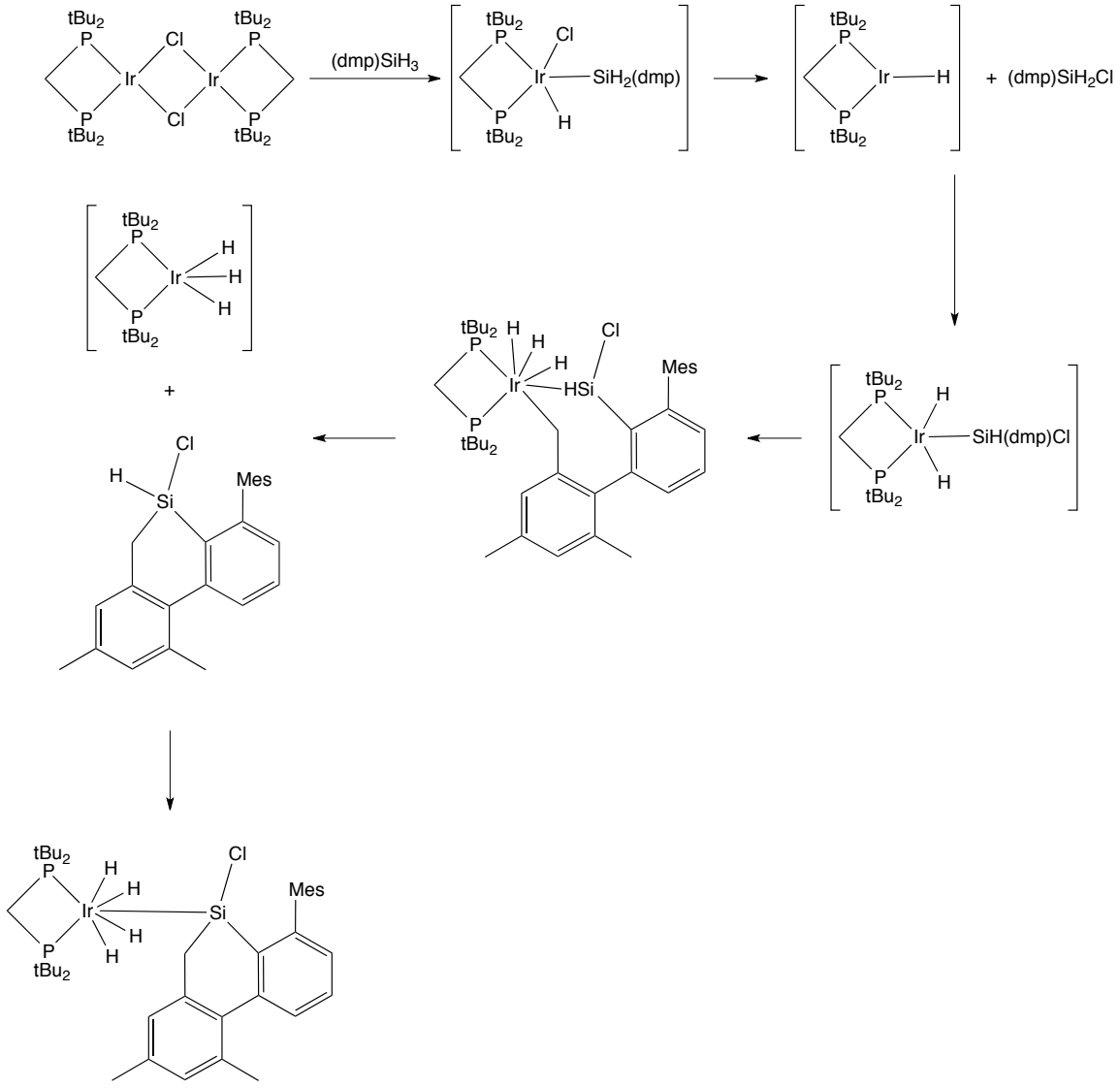
species, and unlike **12**, the Ir–P bond lengths are very similar (2.378(4) and 2.365(4) Å). The Si–Cl bond length (2.142(6) Å) is normal, and the Si–C bond lengths are very similar (1.890(15) and 1.868(14) Å). The hydride ligands were not located.

Figure 6. Molecular structure of **14** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Ir(1) – Si(1) = 2.323(4), Ir(1) – P(1) = 2.378(4), Ir(1) – P(2) = 2.365(4), Si(1) – Cl(1) = 2.142(6), Si(1) – C(1) = 1.890(15), Si(1) – C(15) = 1.868(14).



The ^{1}H NMR spectrum at room temperature displays 5 distinct methyl groups, correlating to the CH_3 groups of the dmp ligand. Additionally, two new CH_2 resonances are present at 3.64 and 2.64 ppm, each integrating to 1 H. Four equivalent hydride ligands appear as a triplet at -11.58 (J_{PH} = 18.0 Hz). The ^{29}Si NMR spectrum displays a resonance at -1.96 ppm that is typical for metal silyl complexes. Thus, complex **14** results from three Si–H bond activations, migration of Cl to the Si atom, and a C–H bond activation of the dmp group. As observed for **11**, a Si – C bond is formed to create a six-membered silacycle, rather than a metallocycle. Unlike **11**, complex **14** is stable at elevated temperatures and does not release a tertiary silane product upon heating to 80 °C for 18 h. As proposed for the syntheses of **1** – **2**, **5** – **9**, and **11**, the formation of **14**, shown in Scheme 7, could proceed through a series of oxidative addition and reductive elimination steps. A similar complex was reported from the reaction of $(Et_2PhP)_3IrCl$ with $(dmp)SiH_3$ and was suggested to form via an Ir silylene complex.[29] While both of these postulated mechanisms are reasonable, the reaction mixture must be heated to achieve the synthesis of **14**, which is not consistent with conditions typically observed for reactive silylene intermediates.

Scheme 7.



Conclusion

The complexes (dtbpe)Rh(CH_2Ph), (dtbpm)Rh(CH_2Ph), and [(dtbpm)IrCl]$_2$ have been shown to undergo reactions with various organosilanes, and several themes can be deduced from studying the reactivity patterns of these bis(phosphine)-supported group 10 metal complexes. Most notable is the prevalence of Si–C bond formation in these systems. The complex (dtbpe)Rh(CH_2Ph) undergoes reactions with secondary silanes in which the benzyl group is transferred to the silicon atom to give the tertiary silyl complexes **1** and **2**. Benzyl reagents often lose the benzyl group as toluene (e.g., in the reaction of (dtbpm)Rh(CH_2Ph) with Mes_2SiH_2). The sila- and germaallyl complexes **5** – **9** result from the net insertion of an alkyne into an E – H bond. Interestingly, this Si–C bond formation appears to be reversible based on the conversion of **8** and **9** back to **3** and **4**, respectively, under an applied vacuum. Complex **11** is produced from a C–H bond activation and subsequent Si–C bond formation to give a silacycle, and both (dtbpm)Rh(CH_2Ph) and **11** have been demonstrated to catalyze Si–C bond formation in the

transformation of $TripPhSiH_2$ to 5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindole. Like **11**, the iridium complex **14** also contains a silacycle produced by an intramolecular Si – C bond formation.

Another common theme encountered in this study of rhodium and iridium complexes supported by chelating, bulky diphosphines is the apparent participation of reactive [(P_2)M-H] species as key intermediates in many of the observed transformations. In the proposed mechanisms for the formations of **1, 2**, and **11**, the Si–C bond-forming step appears to produce a [(P_2)Rh-H] species, which can then undergo further reaction with the released silane. Similarly, the Si–C bond-forming step in the synthesis of **14** appear to generate a [(dtbpm)IrH_3] species. Several [(P_2)M-H] complexes with group 10 metals have been isolated as dinuclear complexes, such as $[(dippe)RhH]_2$[9] and $[(dippe)NiH]_2$,[30] and these complexes are active catalysts for deuterium exchange or dehydrocoupling of silanes. Currents efforts to synthesize $[(dtbpm)RhH]_2$ and $[(dtbpm)IrH]_2$ and explore their catalytic reactivity is underway.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and then $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene and toluene were then dried over $CaCl_2$ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. The complexes (dtbpe)Rh(CH_2Ph),[10] (dtbpm)Rh(CH_2Ph),[11] and $[(dtbpm)IrCl]_2$[27] were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H unless otherwise noted. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{19}F\{^1H\}$ spectra were referenced relative to a C_6F_6 external standard. $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^1H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^1H ^{29}Si HMBC unless specified otherwise. The following abbreviations have been used to describe peak multiplicities in the reported NMR spectroscopic data: "m" for complex multiplet, and "br" for broadened resonances. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

(dtbpe)Rh(H)$_2$(SiBnPh$_2$) (1). To a 2 mL pentane solution of (dtbpe)Rh(CH_2Ph) (0.030 g, 0.058 mmol) was added a 1 mL pentane solution of Ph_2SiH_2 (0.011 g, 0.060 mmol). The reaction mixture was allowed to stand for 24 h at room temperature, after which the resulting orange-red solution was cooled to –35° C. After 3 d, orange crystals were collected by filtration in 69% yield (0.028 g). ^1H NMR (C_6D_6, 500 MHz): δ 7.93 (4H, d, J = 7.0 Hz, Ar*H*), 7.29 (4H,

t, J = 7.5 Hz, Ar*H*), 7.20 (4H, t, J = 7.5 Hz, Ar*H*), 7.08 (2H, t, J = 7.5 Hz, Ar*H*), 6.98 (1H, t, J = 7.0 Hz, Ar*H*), 3.28 (2H, s, CH_2Ar), 1.37 (4H, d, J = 12.0 Hz, PCH_2CH_2P), 1.00 (36H, m, PC(CH_3)$_3$), -5.35 (2H, m, J_{PH} = 19.6 Hz, J_{RhH} = 33.8 Hz, J_{SiH} = 44.4 Hz, Rh*H)*. ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 147.9 (Ar*C*), 143.4 (Ar*C*), 136.1 (Ar*C*), 130.4 (Ar*C*), 127.3 (Ar*C*), 123.8 (Ar*C*), 37.4 (*C*H$_2$), 35.2 (P*C*(CH$_3$)$_3$), 35.0 (P(*C*H$_2$)$_2$P), 30.5 (PC(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 111.3 (d, $^1J_{RhP}$ = 114 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ -5.6. Anal. Calcd for $C_{37}H_{59}P_2RhSi$: C, 63.78; H, 8.53. Found: C, 63.39; H, 8.70.

(dtbpe)Rh(H)$_2$(SiBnEt$_2$) (2). To a 2 mL pentane solution of (dtbpe)Rh(CH$_2$Ph) (0.050 g, 0.098 mmol) was added a 1 mL pentane solution of Et$_2$SiH$_2$ (0.009 g, 0.10 mmol). The reaction mixture was cooled to –35° C. After 3 d, yellow crystals were collected in 70% yield (0.041 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.36 (2H, d, J = 7.6 Hz, Ar*H*), 7.22 (2H, t, J = 7.6 Hz, Ar*H*), 7.04 (1H, t, J = 7.6 Hz, Ar*H*), 2.81 (2H, s, CH_2), 1.40 (10H, m, CH_2CH_3), 1.11 (36H, d, J = 12.2 Hz, PC(CH_3)$_3$), 0.88 (4H, t, J = 7.0 Hz, PCH_2CH_2P), -5.63 (2H, m, J_{PH} = 19.1 Hz, J_{RhH} = 27.3 Hz, J_{SiH} = 52.1 Hz, Rh*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 144.3 (Ar*C*), 141.6 (Ar*C*), 139.9 (Ar*C*), 132.5 (Ar*C*), 125.8 (Ar*C*), 123.1 (Ar*C*), 37.8 (*C*H$_2$), 34.6 (P(*C*H$_2$)$_2$P), 31.5 (P*C*(CH$_3$)$_3$), 30.3 (PC(*C*H$_3$)$_3$), 7.83 (*C*H$_2$CH$_3$), 2.39 (CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 114.7 (d, $^1J_{RhP}$ = 136 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 0.8 ppm. Anal. Calcd for $C_{29}H_{59}P_2RhSi$: C, 57.98; H, 9.90. Found: C, 57.70; H, 10.36.

(dtbpm)Rh(SiHMes$_2$) (3). A solution of Mes$_2$SiH$_2$ (0.040 g, 0.15 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh(CH$_2$Ph) (0.075 g, 0.15 mmol) in 2 mL of pentane. After 1 h, the solution was concentrated (to ca. 2 mL) and cooled to -35 ºC to afford orange crystals in 81% yield (0.081 g). ^{1}H NMR (20 °C, toluene-d_8, 500 MHz): δ 6.81 (4H, s, Ar*H*), 3.01 (2H, t, J = 7.5 Hz, PCH_2P), 2.56 (9H, br s, ArCH_3), 2.24 (6H, s, ArCH_3), 1.21 (36H, d, J = 15.0 Hz, PC(CH_3)$_3$). ^{1}H NMR (-80 °C, toluene-d_8, 500 MHz): δ 7.06 (1H, s, Ar*H*), 6.96 (1H, s, Ar*H*), 6.76 (1H, s, Ar*H*), 6.74 (1H, s, Ar*H*), 6.81 (1H, br s, Si*H*), 3.15 (3H, s, ArCH_3), 2.77 (5H, s, ArCH_3 + PCH_2P), 2.60 (3H, s, ArCH_3), 2.34 (3H, s, ArCH_3), 2.30 (3H, s, ArCH_3), 1.44 (9H, d, J = 12.5 Hz, PC(CH_3)$_3$), 1.18 (9H, d, J = 11.5 Hz, PC(CH_3)$_3$), 1.05 (9H, d, J = 11.5 Hz, PC(CH_3)$_3$), 0.95 (9H, d, J = 12.5 Hz, PC(CH_3)$_3$). ^{13}C{^{1}H} NMR (-80 °C, toluene-d_8, 150.9 MHz): δ 144.8 (Ar*C*), 144.2 (Ar*C*), 144.1 (Ar*C*), 143.4 (Ar*C*), 142.8 (Ar*C*), 142.2 (Ar*C*), 136.3 (Ar*C*), 134.9 (Ar*C*), 126.1 (Ar*C*), 36.3 (P*C*(CH$_3$)$_3$), 36.0 (P*C*(CH$_3$)$_3$), 34.0 (P*C*(CH$_3$)$_3$), 33.8 (P*C*(CH$_3$)$_3$), 31.9 (P*C*H$_2$P), 31.0 (PC(*C*H$_3$)$_3$), 30.7 (PC(*C*H$_3$)$_3$), 30.3 (PC(*C*H$_3$)$_3$), 25.8 (Ar*C*H$_3$), 25.0 (Ar*C*H$_3$), 23.5 (Ar*C*H$_3$), 21.4 (Ar*C*H$_3$), 21.2 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 45.9 (dd, $^2J_{PP}$ = 17.9 Hz, $^1J_{RhP}$ = 226.6 Hz), 10.6 (dd, $^2J_{PP}$ = 17.9 Hz, $^1J_{RhP}$ = 89.7 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ -12.4. Anal. Calcd for $C_{35}H_{61}P_2RhSi$: C, 62.30; H, 9.11. Found: C, 61.94; H, 9.30.

(dtbpm)Rh(GeHMes$_2$) (4). A solution of Mes$_2$GeH$_2$ (0.047 g, 0.15 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh(CH$_2$Ph) (0.075 g, 0.15 mmol) in 2 mL of pentane. After 1 h, the solution was concentrated (ca. 2 mL) and cooled to -35 ºC to afford dark red crystals in 71% yield (0.077 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 6.89 (4H, s, Ar*H*), 5.98 (1H, d, J = 14.0 Hz, Ge*H*), 2.97 (2H, t, J = 7.5 Hz, PCH_2P), 2.71 (6H, br s, ArCH_3), 2.32 (6H, br s, ArCH_3), 2.25 (6H, s, ArCH_3), 1.21 (18H, d, J = 13.4 Hz, PC(CH_3)$_3$), 1.17 (18H, d, J = 12.3 Hz, PC(CH_3)$_3$). ^{1}H NMR (-80 °C, toluene-d_8, 500 MHz): δ 7 .01 (2H, s, Ar*H*), 6.69 (2H, s, Ar*H*), 5.94 (1H, d, J = 14.2 Hz, Ge*H*), 3.05 (3H, s, ArCH_3), 2.71 (2H, m, PCH_2P), 2.56 (6H, s, ArCH_3),

2.28 (3H, s, ArCH_3), 2.23 (3H, s, ArCH_3), 1.99 (3H, s, ArCH_3), 1.33 (9H, d, J = 12.8 Hz, PC(CH_3)$_3$), 1.11 (9H, d, J = 12.2 Hz, PC(CH_3)$_3$), 0.99 (9H, d, J = 11.8 Hz, PC(CH_3)$_3$), 0.88 (9H, d, J = 13.0 Hz, PC(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 146.5 (Ar*C*), 142.5 (Ar*C*), 135.4 (Ar*C*), 37.6 (PCH_2P), 36.5 (P*C*(CH$_3$)$_3$), 34.6 (P*C*(CH$_3$)$_3$), 34.0 (P*C*(CH$_3$)$_3$), 31.7 (PC(*C*H$_3$)$_3$), 30.9 (PC(*C*H$_3$)$_3$), 22.3 (Ar*C*H$_3$), 20.8 (Ar*C*H$_3$), 13.8 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 42.6 (dd, $^2J_{PP}$ = 20.9 Hz, $^1J_{RhP}$ = 218.6 Hz), 9.6 (dd, $^2J_{PP}$ = 20.9 Hz, $^1J_{RhP}$ = 109.1 Hz). Anal. Calcd for $C_{35}H_{61}GeP_2Rh$: C, 58.44; H, 8.55. Found: C, 58.26; H, 8.78.

(dtbpm)Rh(Si(CPh=CHPh)Mes$_2$) (5). A solution of diphenylacetylene (0.008 g, 0.04 mmol) in 1 mL of C_6H_6 was added to a solution of **3** (0.030 g, 0.04 mmol) in 2 mL of C_6H_6. The red reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a bright orange solid in 85% yield (0.032 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.52 (4H, d, J = 7.4 Hz, Ar*H*), 6.98 (4H, t, J = 7.4 Hz, Ar*H*), 6.86 (4H, ov m, Ar*H*), 6.66 (2H, s, Ar*H*), 5.36 (1H, s, C*H*Ph), 3.18 (5H, br s, ArCH_3 + PCH_2P), 2.79 (3H, br s, ArCH_3), 2.67 (6H, s, ArCH_3), 2.20 (3H, s, ArCH_3), 2.04 (3H, s, ArCH_3), 1.27 (18H, br s, PC(CH_3)$_3$), 1.10 (9H, br s, PC(CH_3)$_3$), 0.92 (9H, br s, PC(CH_3)$_3$). ^{1}H NMR (-60 °C, toluene-d_8, 500 MHz): δ 7.46 (4H, s, Ar*H*), 6.95 (4H, s, Ar*H*), 6.80 (4H, s, Ar*H*), 6.59 (2H, s, Ar*H*), 5.24 (1H, t, J_{RhH} = 6.3 Hz, C*H*Ph), 3.11 (5H, br s, ArCH_3 + PCH_2P), 2.72 (3H, s, ArCH_3), 2.59 (6H, s, ArCH_3), 2.19 (3H, s, ArCH_3), 2.01 (3H, s, ArCH_3), 1.21 (18H, d, J = 11.5 Hz, PC(CH_3)$_3$), 1.05 (9H, d, J = 11.3 Hz, PC(CH_3)$_3$), 0.95 (9H, d, J = 11.0 Hz, PC(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 145.7 (Ar*C*), 143.8 (Ar*C*), 143.0 (Ar*C*), 136.9 (Ar*C*), 132.0 (Ar*C*), 130.8 (Ar*C*), 125.0 (Ar*C*), 124.3 (Ar*C*), 124.0 (Ar*C*), 90.3 (*C*PhSi), 83.6 (*C*HPh), 37.4 (P*C*H$_2$P), 36.5 (P*C*(CH$_3$)$_3$), 31.4 (PC(*C*H$_3$)$_3$), 27.1 (Ar*C*H$_3$), 21.3 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 27.8 (dd, $^2J_{PP}$ = 9.1 Hz, $^1J_{RhP}$ = 145.1 Hz), 7.9 (dd, $^2J_{PP}$ = 9.1 Hz, $^1J_{RhP}$ = 89.7 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 3.8. IR: 1550 cm^{-1} (*n*C=C). Anal. Calcd for $C_{49}H_{71}P_2RhSi$: C, 68.99; H, 8.39. Found: C, 68.38; H, 8.72.

(dtbpm)Rh(Ge(CPh=CHPh)Mes$_2$) (6). A solution of diphenylacetylene (0.008 g, 0.04 mmol) in 1 mL of C_6H_6 was added to a solution of **4** (0.030 g, 0.04 mmol) in 2 mL of C_6H_6. The reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a dark orange solid in 83% yield (0.029 g). ^{1}H NMR (C_6D_6, 600 MHz): δ 7.52 (4H, d, J = 6.9 Hz, Ar*H*), 6.99 (4H, m, Ar*H*), 6.88 (2H, br s, Ar*H*), 6.83 (2H, t, J = 7.5 Hz, Ar*H*), 6.70 (2H, br s, Ar*H*), 5.62 (1H, s, C*H*Ph), 3.19 (2H, br s, PCH_2P), 2.94 (6H, br s, ArCH_3), 2.47 (6H, br s, ArCH_3), 2.19 (3H, br s, ArCH_3), 2.10 (3H, br s, ArCH_3), 1.26 (18H, br s, PC(CH_3)$_3$), 1.11 (18H, br s, PC(CH_3)$_3$). ^{1}H NMR (-60 °C, toluene-d_8, 500 MHz): δ 7.31 (2H, t, J = 7.0 Hz, Ar*H*), 7.04 (2H, d, J = 7.0 Hz, Ar*H*), 6.83 (2H, m, Ar*H*), 6.77 (4H, t, J = 7.0 Hz, Ar*H*), 6.63 (4H, s, Ar*H*), 5.46 (1H, s, C*H*Ph), 3.12 (2H, dd, J = 16.0, 8.1 Hz, PCH_2P), 2.38 (6H, s, ArCH_3), 2.04 (12H, s, ArCH_3), 1.24 (9H, d, J = 10.0 Hz, PC(CH_3)$_3$), 1.13 (9H, d, J = 13.0 Hz, PC(CH_3)$_3$), 1.06 (9H, d, J = 11.7 Hz, PC(CH_3)$_3$), 0.93 (9H, d, J = 12.0 Hz, PC(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 147.7 (Ar*C*), 143.6 (Ar*C*), 142.3 (Ar*C*), 135.8 (Ar*C*), 130.2 (Ar*C*), 124.9 (Ar*C*), 123.9 (Ar*C*), 91.1 (*C*HPh), 92.6 (*C*HPh), 35.9 (P*C*H$_2$P), 34.6 (P*C*(CH$_3$)$_3$), 34.0 (P*C*(CH$_3$)$_3$), 31.5 (PC(*C*H$_3$)$_3$), 31.3 (PC(*C*H$_3$)$_3$), 30.9 (PC(*C*H$_3$)$_3$), 22.6 (Ar*C*H$_3$), 22.3 (Ar*C*H$_3$), 20.7 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 31.4 (dd, $^2J_{PP}$ = 8.2 Hz, $^1J_{RhP}$ = 136.7 Hz), 7.8 (dd, $^2J_{PP}$ = 8.2 Hz, $^1J_{RhP}$ = 88.0 Hz). Anal. Calcd for $C_{49}H_{71}GeP_2Rh$: C, 65.57; H, 7.97. Found: C, 65.78; H, 8.04.

(dtbpm)Rh(Si(CH=CHPh)Mes$_2$) (7). An excess of phenylacetylene (*ca.* 0.1 mL) was added to a solution of **3** (0.030 g, 0.04 mmol) in 1 mL of C_6H_6. The reaction solution was stirred for 30 min before being filtered through a Celite plug. The resulting solution was stripped to dryness to give a bright orange solid in 88% yield (0.030 g). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.45 (2H, d, *J* = 7.4 Hz, Ph*H*), 7.06 (2H, t, *J* = 7.4 Hz, Ph*H*), 6.89 (1H, d, *J* = 7.4 Hz, Ph*H*), 6.81 (4H, s, Ar*H*), 5.23 (1H, d, *J* = 16.2 Hz, =C*H*), 4.16 (1H, dd, *J* = 16.2, J_{RhH} = 6.7 Hz, =C*H*), 3.12 (2H, t, *J* = 6.8 Hz, PC*H*$_2$P), 3.01 (6H, br s, ArC*H*$_3$), 2.69 (6H, s, ArC*H*$_3$), 2.18 (3H, s, ArC*H*$_3$), 2.16 (3H, s, ArC*H*$_3$), 1.34 (9H, d, *J* = 12.2 Hz, C(C*H*$_3$)$_3$), 1.26 (9H, d, *J* = 12.0 Hz, C(C*H*$_3$)$_3$)), 1.04 (9H, d, *J* = 12.7 Hz, C(C*H*$_3$)$_3$)), 0.76 (9H, d, *J* = 11.8 Hz, C(C*H*$_3$)$_3$)). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 145.3 (Ar*C*), 144.4 (Ar*C*), 144.0 (Ar*C*), 139.1 (Ar*C*), 131.5 (Ar*C*), 130.6 (Ar*C*), 128.6 (Ar*C*), 127.2 (Ar*C*), 100.7 (*C*Si), 76.9 (*C*HPh), 36.1 (P*C*H$_2$P), 35.4 (P*C*(CH$_3$)$_3$), 31.6 (PC(*C*H$_3$)$_3$), 31.0 (PC(*C*H$_3$)$_3$), 30.8 (PC(*C*H$_3$)$_3$), 30.3 (PC(*C*H$_3$)$_3$), 26.9 (Ar*C*H$_3$), 23.1 (Ar*C*H$_3$), 20.8 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 37.4 (dd, $^2J_{PP}$ = 15.9 Hz, $^1J_{RhP}$ = 187.5 Hz), 6.8 (dd, $^2J_{PP}$ = 15.9 Hz, $^1J_{RhP}$ = 127.4 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 0.6. Anal. Calcd for $C_{37}H_{59}P_2RhSi$: C, 63.78; H, 8.53. Found: C, 63.39; H, 8.70.

***in situ* formation of (dtbpm)Rh(Si(CMe=CHMe)Mes$_2$) (8).** With a 10 μL syringe, 2-butyne (3.1 μL, 0.04 mmol) was added to a solution of **3** (0.030 g, 0.04 mmol) in 1 mL of C_6D_6. The reaction solution was stirred for 30 min before being filtered through a Celite plug. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.81 (4H, s, Ar*H*), 3.91 (1H, s, C*H*Me), 3.10 (2H, s, PC*H*$_2$P), 2.88 (12H, s, ArC*H*$_3$), 2.17 (6H, s, ArC*H*$_3$), 2.14 (3H, s, C*H*$_3$), 2.12 (3H, s, C*H*$_3$), 1.28 (12H, br s, PC(C*H*$_3$)$_3$), 1.18 (12H, br s, PC(C*H*$_3$)$_3$). ^{1}H NMR (-60 °C, toluene-*d*$_8$, 500 MHz): δ 6.83 (1H, s, Ar*H*), 6.74 (2H, s, Ar*H*), 6.58 (1H, s, Ar*H*), 3.47 (1H, m, C*H*Me), 3.33 (3H, s, ArC*H*$_3$), 2.99 (2H, m, PC*H*$_2$P), 2.81 (6H, s, ArC*H*$_3$), 2.64 (3H, s, ArC*H*$_3$), 2.22 (3H, s, ArC*H*$_3$), 2.13 (6H, s, ArC*H*$_3$), 2.10 (3H, s, ArC*H*$_3$), 1.32 (9H, d, *J* = 11.5 Hz, PC(C*H*$_3$)$_3$), 1.17 (9H, d, *J* = 11.4 Hz, PC(C*H*$_3$)$_3$), 1.07 (9H, d, *J* = 10.8 Hz, PC(C*H*$_3$)$_3$), 0.94 (9H, d, *J* = 12.1 Hz, PC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 143.5 (Ar*C*), 136.5 (Ar*C*), 89.8 (*C*MeSi), 79.9 (*C*HMe), 37.2 (P*C*H$_2$P), 36.0 (P*C*(CH$_3$)$_3$), 34.9 (P*C*(CH$_3$)$_3$), 31.5 (PC(*C*H$_3$)$_3$), 31.3 (PC(*C*H$_3$)$_3$), 27.3 (Ar*C*H$_3$), 23.4 (CH*Me*=C*Me*Si), 21.1 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 30.2 (dd, $^2J_{PP}$ = 7.5 Hz, $^1J_{RhP}$ = 154.9 Hz), 13.95 (dd, $^2J_{PP}$ = 7.5 Hz, $^1J_{RhP}$ = 99.4 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 5.2.

***in situ* formation of (dtbpm)Rh(Ge(CMe=CHMe)Mes$_2$) (9).** With a 10 μL syringe, 2-butyne (3.3 μL, 0.04 mmol) was added to a solution of **4** (0.030 g, 0.04 mmol) in 1 mL of C_6D_6. The dark red reaction solution was stirred for 30 min before being filtered through a Celite plug. ^{1}H NMR (C_6D_6, 600 MHz): δ 6.83 (4H, s, Ar*H*), 4.39 (1H, br m, C*H*Me), 3.14 (2H, t, *J* = 6.6 Hz, PC*H*$_2$P), 2.80 (12H, s, ArC*H*$_3$), 2.18 (6H, s, ArC*H*$_3$), 2.15 (3H, m, C*H*$_3$), 2.13 (3H, s, C*H*$_3$), 1.27 (18H, d, *J* = 11.4 Hz, PC(C*H*$_3$)$_3$), 1.19 (18H, d, *J* = 12.4 Hz, PC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 142.4 (Ar*C*), 135.5 (Ar*C*), 87.7 (*C*MeSi), 79.5 (*C*HMe), 38.2 (P*C*H$_2$P), 35.4 (P*C*(CH$_3$)$_3$), 34.8 (P*C*(CH$_3$)$_3$), 31.5 (PC(*C*H$_3$)$_3$), 31.1 (PC(*C*H$_3$)$_3$), 30.8 (PC(*C*H$_3$)$_3$), 26.4 (Ar*C*H$_3$), 23.6 (CH*Me*=C*Me*Ge), 22.6 (CH*Me*=C*Me*Ge), 20.7 (Ar*C*H$_3$), 18.4 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 32.6 (dd, $^2J_{PP}$ = 9.8 Hz, $^1J_{RhP}$ = 117.4 Hz), 13.7 (dd, $^2J_{PP}$ = 9.8 Hz, $^1J_{RhP}$ = 92.9 Hz).

(dtbpm)Rh(SiHMes$_2$)(DMAP) (10). A solution of DMAP (0.009 g, 0.07 mmol) in 1 mL of pentane was added to a solution of **3** (0.050 g, 0.07 mmol) in 2 mL of C_6H_6. After 30 min, the solution was concentrated (ca. 2 mL) and cooled to -35 ºC to afford yellow crystals in 95% yield (0.053 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.48 (1H, d, *J* = 5.6 Hz, Ar*H*), 8.10 (1H, d, *J* = 6.0 Hz, Ar*H*), 6.10 (1H, d, *J* = 5.6 Hz, Ar*H*), 5.53 (1H, d, *J* = 6.0 Hz, Ar*H*), 2.87 (2H, t, *J* = 6.9 Hz, PC*H*$_2$P), 2.23 (3H, s, NC*H*$_3$), 2.04 (3H, s, NC*H*$_3$), 1.48 (18H, br s, PC(C*H*$_3$)$_3$), 1.25 (18H, d, *J* = 10.0 Hz, PC(C*H*$_3$)$_3$). ^{1}H NMR (-60 °C, toluene-*d*$_8$, 500 MHz): δ 8.38 (1H, br s, Ar*H*), 7.59 (1H, br s, Ar*H*), 7.21 (1H, s, Mes*H*), 6.95 (1H, s, Mes*H*), 6.78 (1H, s, Mes*H*), 6.14 (1H, s, Mes*H*), 6.06 (1H, m, Si*H*), 5.40 (1H, br s, Ar*H*), 5.15 (1H, br s, Ar*H*), 4.48 (3H, s, MesC*H*$_3$), 3.20 (3H, s, MesC*H*$_3$), 2.70 (5H, s, ArC*H*$_3$ + PC*H*$_2$P), 2.26 (3H, s, MesC*H*$_3$), 2.19 (3H, s, ArC*H*$_3$), 2.03 (3H, s, ArC*H*$_3$), 1.76 (9H, d, *J* = 10.8 Hz, PC(C*H*$_3$)$_3$), 1.44 (3H, s, MesC*H*$_3$), 1.38 (9H, d, *J* = 10.6 Hz, PC(C*H*$_3$)$_3$), 1.18 (9H, d, *J* = 11.0 Hz, PC(C*H*$_3$)$_3$), 0.95 (9H, d, *J* = 10.6 Hz, PC(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): δ 152.3 (Ar*C*), 151.9 (Ar*C*), 105.4 (Ar*C*), 37.8 (P*C*H$_2$P), 34.0 (P*C*(CH$_3$)$_3$), 31.1 (PC(*C*H$_3$)$_3$), 22.3 (PC(*C*H$_3$)$_3$), 20.9 (Ar*C*H$_3$), 13.9 (Ar*C*H$_3$), 8.6 (Ar*C*H$_3$). ^{13}C{^{1}H} NMR (-60 °C, toluene-*d*$_8$, 150.9 MHz): δ 151.9 (Ar*C*), 145.5 (Ar*C*), 145.3 (Ar*C*), 143.5 (Ar*C*), 105.8 (Ar*C*), 105.4 (Ar*C*), 38.5 (Ar*C*H$_3$), 37.6 (P*C*H$_2$P), 36.1 (P*C*(CH$_3$)$_3$), 35.6 (PC(*C*H$_3$)$_3$), 35.1 (P*C*(CH$_3$)$_3$), 33.9 (P*C*(CH$_3$)$_3$), 33.3 (PC(*C*H$_3$)$_3$), 32.3 (PC(*C*H$_3$)$_3$), 31.3 (PC(*C*H$_3$)$_3$), 30.8 (PC(*C*H$_3$)$_3$), 26.5 (Ar*C*H$_3$), 25.8 (Ar*C*H$_3$), 24.8 (Ar*C*H$_3$), 23.7 (Ar*C*H$_3$), 21.9 (Ar*C*H$_3$), 15.2 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 39.14 (dd, $^2J_{PP}$ = 9.0, $^1J_{RhP}$ = 169.5 Hz), 3.63 (dd, $^2J_{PP}$ = 9.0, $^1J_{RhP}$ = 97.8 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ -33.8. Anal. Calcd for $C_{42}H_{71}N_2P_2RhSi$: C, 63.30; H, 8.98; N, 3.52. Found: C, 62.96; H, 9.23; N, 3.24

(dtbpm)Rh(H)$_2$[5,7-diisopropyl-3-methyl-1-phenyl-2,3-dihydro-1*H*-silaindenyl-κSi] (11). A solution of TripPhSiH$_2$ (0.032 g, 0.10 mmol) in 2 mL of pentane was added to a solution of (dtbpm)Rh(CH$_2$Ph) (0.050 g, 0.10 mmol) in 2 mL of pentane. The solution was immediately cooled to -35 ºC to afford orange crystals in 65% yield (0.047 g). ^{1}H NMR (0 °C, toluene-*d*$_8$, 500 MHz): δ 8.14 (2H, d, *J* = 6.7 Hz, Ph*H*), 7.26 (2H, m, Ph*H*), 7.08 (1H, s, Ph*H*), 7.03 (2H, s, Ar*H*), 3.76 (1H, sept, *J* = 6.7 Hz, C*H*), 3.58 (1H, sextet, *J* = 6.9 Hz, C*H*), 3.14 (2H, t, *J* = 6.9 Hz, PC*H*$_2$P), 2.96 (1H, sept, *J* = 6.8 Hz, C*H*), 1.99 (1H, dd, *J* = 13.5, 6.9 Hz, SiC*H*$_2$), 1.76 (3H, d, *J* = 6.7 Hz, C*H*$_3$), 1.61 (1H, m, SiC*H*$_2$), 1.50 (3H, d, *J* = 6.9 Hz, C*H*$_3$), 1.39 (6H, d, *J* = 6.8, *CH*$_3$), 1.23 (18H, d, *J* = 12.6 Hz, PC(C*H*$_3$)$_3$), 1.10 (18H, d, *J* = 12.8 Hz, PC(C*H*$_3$)$_3$), 1.05 (3H, d, *J* = 6.9 Hz, C*H*$_3$), -7.04 (2H, m, J_{SiH} = 51.8 Hz, Rh*H*$_2$). ^{13}C{^{1}H} NMR (0 °C, toluene-*d*$_8$, 150.9 MHz): δ 155.5 (Ar*C*), 152.9 (Ar*C*), 148.8 (Ar*C*), 144.5 (Ar*C*), 126.63 (Ar*C*), 120.4 (Ar*C*), 118.9 (Ar*C*), 37.8 (*C*H$_2$), 35.1 (P*C*H$_2$P), 34.9 (P*C*(CH$_3$)$_3$), 34.6 (P*C*(CH$_3$)$_3$), 33.8 (PC(*C*H$_3$)$_3$), 32.9 (PC(*C*H$_3$)$_3$), 30.5 (PC(*C*H$_3$)$_3$), 30.3 (PC(*C*H$_3$)$_3$), 25.2 (Ar*C*H$_3$), 24.5 (Ar*C*H$_3$), 24.3 (Ar*C*H$_3$), 23.8 (Ar*C*H$_3$), 22.8 (Ar*C*H$_3$). ^{31}P{^{1}H} NMR (0 °C, toluene-*d*$_8$, 163.0 MHz): δ 19.8 (d, $^1J_{RhP}$ = 113.9 Hz). ^{29}Si NMR (0 °C, toluene-*d*$_8$, 99.4 MHz): δ 0.89. Anal. Calcd for $C_{38}H_{67}P_2RhSi$: C, 63.67; H, 9.42. Found: C, 63.73; H, 9.54.

[(dtbpm)IrH](μ-SiPh$_2$)(μ-Cl)$_2$[(dtbpm)IrH] (12). A solution of H_2SiPh_2 (0.023 g, 0.12 mmol) in C_6H_6 was added to a stirring solution of [(dtbpm)IrCl]$_2$ (0.10 g, 0.09 mmol) in C_6H_6. The solution was stirred at room temperature for 40 min. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove remaining H_2SiPh_2. Further drying gave **12** as a yellow-orange powder in 89% yield (0.102 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.89 (4H, br s, Ar*H*), 7.44 (4H, t, *J* = 7.4 Hz,

Ar*H*), 7.26 (2H, t, *J* = 7.4 Hz, Ar*H*), 3.15 (2H, m, PCH_2P), 2.85 (2H, m, PCH_2P), 1.55 (18H, d, J_{PH} = 11.5 Hz, PC(CH_3)$_3$), 1.43 (18, d, J_{PH} = 11.5 Hz, PC(CH_3)$_3$), 1.03 (18H, d, J_{PH} = 13.5 Hz, PC(CH_3)$_3$), 0.85 (18H, d, J_{PH} = 13.5 Hz, PC(CH_3)$_3$), -23.3 (2H, d, J_{PH} = 24.8 Hz, Ir*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): δ 136.5 (Ar*C*), 135.6 (Ar*C*), 134.5 (Ar*C*), 129.7 (Ar*C*), 128.1 (Ar*C*), 36.0 (P*C*H_2P), 35.3 (P*C*H_2P), 33.3 (P*C*(CH$_3$)$_3$), 32.3 (P*C*(CH$_3$)$_3$), 31.1 (PC(*C*H$_3$)$_3$), 30.9 (PC(*C*H$_3$)$_3$), 30.3 (PC(*C*H$_3$)$_3$), 29.1 (PC(*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ 8.9 (d, $^2J_{PP}$ = 6.1 Hz), -3.7 (d, $^2J_{PP}$ = 6.1 Hz). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ -34.4. IR: 2328, 2288 (*n*Ir-H). Anal. Calcd for $C_{46}Cl_2H_{88}Ir_2P_4Si$: C, 44.25; H, 7.10. Found: C, 45.42; H, 7.08.

[(dtbpm)IrH](μ-SiMesCl)(μ-Cl)(μ-H)[(dtbpm)IrH] (13). A solution of H_3SiMes (0.018 g, 0.12 mmol) in C_6H_6 was added to a stirring solution of [(dtbpm)IrCl]$_2$ (0.102 g, 0.096 mmol) in C_6H_6. The solution was stirred at room temperature for 40 min. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove remaining H_3SiMes. Further drying under reduced pressure gave **13** as a yellow powder in 90% yield (0.104 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.92 (1H, s, Ar*H*), 6.83 (1H, s, Ar*H*), 3.72 (2H, m, PCH_2P), 3.51 (2H, m, PCH_2P), 3.36 (3H, s, ArCH_3), 3.16 (3H, s, ArCH_3), 2.17 (3H, s, ArCH_3), 1.51 (18H, d, J_{PH} = 11.9 Hz, PC(CH_3)$_3$), 1.41 (18H, d, J_{PH} = 9.9 Hz, PC(CH_3)$_3$), 1.35 (18H, d, J_{PH} = 9.9 Hz, PC(CH_3)$_3$), 1.08 (18H, d, J_{PH} = 11.6 Hz, PC(CH_3)$_3$), -12.59 (1H, tt, J_{PH} = 5.3, 63.3 Hz, μ-Ir*H*), -24.66 (2H, dd, J_{PH} = 2.4, 18.0 Hz, Ir*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): δ 144.5 (Ar*C*), 139.1 (Ar*C*), 135.6 (Ar*C*), 130.5 (Ar*C*), 37.3 (P*C*H_2P), 35.2 (P*C*H_2P), 32.3 (P*C*(CH$_3$)$_3$), 31.6 (P*C*(CH$_3$)$_3$), 30.8 (PC(*C*H$_3$)$_3$), 30.2 (PC(*C*H$_3$)$_3$), 29.9 (PC(*C*H$_3$)$_3$), 29.3 (PC(*C*H$_3$)$_3$), 26.5 (Ar*C*H$_3$), 24.0 (Ar*C*H$_3$), 22.3 (Ar*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ 18.50 (d, $^2J_{PP}$ = 14.5), 3.28 (d, $^2J_{PP}$ = 14.5). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 75.0 (t, J_{SiP} ~ 150 Hz). IR: 2391, 2327 (*n*Ir-H). Anal. Calcd for $C_{43}Cl_2H_{92}Ir_2P_4Si$: C, 42.45; H, 7.62. Found: C, 42.69; H, 7.24.

(dtbpm)Ir(H)$_4$(10-chloro-1-mesityl-5,7-dimethyl-9,10-dihydrosilaphenanthrene-κSi) (14). A solution of H_3Si(dmp) (0.032 g, 0.094 mmol) in C_6H_6 was added to a stirring solution of [(dtbpm)IrCl]$_2$ (0.050 g, 0.046 mmol) in C_6H_6. The solution was stirred at 55 ºC for 18 h. The solvent was removed under reduced pressure. The resulting yellow-orange solid was washed twice with 1 mL of cold pentane to remove remaining H_3Si(dmp). Further drying under reduced pressure gave **14** as a yellow powder in 72% yield (0.058 g). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.34 (1H, s, Ar*H*), 7.25 (1H, t, *J* = 7.5 Hz, Ar*H*), 7.06 (1H, s, Ar*H*), 7.01 (1H, d, *J* = 7.5, Ar*H*), 6.92 (2H, d, *J* = 7.5 Hz, Ar*H*), 6.79 (1H, s, Ar*H*), 3.64 (1H, d, *J* = 13.4 Hz, CH_2), 3.13 (2H, t, *J* = 7.7 Hz, PCH_2P), 2.64 (1H, d, *J* = 13.4 Hz, CH_2), 2.56 (3H, s, ArCH_3), 2.46 (3H, s, ArCH_3), 2.42 (3H, s, ArCH_3), 2.34 (3H, s, ArCH_3), 2.20 (3H, s, ArCH_3), 1.10 (18H, d, J_{PH} = 13.5 Hz, PC(CH_3)$_3$), 1.00 (18H, d, J_{PH} = 13.6 Hz, PC(CH_3)$_3$), -11.58 (4H, t, J_{PH} = 15.1 Hz, Ir*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz): δ 145.6 (Ar*C*), 145.1 (Ar*C*), 142.9 (Ar*C*), 140.6 (Ar*C*), 139.8 (Ar*C*), 138.2 (Ar*C*), 136.4 (Ar*C*), 135.4 (Ar*C*), 135.1 (Ar*C*), 134.9 (Ar*C*), 129.8 (Ar*C*), 129.7 (Ar*C*), 125.6 (Ar*C*), 41.6 (*C*H$_2$), 37.6 (P*C*H$_2$P), 33.5 (P*C*(CH$_3$)$_3$), 32.8 (P*C*(CH$_3$)$_3$), 31.9 (PC(*C*H$_3$)$_3$), 30.5 (P*C*(CH$_3$)$_3$), 29.7 (P*C*(CH$_3$)$_3$), 24.0 (Ar*C*H$_3$), 23.0 (Ar*C*H$_3$), 22.7 (Ar*C*H$_3$), 21.4 (Ar*C*H$_3$), 21.1 (Ar*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 163.0 MHz): δ -2.12. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ -1.96. Anal. Calcd for $C_{41}H_{66}ClIrP_2Si$: C, 56.17; H, 7.59. Found: C, 55.86; H, 7.86.

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Chapter 6

Interligand H···Si Interactions in Tungsten Silyl Trihydride Complexes

Introduction

In recent years the use of amidinates as ligands for early transition metal complexes has gained considerable popularity.[1-3] Amidinates are easily synthesized and can be readily modified to induce either small or drastic steric and electronic changes. Futhermore, multiple methods for installing amidinate ligands onto metal fragments have proven effective.[4,5] Amidinate-supported Group 4 complexes are active olefin polymerization catalysts, and the amidinate ligand is not directly involved in observed reactivity.[6-9] Recent work from Sita and co-workers with Group 6 complexes of the type $Cp^*(Am)MCl_2$ (Am = $[(iPrN)_2CMe]^-$; M = Mo, W)[10] inspired the exploration of reactivity of $Cp^*(Am)WCl_2$ (**1**) with organosilanes.

Research in this laboratory has focused on fundamental chemistry involving Si – H activations and the formation of silylene complexes. In particular, $[(\eta^7\text{-}C_5Me_3(CH_2)_2)(dmpe)W(H)_2][B(C_6F_5)_4]$ has been shown to perform double Si – H activations to result in high oxidation state silylene complexes of the type $[Cp^*(dmpe)W{=}SiR_2][B(C_6F_5)_4]$.[11,12] Similar chemistry was envisioned to occur with a Cp*(amidinate)W fragment, such as $Cp^*(Am)WR_2$. Herein we present the synthesis of new tungsten complexes supported by the amidinate ligand (Am = $[(iPrN)_2CMe]^-$) in which a non-classical Si···H interaction is observed.

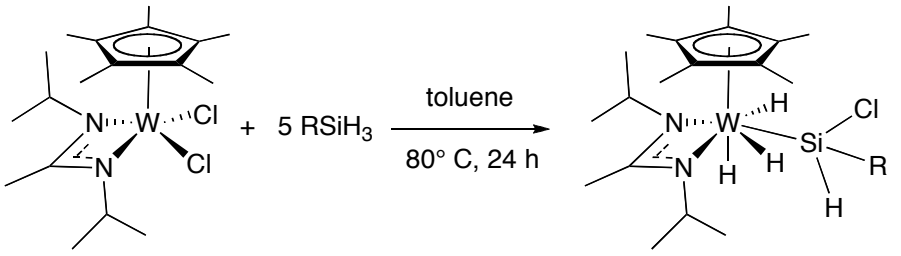
A number of interesting non-classical interactions have been observed in organometallic complexes containing silicon, which have been characterized as involving σ-complexes (η^2- and η^3-silane complexes), agostic interactions, and interligand hypervalent interactions,[13-16] and such species have been proposed as intermediates in catalytic transformations of organosilanes.[17-20] An interligand hypervalent interaction is described as involving primarily electron donation from a metal hydride bond into an antibonding orbital of a silicon – X bond, where X is a good leaving group. This interaction results in elongation of the Si – X bond, shortening of the M – Si bond, and often but not always, increased Si – H coupling constants.[15, 21] Such interactions have been well documented for Ru, Ta, and Nb complexes.[22-26]

Results and Discussion

Reactions of primary silanes with $Cp^*(Am)WCl_2$. Complex **1** was found to react with a 5-fold excess of phenylsilane at 80° C over 24 h in toluene to give $Cp^*(Am)W(H)_3(SiHRCl)$ (**2**) as a light brown solid in 42% yield after recrystallization from pentane at –30 °C (eq 1). The yield is significantly lowered by the similar solubility properties of **2** and phenylsilane, making isolation of pure **2** difficult. In an analogous manner, **1** was found to react with *p*-tolylsilane, 3,5-xylylsilane, and (pentafluorophenyl)silane to give complexes **3** – **5**, respectively. Reactions with the bulkier silanes $MesSiH_3$, $TripSiH_3$, and $DMPSiH_3$ did not proceed, even with heating at 80° C for one week, presumably for steric reasons.

The ^{1}H NMR spectrum of **2** contains three chemically inequivalent hydride resonances at 5.24 ppm (J_{SiH} = < 7 Hz), 0.92 ppm (J_{SiH} = 11.1 Hz), and -1.28 ppm (J_{SiH} = 24.6 Hz). The Si-H resonance at 8.41 ppm (J_{SiH} = 199.5 Hz) is shifted downfield relative to that of the free silane (4.23 ppm). The ^{29}Si NMR spectrum contains a single resonance for the silyl ligand at 43.9 ppm. The isopropyl groups of the ligand exhibit two methine resonances and four methyl resonances, indicating C_1 symmetry for the complex. Tungsten satellites were observable for the hydride resonances, and the W – H coupling constant for all hydrides of ca. 40 Hz is similar to those reported for $[C_5Me_5(dmpe)W(H)_2]$-based compounds.[11,12] The NMR data for complexes **3** – **5** follow similar trends (Table 1). The NMR spectra were found to remain unchanged over the temperature range of –50 to 80 °C. Using the inversion recovery method, the minimum T_1

relaxation times were found to be 950 (H_a), 800 (H_b), and 980 ms (H_c), indicative of classical hydrides.



(1)

1

R = Phenyl (**2**)
p-Tolyl (**3**)
3,5-Xylyl (**4**)
C_6F_5 (**5**)

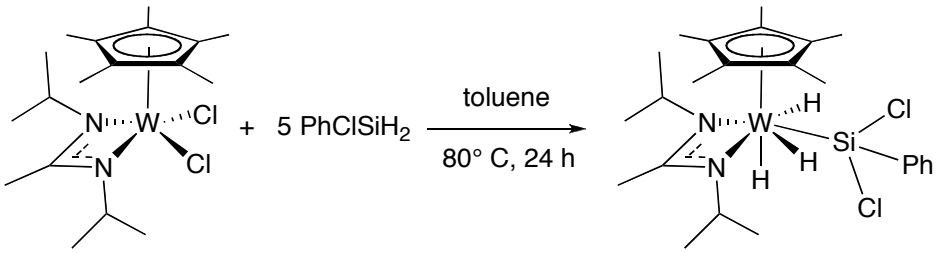
Complexes **2** – **5** appear to be quite stable and relatively unreactive. Heating at 100° C for 24 h in C_6D_6 resulted in no detectable decomposition of **2** (by ^{1}H NMR sprectroscopy). Addition of an excess of PMe_3 to **2** gave no reaction with heating to 100° C for 24 h. Reactions with diphenylacetylene, benzophenone, acetophenone, norbornene, and 3,3-dimethylbut-1-ene did not proceed at room temperature but resulted in numerous unidentified organometallic species upon heating to 80° C for 6 h.

Table 1. NMR data for complexes **2** – **5**

Complex	δ ^{1}H (H_a) ($^2J_{SiH}$)	δ ^{1}H (H_b) ($^2J_{SiH}$)	δ ^{1}H (H_c) ($^2J_{SiH}$)	δ ^{1}H (SiH) ($^1J_{SiH}$)	δ ^{29}Si
Cp*(Am)WH$_3$(SiHPhCl) (2)	5.24 (<7)	0.92 (11.1)	-1.28 (24.6)	8.41 (199.5)	43.9
Cp*(Am)WH$_3$(SiHTolylCl) (3)	5.35 (14.4)	0.95 (9.3)	-1.15 (26.5)	8.44 (198.0)	43.2
Cp*(Am)WH$_3$(SiHXylylCl) (4)	5.39 (7.8)	0.94 (15.4)	-1.11 (31.9)	8.43 (198.1)	43.3
Cp*(Am)WH$_3$[SiH(C$_6$F$_5$)Cl] (5)	4.74 (22.7)	0.58 (10.6)	-1.61 (21.6)	8.52 (215.5)	22.1

Reactions of secondary silanes with Cp*(Am)WCl$_2$. In reactions of primary silanes with complex **1**, use of less than 5 equiv of $RSiH_3$ resulted in a tertiary silyl-containing product (*vida infra*). It was therefore of interest to explore the reactivity of **1** with secondary silanes in order to isolate such species. Using the same reaction conditions employed for the synthesis of **2** – **5**, complex **1** was found to react with $H_2SiPhCl$ to afford Cp*(Am)W(H)$_3$($SiPhCl_2$) (**6**) as a light green solid in 27% isolated yield (eq 2). The ^{1}H NMR spectrum reveals only two inequivalent hydride resonances, integrating for three hydrides total, at 4.61 ppm (1H, J_{SiH} = 9.9 Hz) and 1.05 ppm (2H, J_{SiH} = 17.8 Hz). The ^{29}Si NMR spectrum displays a single

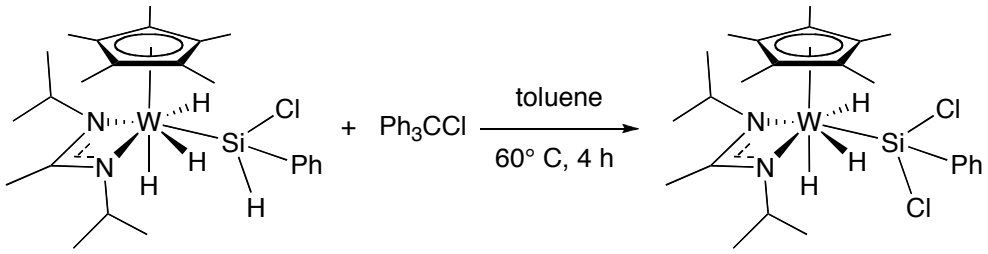
resonance at 47.8 ppm. Interestingly, the isopropyl groups of the amidinate ligand are equivalent, indicating that the ligand lies on a plane of symmetry. Reactions of **2** with the secondary silanes Ph_2SiH_2, Et_2SiH_2, and $MesClSiH_2$ did not proceed after one week of heating at 80 °C in C_6D_6.



(2)

1 **6**

Complex **6** can alternatively be synthesized from reaction of **2** with one equiv of trityl chloride at 60° C for 4 h in toluene, quantitatively by NMR spectroscopy (eq 3). This method is a more convenient route to the dichlorosilyl species. Complex **6** does not react further with Ph_3CCl in C_6D_6 at 100° C for 24 h. Thus, the Si-H bond of **2** appears to represent the most hydridic center in these type of complexes.

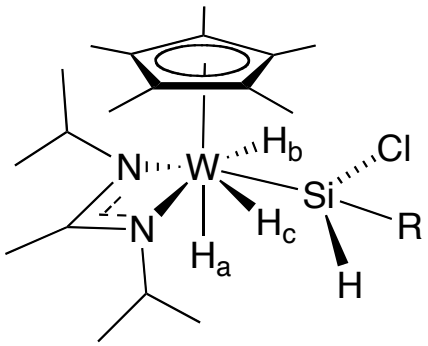


(3)

2 **6**

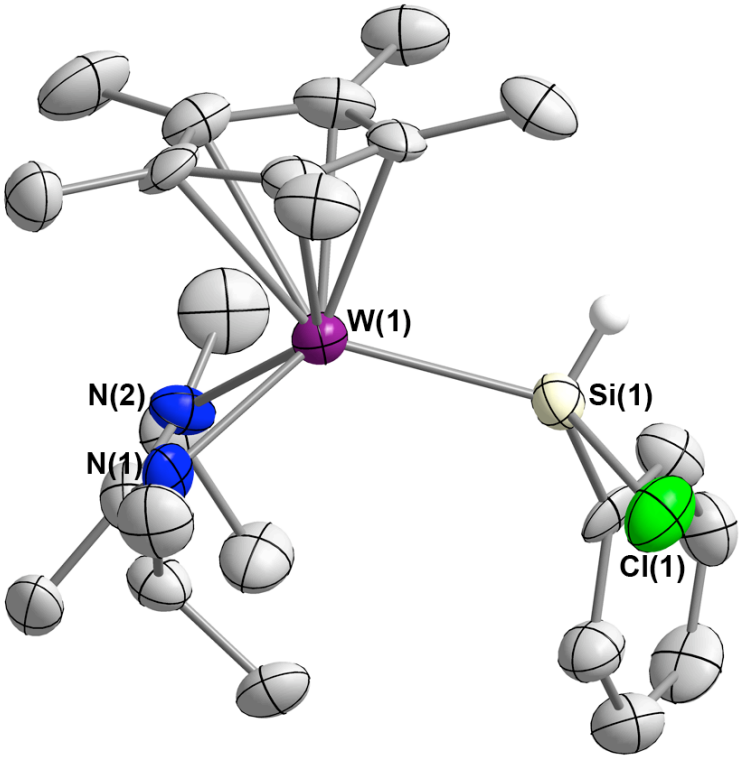
Comparison of the NMR spectra of complexes **2** and **6** allows for definitive assignments of the hydride resonances (Figure 1). Thus, the resonance at ca. 5 ppm (H_a) observed in **2** and **6** corresponds to a hydride ligand that is *trans* to the Cp* ligand. The shift at ca. 1 ppm (H_b) for **2** and **6** corresponds to hydride ligands in close proximity to the Cl atom of the silyl ligand. The furthest upfield signal at ca. -1 ppm (H_c), observed only in **2**, correlates to the hydride nearest to the Si – H group. In complex **2**, H_c exhibits the largest coupling to Si (J_{SiH} = 24.6 ppm). This increased coupling is suggestive of a significant Si···H–W interaction (IHI). H_c is approximately *trans* to the Cl group on silicon, allowing for overlap with the Si – Cl antibonding orbital. Two such interactions are seen in complex **6** with the H_b hydrides (J_{SiH} = 17.8 Hz).

Figure 1. Assignment of hydrides based on NMR spectroscopy.



Solid-state structure of 2. Suitable crystals of **2** for single-crystal X-ray diffraction were grown by slow evaporation of pentane at room temperature over one week. The X-ray structure of **2** reveals a 3-legged piano stool geometry of the Cp*, amidinate ligand, and silyl ligands about W, and the W – Si bond length of 2.490(4) Å is typical for a W – Si single bond (Figure 2). The N(1)-W(1)-N(2) angle of 63.5(4)° is as expected for an amidinate ligand, and the silyl group is canted slightly towards N(2) as seen by the N(1)-W(1)-Si(1) angle of 124.9(3)° and the N(2)-W(1)-Si(1) angle of 113.3(3)°. The elongated Si – Cl bond length of 2.138(5) Å supports the identification of an interligand H···Si interaction between a W – H and the Si – Cl antibonding orbital. Due to insufficient data, the hydrides were not located.

Figure 2. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity.

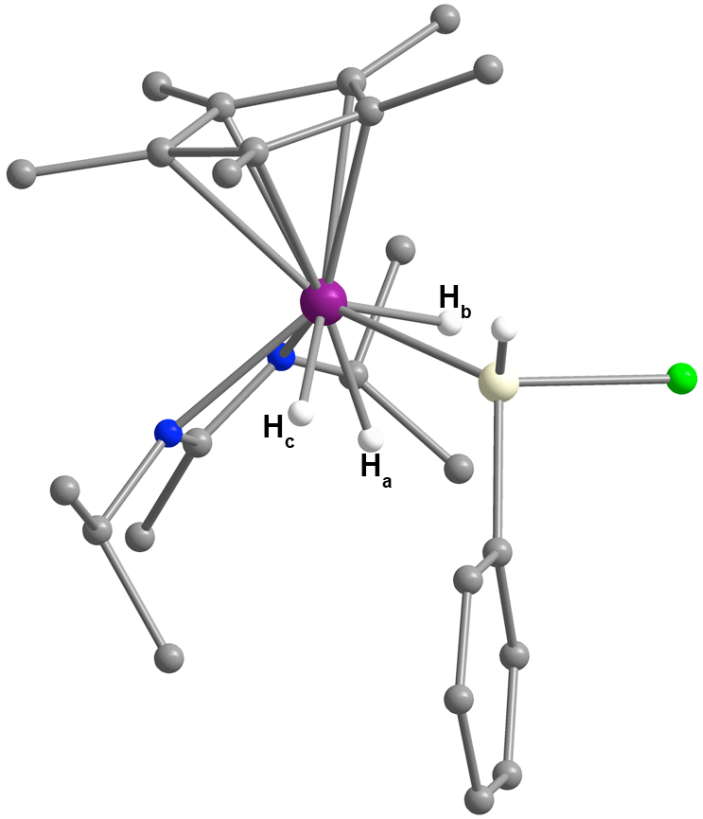


A similar compound, $Cp^*(CO)_2W(H)_2(SiHCl_2)$, has been reported in the literature.[26] Interestingly, this complex adopts a pseudo-octahedral structure (with the Cp* ligand considered as occupying a single site) and has a W – Si bond length of 2.4902(9) Å. This is a significantly different geometry than that observed for **2**. Additionally, both W – H bonds of

$Cp^*(CO)_2W(H)_2(SiHCl_2)$ interact much more strongly with the silicon center, based on the Si···H distances of 1.91(3) and 1.90(3) Å. Coupling constants were not reported for this compound. Although two interligand hypervalent interactions have been implicated for the lengthened Si – Cl bonds (2.0981(14) and 2.1084(13) Å), the Si – Cl distance in **2** is slightly longer, indicating a stronger interaction, and this would be consistent with a more electron-rich W center in **2**.

DFT Calculations of 2. Because the hydride ligands of **2** were not located by X-ray crystallography, DFT calculations at the B3LYP/LANL2DZ level of theory were undertaken. Using the crystal structure as a starting point, several different arrangements of the hydrides were minimized, resulting in the lowest energy structure shown in Figure 4. The bond distances and angles are in agreement with those observed by X-ray crystallography, including the elongated Si – Cl bond distance of 2.16 Å. One hydride, H_a, is located *trans* to the Cp* centroid, with a W – H bond distance of 1.69 Å. The other two hydride ligands occupy the open pockets between the amidinate and silyl ligands. The W – H group *cis* to Cl, H_b, is associated with a bond distance of 1.68 Å. The other hydride, H_c, is approximately *trans* (156º) to the Cl atom on the silyl group and is involved with a slightly longer W – H bond distance of 1.71 Å. Additionally, H_c is associated with the shortest Si – H distance (2.10 Å). These structural features correlate well with the structure hypothesized from NMR data.

Figure 3. Optimized geometry of $Cp^*(Am)W(H)_3(SiHPhCl)$.



To further probe the nature of the H···Si interations in **2**, NMR spin-spin coupling predictions and NBO calculations were performed. The following J_{Si-H} values were found: H_a = 2 Hz, H_b = 11 Hz, and H_c = 39 Hz. These coupling constants agree very well with experimentally obtained values (H_a = <7 Hz, H_b = 11.1 Hz, and H_c = 24.6 Hz) and indicate that

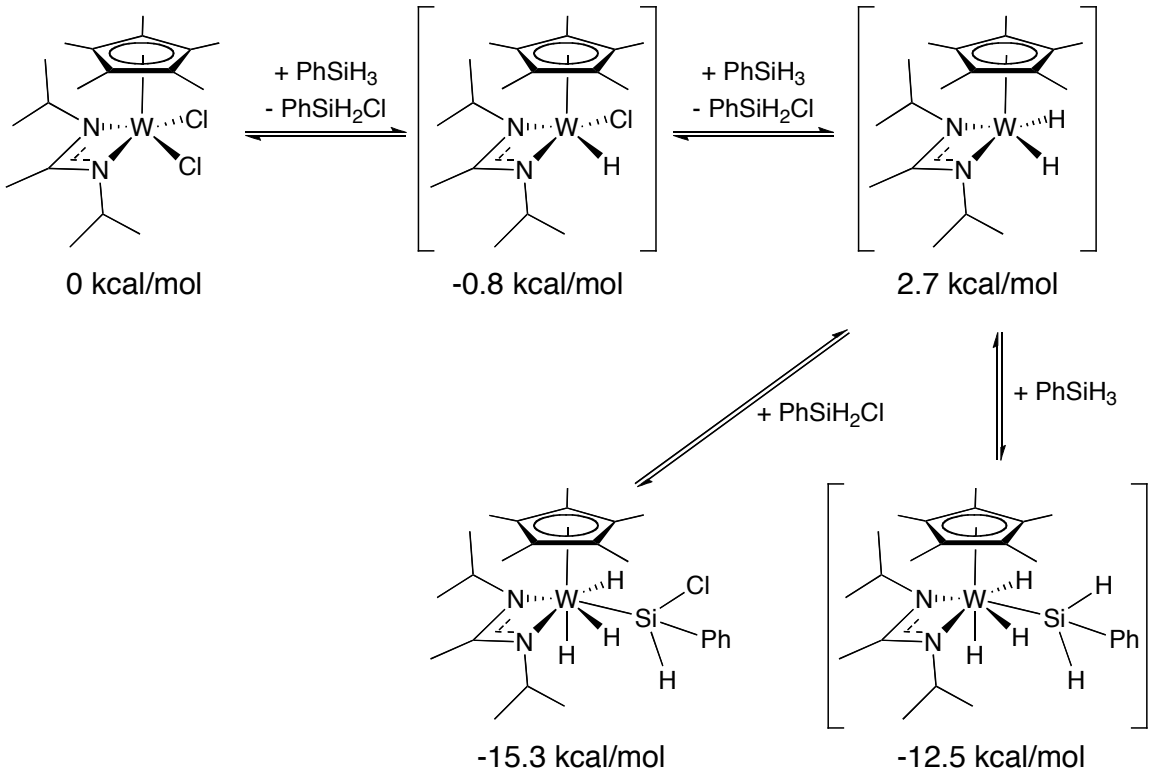
H_c has the strongest interaction with Si. The other two hydride ligands show little Si – H bonding. Donation from the W – H_c bonding orbital to the Si – Cl antibonding orbital was found to be present in the NBO analysis. Additional weak interactions between all W – H bonding orbitals and the W – Si antibonding orbital were identified.

Proposed Mechanism. Several experiments were conducted to probe the reaction mechanism for the formation of a chlorosilyl ligand starting from a primary silane. Under the reaction conditions of eq 1, lower quantities of phenylsilane (2 – 4 equiv) resulted in unreacted **1**, complex **2,** and a side product, Cp*(Am)W$(H)_3(SiPhCl_2)$ (**6**), as determined from an independently synthesized sample. For example, 3 equiv of phenylsilane was found to react with **1** at 80° C for 16 h to give 10% of **1**, 20% of **6**, and 70% of **2** by NMR spectroscopy. The use of 5 equiv or more of phenylsilane cleanly yielded **2**, along with 1 equiv $H_2SiPhCl$ and 3 equiv of unreacted $PhSiH_3$. Complex **1** was heated to 80° C for 24 h with 25 equiv of $PhSiH_3$ to give only **2** and 1 equiv of $PhSiH_2Cl$. Similarly, **1** was heated to 80° C for 24 h with 25 equiv of $PhSiH_2Cl$ to give only **6** and 1 equiv of $PhSiHCl_2$. Thus, the complex with more chloro substituents on the silyl group appears to be the most stable product. Additionally, the formation of strong Si – Cl bonds appears to be a driving force of the reaction. For comparison, the analogous treatment of **1** with 5 equiv $PhGeH_3$ in C_6D_6 for 24 h at 80° C results in no reaction.

The proposed mechanism, detailed in Figure 4, involves a series of Si – H bond oxidative additions and Si – Cl bond reductive eliminations. DFT calculations were performed to determine the thermodynamic stability of each proposed intermediate, taking into account both the complexes and organosilanes. The formation of Cp*(Am)WHCl from **1** and the subsequent formation of Cp*(Am)WH_2 appear to be essentially isoenergetic. Further reaction to form the isolable product **2** is downhill by 15 kcal/mol. Formation of the Cp*(Am)$H_3(SiH_2Ph)$ is calculated to be ca. 3 kcal/mol less favorable than **2**, large enough to explain the exclusive observation of **2**.

Multiple attempts to isolate or observe the Cp*(Am)WH_2 species were undertaken to gain further insight into the formation of **2**. No reaction was observed after heating **1** with an excess of Et_3SiH in C_6D_6 for 24 h at 80° C. Complex **1** was also unreactive towards nBu_3SnH under identical conditions. Conversely, reactions with reagents such as $LiEt_3BH$, $LiAlH_4$, and $NaBH_4$ resulted in complex mixtures of products. Additionally, conversion of **1** to Cp*(Am)WR_2 complexes using MeMgCl, Bn_2Mg, nBuLi, and MeLi resulted in multiple unidentified products. In all experiments, no evidence for the targeted complex was observed.

Figure 4. Proposed mechanism for the formation of complex **2** (relative energies indicated).



Concluding Remarks

In conclusion, a variety W(VI) silyltrihydride complexes are accessable starting from the W(IV) complex, Cp*(Am)WCl_2. Multiple Si – H bond activations are proposed for the formation of such complexes. Limitations of silane activations appear to be driven by steric bulk, and one driving force for the reaction seems to be the formation of Si – Cl bonds. An interligand interaction between one W – H bond and the silyl ligand is observed by NMR spectroscopy and X-ray crystallography – specifically an increased Si – H coupling constant and elongated Si – Cl bond. DFT calculations support the experimental findings. Additionally, Cp*(Am)WH_3(SiHPhCl) undergoes Si – H activation with CPh_3Cl to selectively form Cp*(Am)$WH_3(SiPhCl_2)$. All attempts to synthesize complexes of the type Cp*(Am)WR_2 (R = H, aryl, alkyl) have so far been unsuccessful. Reactions of hydrosilanes in this Cp*(Am)W system appear to be strongly driven to hexavalent hydrido silyl species such as those described above.

Experimental

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene and pentane were dried over Na and distilled under N_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy.

Cp*(Am)WCl_2 (**1**) was prepared according to literature methods.[10] All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^{1}H. ^{31}P{^{1}H} NMR spectra were referenced relative to 85% H_3PO_4 external standard (δ = 0). ^{13}C{^{1}H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For ^{13}C{^{1}H} NMR spectra, resonances obscured by the solvent signal are omitted. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^{1}H ^{29}Si HMBC unless specified otherwise. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

Cp*(Am)W(H)$_3$(SiHPhCl) (2). To a 20 mL toluene solution of Cp*(Am)WCl_2 (0.100 g, 0.188 mmol) was added an excess of phenylsilane (0.108 g, 1.00 mmol). The reaction mixture was stirred at 80° C for 24 h, after which the resulting transparent brown solution was evacuated to dryness. The remaining brown residue was then dissolved in 15 mL pentane, and the solution was filtered through Celite. The solution was then concentrated to approximately 2 mL and cooled to –35° C. The brown precipitate was isolated by decantation and drying under vacuum to give a light tan solid in 42% yield (0.045 g, 0.079 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.41 (1H, d, J = 5.8 Hz, $^1J_{SiH}$ = 199.5 Hz, Si*H*), 8.16 (2H, d, J = 7.4 Hz, Ar*H*), 7.34 (2H, t, J = 7.4 Hz, Ar*H*), 7.17 (1H, t, J = 7.4 Hz, Ar*H*), 5.24 (1H, m, $^1J_{WH}$ = 34.0 Hz, W*H*), 3.24 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 3.07 (1H, sept, J = 6.5 Hz, C*H*^{i}Pr$_2$), 1.76 (15H, s, C_5*Me$_5$*), 1.26 (3H, s, C*Me*), 1.15 (3H, d, J = 6.5, CH^i*Pr$_2$*), 1.03 (3H, d, J = 6.5, CH^i*Pr$_2$*), 0.92 (1H, dd, J = 4.5 Hz, 9.5 Hz, $^1J_{SiH}$ = 11.1 Hz, $^1J_{WH}$ = 45.8 Hz, W*H*), 0.76 (3H, d, J = 6.5, CH^i*Pr$_2$*), 0.58 (3H, d, J = 6.5, CH^i*Pr$_2$*), -1.28 (1H, m, $^1J_{SiH}$ = 24.6 Hz, $^1J_{WH}$ = 47.6 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.9 (*C*Me), 151.7 (Ar*C*), 133.24 (Ar*C*), 127.9 (Ar*C*), 129.1 (Ar*C*), 103.0 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr$_2$*), 24.9 (CH^i*Pr$_2$*), 23.9 (CH^i*Pr$_2$*), 23.8 (CH^i*Pr$_2$*), 15.2 (C*Me*), 10.6 (C_5*Me$_5$*). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 43.9. Anal. Calcd for $C_{24}H_{41}N_2ClSiW$: C, 47.65; H, 6.84; N, 4.63. Found: C, 47.54; H, 6.91; N, 4.57.

Cp*(Am)W(H)$_3$(SiH(Tolyl)Cl) (3). By a procedure analogous to that for **2**, complex **3** was obtained as a light tan solid in 34% yield (0.040 g, 0.065 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.44 (1H, d, J = 5.9 Hz, $^1J_{SiH}$ = 198.0 Hz, Si*H*), 8.14 (2H, d, J = 7.8 Hz, Ar*H*), 7.21 (2H, d, J = 7.8 Hz, Ar*H*), 5.35 (1H, m, $^1J_{SiH}$ = 14.4 Hz, $^1J_{WH}$ = 35.4 Hz, W*H*), 3.29 (1H, sept, J = 6.6 Hz, C*H*^{i}Pr$_2$), 3.16 (1H, sept, J = 6.6 Hz, C*H*^{i}Pr$_2$), 2.21 (3H, s, ArC*H$_3$*), 1.81 (15H, s, C_5*Me$_5$*), 1.32 (3H, s, C*Me*), 1.18 (3H, d, J = 6.6, CH^i*Pr$_2$*), 1.07 (3H, d, J = 6.6, CH^i*Pr$_2$*), 0.95 (1H, dd, J = 5.1 Hz, 9.5 Hz, $^1J_{SiH}$ = 9.3 Hz, $^1J_{WH}$ = 32.2 Hz, W*H*), 0.83 (3H, d, J = 6.6, CH^i*Pr$_2$*), 0.68 (3H, d, J = 6.6, CH^i*Pr$_2$*), -1.15 (1H, m, $^1J_{SiH}$ = 26.5 Hz, $^1J_{WH}$ = 47.3 Hz, W*H*). ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz): 173.8 (*C*Me), 148.2 (Ar*C*), 136.8 (Ar*C*), 133.5 (Ar*C*), 127.9 (Ar*C*), 102.9 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr$_2$*), 25.1 (CH^i*Pr$_2$*), 24.0 (CH^i*Pr$_2$*), 23.9 (CH^i*Pr$_2$*), 21.0 (Ar*C*H$_3$), 15.2 (C*Me*), 10.7 (C_5*Me$_5$*). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 43.2. Anal. Calcd for $C_{26}H_{45}N_2ClSiW$: C, 48.51; H, 7.00; N, 4.53. Found: C, 49.01; H, 6.68; N, 3.94.

Cp*(Am)W(H)$_3$(SiH(Xylyl)Cl) (4). By a procedure analogous to that for **2**, complex **4** was obtained as a light tan solid in 37% yield (0.041 g, 0.069 mmol). ^{1}H NMR (C_6D_6, 600 MHz): δ 8.43 (1H, d, J = 6.0 Hz, $^1J_{SiH}$ = 198.1 Hz, Si*H*), 7.88 (2H, s, Ar*H*), 6.67 (1H, s, Ar*H*),

5.39 (1H, m, $^1J_{SiH}$ = 7.8 Hz, $^1J_{WH}$ = 36.7 Hz, W*H*), 3.28 (1H, sept, *J* = 6.5 Hz, C*H*^{i}Pr$_2$), 3.19 (1H, sept, *J* = 6.5 Hz, C*H*^{i}Pr$_2$), 2.28 (6H, s, ArC*H*$_3$), 1.81 (15H, s, C$_5$*Me*$_5$), 1.34 (3H, s, C*Me*), 1.20 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 1.07 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 0.92 (1H, dd, *J* = 5.5 Hz, 10.4 Hz, $^1J_{SiH}$ = 7.4 Hz, $^1J_{WH}$ = 35.4 Hz, W*H*), 0.86 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 0.78 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), -1.11 (1H, m, $^1J_{SiH}$ = 31.9 Hz, $^1J_{WH}$ = 46.3 Hz, W*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 173.7 (*C*Me), 151.1 (Ar*C*), 135.7 (Ar*C*), 131.4 (Ar*C*), 129.4 (Ar*C*), 102.9 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.1 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 25.0 (CH^i*Pr*$_2$), 24.0 (CH^i*Pr*$_2$), 22.9 (CH^i*Pr*$_2$), 21.29 (Ar*C*H$_3$), 21.27 (Ar*C*H$_3$), 15.3 (C*Me*), 10.6 (C$_5$*Me*$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 43.3. Anal. Calcd for $C_{26}H_{45}N_2ClSiW$: C, 49.33; H, 7.17; N, 4.43. Found: C, 49.37; H, 7.18; N, 4.22.

Cp*(Am)W(H)$_3$(SiH(C$_6$F$_5$)Cl) (5). By a procedure analogous to that for **2**, complex **5** was obtained as a light tan solid in 35% yield (0.046 g, 0.0696 mmol). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 8.52 (1H, br s, $^1J_{SiH}$ = 215.5 Hz, Si*H*), 4.74 (1H, m, $^1J_{SiH}$ = 22.7 Hz, $^1J_{WH}$ = 35.9 Hz, W*H*), 3.18 (1H, sept, *J* = 6.5 Hz, C*H*^{i}Pr$_2$), 2.99 (1H, sept, *J* = 6.5 Hz, C*H*^{i}Pr$_2$), 1.73 (15H, s, C$_5$*Me*$_5$), 1.23 (3H, s, C*Me*), 1.10 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 0.98 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 0.66 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), 0.58 (1H, m, $^1J_{SiH}$ = 10.6 Hz, $^1J_{WH}$ = 39.9 Hz, W*H*), 0.45 (3H, d, *J* = 6.5, CH^i*Pr*$_2$), -1.61 (1H, m, $^1J_{SiH}$ = 21.6 Hz, $^1J_{WH}$ = 45.8 Hz, W*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 174.9 (*C*Me), 128.2 (Ar*C*), 127.9 (Ar*C*), 127.5 (Ar*C*), 103.6 (*C*$_5$Me$_5$), 49.4 (*C*H^{i}Pr$_2$), 48.6 (*C*H^{i}Pr$_2$), 25.1 (CH^i*Pr*$_2$), 24.4 (CH^i*Pr*$_2$), 23.6 (CH^i*Pr*$_2$), 23.5 (CH^i*Pr*$_2$), 14.9 (C*Me*), 10.5 (C$_5$*Me*$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 22.1. Anal. Calcd for $C_{24}H_{36}N_2ClFSiW$: C, 41.48; H, 5.22; N, 4.03. Found: C, 41.67; H, 5.13; N, 3.78.

Cp*(Am)W(H)$_3$(SiPhCl$_2$) (6). By a procedure analogous to that for **2**, complex **6** was obtained as a light green solid in 27% yield (0.040 g, 0.063 mmol). ^{1}H NMR (C$_6$D$_6$, 600 MHz): δ 8.38 (2H, d, *J* = 7.5 Hz, Ar*H*), 7.34 (2H, t, *J* = 7.5 Hz, Ar*H*), 7.09 (1H, t, *J* = 7.4 Hz, Ar*H*), 4.61 (1H, t, *J* = 8.5, $^1J_{SiH}$ = 9.9 Hz, $^1J_{WH}$ = 25.7 Hz, W*H*), 3.16 (2H, sept, *J* = 7.0 Hz, C*H*^{i}Pr$_2$), 1.87 (15H, s, C$_5$*Me*$_5$), 1.19 (3H, s, C*Me*), 1.05 (2H, d, *J* = 8.5, $^1J_{SiH}$ = 17.8 Hz, $^1J_{WH}$ = 32.8 Hz, W*H*), 0.89 (12H, ov dd, *J* = 7.0, CH^i*Pr*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz): 173.9 (*C*Me), 151.7 (Ar*C*), 133.24 (Ar*C*), 127.9 (Ar*C*), 129.1 (Ar*C*), 103.0 (*C*$_5$Me$_5$), 49.3 (*C*H^{i}Pr$_2$), 49.0 (*C*H^{i}Pr$_2$), 25.5 (CH^i*Pr*$_2$), 24.9 (CH^i*Pr*$_2$), 23.9 (CH^i*Pr*$_2$), 23.8 (CH^i*Pr*$_2$), 15.2 (C*Me*), 10.6 (C$_5$*Me*$_5$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 47.8. Anal. Calcd for $C_{24}H_{40}N_2Cl_2SiW$: C, 45.08; H, 6.31; N, 4.38. Found: C, 45.80; H, 6.24; N, 3.98.

X-ray Crystallography. The X-ray analysis of **2** was carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on an APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Data was integrated and empirical absorption corrections were made using the APEX2 program package. The structure as solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Computational Details. All calculations were performed in the molecular graphics and computing facility of the College of Chemistry, University of California, Berkeley (NSF grant CHE-0233882). Calculations were performed using the Gaussian '09 suite of programs[28] at the B3LYP/LANL2DZ level of theory with LANL2DZdp ECP polarization functions for W.[29] The crystal structures of **1** and **2** were used as starting geometries. Vibrational frequencies were

calculated for all converged structures and confirm that these structures lie on a minimum. Graphical representations of the structures were generated using Mercury. The natural bond orbital (NBO) program in Gaussian 03 was utilized to determine the presence of a significant interaction between the W – H bonding orbital and the Si – Cl antibonding orbital.

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Chapter 7

Unusual Ruthenium Hydride Complexes Supported by the [N(2-PPh_2-4-Me-C_6H_3)$_2$] Pincer Ligand

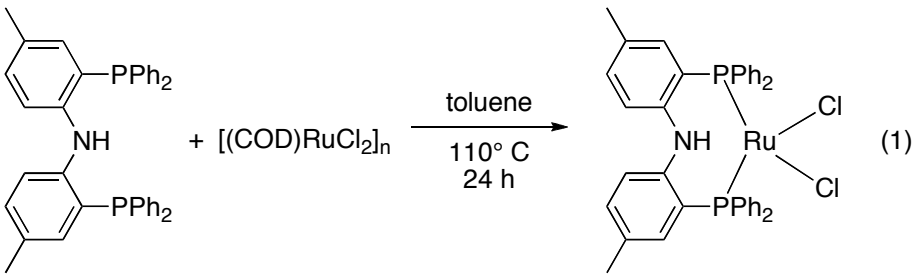
Introduction

Transition metal complexes supported by multiple hydride and dihydrogen ligands have been of considerable interest since stable non-classical hydrides were first isolated by Kubas and co-workers in 1984.[1-6] A number of such complexes have been synthesized, with a particular focus on the Group 8 metals.[7] The characterization of dihydrogen complexes can be based on a variety of experiments, including T_1 measurements, determination of $J_{H\text{-}D}$ coupling constants, and neutron diffraction.[8-11] However, a continuum of possible structures exist, ranging from dihydrogen ligands to dihydrides, making exact classification and determination both difficult and subjective.[4,7] Additionally, recent calculations suggest that many dihydrogen structures are nearly equal in energy to dihydride structures, with a very low energy barrier between the two, which can make it difficult to assign a definitive structure.[12,13]

This group has long been interested in silyl and silylene ligands on transition metal complexes.[14] Recent success with PNP pincer ligands on Ir and Rh sparked an interest in exploration of related chemistry on Ru, a metal that has supported a number of interesting silylene complexes.[15-17] Within these contexts, we envisioned a (PNP^{Ph})$RuH(H_2)$ (PNP^{Ph} = [$^-$N(2-PPh_2-4-Me-C_6H_3)$_2$]) complex, analogous to the (PNP^{iPr})$RuH(H_2)$ complex reported by Ozerov and co-workers,[18] to be a suitable starting material for reactions with organosilanes. However, we found that attempts to prepare a ruthenium hydride complex supported by PNP^{Ph} resulted in an unusual bimetallic complex with non-classical H_2/$(H)_2$ ligands. While a large number of H_2 complexes have been reported, a much smaller number of dinuclear species have been observed.[19-24] Herein we report the synthesis and characterization of this dimer and its reactions with Lewis bases.

Results and Discussion

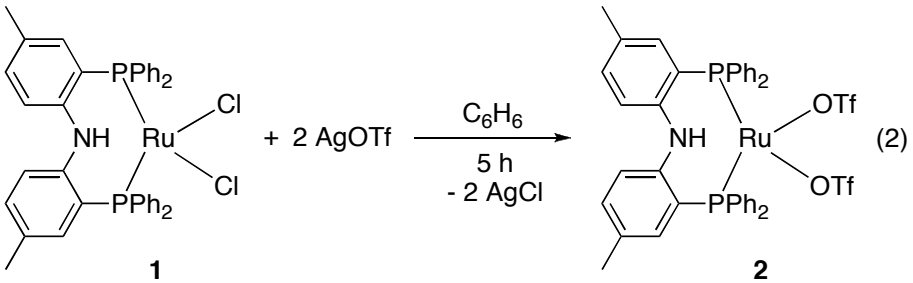
Synthesis of Ru(II) complexes supported by $PNP^{Ph}H$. The reaction of 1 equiv of $PNP^{Ph}H$ with 1 equiv of $[(COD)RuCl_2]_n$ in toluene at 110° C for 24 h produced ($PNP^{Ph}H$)$RuCl_2$ (**1**) as an orange solid in 85% yield (eq 1). The ^{1}H NMR spectrum displays at broad singlet at 9.51 ppm for the intact amine resonance and a single methyl resonance at 2.24 ppm for the ligand. The $^{31}P\{^1H\}$ NMR spectrum possesses a single resonance for the PNP ligand at 65.6 ppm, indicating the presence of equivalent phosphorus groups. The infrared spectrum of the complex exhibits a broad ν(N-H) band at 3015 cm^{-1}. The analogous $[(PNP^{iPr}H)RuCl_2]_n$ complex synthesized by Ozerov and co-workers was found to be an insoluble coordination polymer, [18] while **1** was found to be soluble in halogenated solvents such as $CHCl_3$, CH_2Cl_2, and C_6H_5F. However, reactions of **1** with reagents such as MeLi, nBuLi, $LiN(SiMe_3)_2$, and LDA in THF resulted in multiple unidentifiable products. Complex **1** did not react with silanes such as $PhSiH_3$, Ph_2SiH_2, and Et_3SiH at 80 ºC for 2 days in C_6D_6 or C_6D_5Br.



(1)

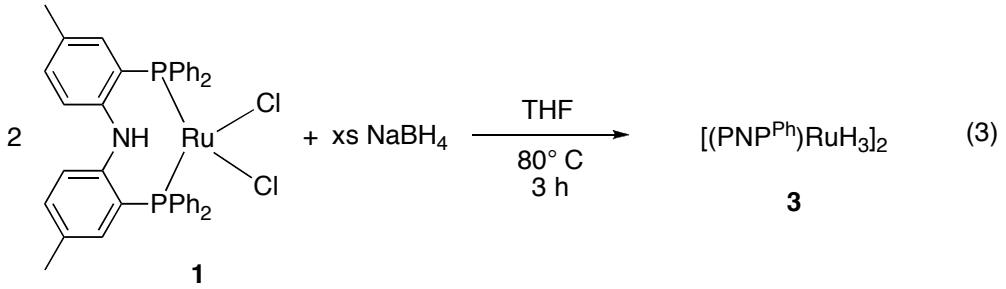
1

Treatment of **1** with 2 equiv of AgOTf in benzene in the absence of light resulted in the formation of $(PNP^{Ph}H)Ru(OTf)_2$ (**2**) as a light yellow solid in 65% yield (eq 2). The ^1H NMR spectrum displays a broad singlet at a downfield resonance of 11.72 ppm for the amine, and a broad ν(N-H) band at 3374 cm^{-1} was observed by infrared spectroscopy. A single methyl resonance is observed for the ligand backbone at 1.68 ppm, indicating a symmetric arrangement of the ligand about the Ru center. The $^{31}P\{^1H\}$ NMR spectrum reveals an upfield shift for the PNP^{Ph} ligand to 48.1 ppm. In contrast to **1**, complex **2** was found to be soluble in both polar and nonpolar solvents, allowing for reactivity studies with various alkylating reagents and silanes. Reactions to derivatize **2** with reagents like $Bn_2Mg\bullet(Et_2O)_n$, MeLi, or LDA were found to be unproductive due to rapid conversion of complex mixtures of unidentified products. Reactions of the organosilanes $MesSiH_3$ and Ph_3SiH with **2** did not proceed even with heating at 80 ºC for 3 days.



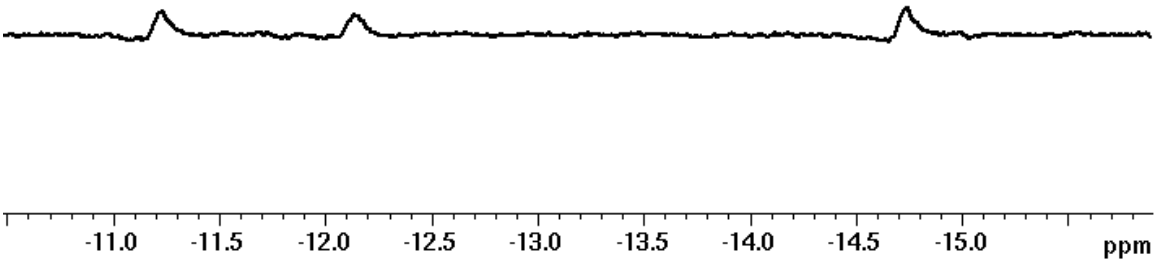
1 **2** (2)

Synthesis and Characterization of $[(PNP^{Ph})RuH_3]_2$. The reaction of **1** with an excess of $NaBH_4$ in THF at 80° C for 3 h generated a new complex (**3**) in high yield as a red-brown solid (eq 3). Complex **3** exhibits good stability at room temperature under N_2 in both the solid state and in solution. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** indicate that the PNP^{Ph} ligand lies on a plane of symmetry, with one methyl resonance observed at 2.27 ppm and only one phosphorus resonance appearing at 56.1 ppm. Interestingly, the ^1H NMR spectrum of **3** possesses three chemically inequivalent upfield hydride resonances at -12.08, -13.17, and -15.55 ppm, each of which integrate to one with respect to the methyl groups on the ligand. These hydride resonances are broad and exhibit no splitting due to coupling to phosphorus nuclei. Additionally, H-H coupling is not observed due to the broadness of the resonances (width at half height = 34 Hz). The inequivalent resonances are surprising because they seem to indicate that full oxidative addition of an H_2 ligand has taken place to give a Ru(IV) trihydride complex. In contrast, $(PNP^{iPr})RuH(H_2)$ displays a single broad resonance in the hydride region integrating to 3 and resulting from exchange of the hydride and H_2 ligand.[25] The ^1H NMR spectra of **3** (Figure 1) observed at temperatures ranging from -90° C to 80° C exhibited neither sharpening nor coalescence of all three hydride resonances. Using the inversion recovery method, the average T_1 relaxation times were found to be 115 ms for each hydride, which is longer than expected for a dihydrogen ligand.[7] ^{11}B NMR spectroscopy supports the absence of any borohydride ligands in **3**.



The gross connectivity in **3** was determined by X-ray crystallography, with dark red needles grown by vapor diffusion of heptane into a toluene solution of **3** at room temperature over one week. Due to poor crystallinity, the X-ray data is not of sufficient quality to report accurate bond distances and angles; however, general comments on the structure of **3** can be made. Complex **3** is a dimeric species consisting of two Ru atoms, two PNP ligands, and therefore six hydride-like ligands (not located crystallographically). The Ru – Ru distance of 2.6 Å is typical of two Ru atoms bridged by hydride ligands. The pincer ligand is bound to the metal in a facial arrangement rather than the more common meridinal binding. The angles around the N atom of the ligand sum to 360°. An empty coordination site is located *trans* to the N atom of each PNP ligand, presumably filled by a hydride ligand.

Figure 1. Upfield region of ^{1}H NMR spectrum of **3** at 300 K.



DFT studies at the B3LYP/LANL2DZ level of theory were undertaken to provide further insight into the geometric structure of **3** and the optimized DFT structure is designated as **3***. The connectivity found via X-ray analysis was utilized as a starting point, and different arrangements of the hydride ligands were examined. No PNP^{Ph} ligand simplifications were made. The geometries of a number of structures were optimized, and all converged to the same structure, represented by **3*** in Figure 2. Rather than displaying three hydrides, a non-classical dihydrogen ligand with an H – H bond distance of 0.842 Å is observed. Other bond distances and bond angles of **3*** are consistent with the experimental data (Table 1).

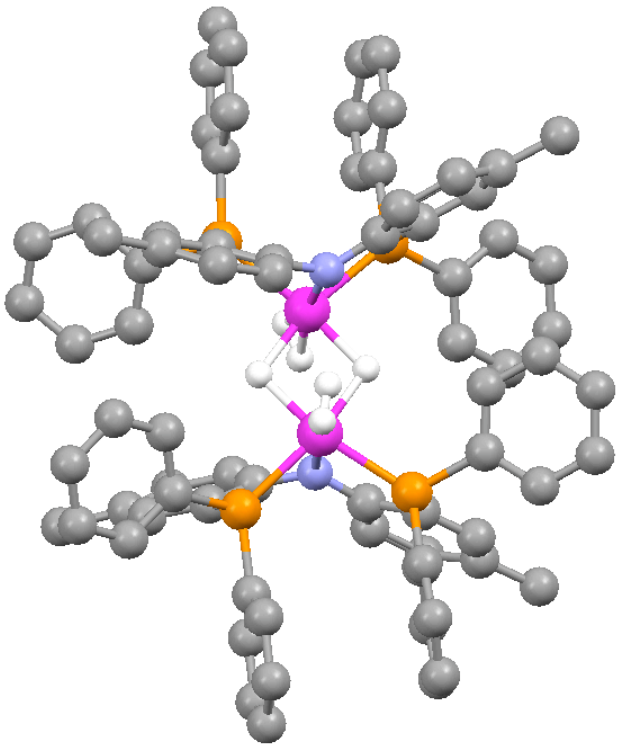
Table 1. Selected Bond Distances in Å of **3***

Ru(1) – P(1)	2.3595	Ru(2) – P(3)	2.3590
Ru(1) – P(2)	2.3249	Ru(2) – P(4)	2.3274
Ru(1) – N(1)	2.1372	Ru(2) – N(2)	2.1380
Ru(1) – H(1a)	1.7506	Ru(2) – H(2a)	1.7564
Ru(1) – H(1b)	1.7570	Ru(2) – H(2b)	1.7501

H(1a) – H(1b)	0.842	H(2a) – H(2b)	0.842
Ru(1) – H(3)	1.8073	Ru(2) – H(3)	1.8108
Ru(1) – H(4)	1.8442	Ru(2) – H(4)	1.8398
Ru(1) – Ru(2)	2.824		

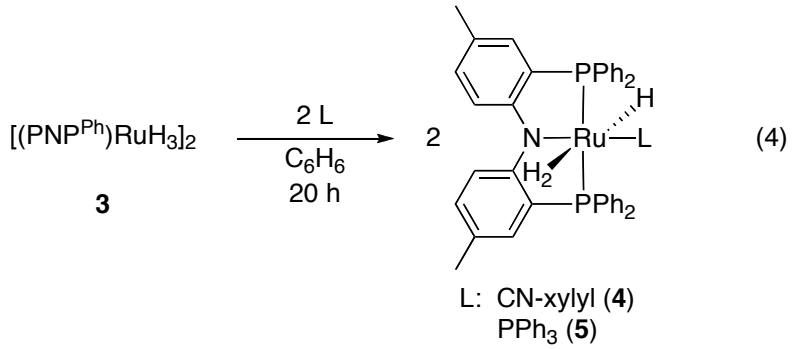
Thus, the computational studies suggest a structure that seems inconsistent with the NMR data in that rapid exchange (e.g., by rotation about the Ru – H_2 bond) would be expected to give rise to one hydride resonance for the H_2 ligand. Although the detailed structure of **3** is yet to be determined, it seems reasonable to conclude that it is a dimeric hydride of the type $[(PNP^{Ph})RuH_3]_2$, involving bridging hydrogen ligands.

Figure 2. Optimized geometry of **3***.



Addition of Lewis Bases to $[(PNP^{Ph})RuH_3]_2$. Reactions of **3** with Lewis bases resulted in $(PNP^{Ph})Ru(H)(H_2)L$, L = (xylyl)isocyanide (**4**) and triphenylphosphine (**5**) (eq 4). The ^1H NMR spectra of **4** and **5** display two new characteristic upfield resonances: a broad peak integrating to two hydrogens (-4.38 and -4.59 ppm, respectively, for **4** and **5**) and a sharp peak at higher field corresponding to one hydrogen that exhibits fine coupling. In the case of **4**, this peak is a triplet (J_{HP} = 20.6 Hz) at -8.80 ppm. For complex **5**, a doublet of triplets (J_{HP} = 21.7, 22.4 Hz) is observed at -9.73 ppm. The small coupling constants to phosphorus indicate that this hydride ligand is *cis* to all P-atoms in each complex. The $^{31}P\{^1H\}$ NMR spectrum of **4** displays a single resonance at 55.6 ppm, while the spectrum of **5** possesses two resonances: a triplet at 71.1 ppm for the PPh_3 ligand and a doublet at 55.3 ppm for the PNP ligand. The P-P coupling

constant of 29.4 Hz is indicative of a *cis* arrangement of the two types of phosphorus donor atoms.



(4)

The T_1 times were measured for **4** and **5**. In complex **4**, the resonance at -4.38 ppm has a T_1 of 100 ms, while the resonance at -8.80 ppm has a T_1 of 300 ms. The T_1 times for **5** follow a similar pattern: 90 ms (-4.59 ppm) and 650 ms (-9.73 ppm). These times are consistent with the integrations, splitting patterns, and the assignment of the downfield resonance (~ 4.5 ppm) to an H_2 ligand and the upfield resonance (~ 9 ppm) to a classical hydride ligand. Both **4** and **5** react rapidly with 1 atm D_2 gas at room temperature to give (PNP)Ru(D)(D_2)L. The ^{1}H NMR spectra were obtained from -30 ºC to 60 ºC, but $J_{H\text{-}D}$ was not observable for either complex. However, a number of ruthenium complexes with a classical hydride ligand *trans* to an H_2 ligand have been documented, with a narrow range of $d_{H\text{-}H}$ values (0.84 to 0.94 Å).[7] The shorter T_1 times for **4** and **5**, as compared to **3**, indicate that the H-H distances in these complexes are similar to those described in the literature for related *trans*-(H_2)(H) complexes.

Conclusion

New Ru hydride complexes supported by a PNP^{Ph} pincer ligand have been obtained. The exact structural nature of the hydride **3** has yet to be determined, but it has been shown to behave as a synthon for the [(PNP^{Ph})RuH_3] fragment. The Ru dimer undergoes attack by a Lewis base to give a monomeric species containing a non-classical H_2 ligand. These complexes represent the first Ru complexes supported by the PNP^{Ph} ligand.

Experimental

General Procedures. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and $NaHCO_3$. Pentane was then dried over $MgSO_4$ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene, toluene, tetrahydrofuran, diethyl ether, dichloromethane, hexanes, and pentane were dried using a VAC Atmospheres solvent purification system. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. Dichloromethane-d_2 was dried by vacuum distillation from CaH_2. PNP^{Ph}H[25] and [(COD)RuCl]$_n$[26] were prepared according to literature methods. All other chemicals were purchased from commercial sources, and used without further purification.

^{1}H, ^{2}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room

temperature and referenced to the residual protonated solvent for ^{1}H. $^{31}P\{^{1}H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{13}C\{^{1}H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For $^{13}C\{^{1}H\}$ NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Infrared spectra were recorded on a Nicolet Nexus 6700 FTIR spectrometer with a liquid-nitrogen-cooled MCT-B detector. Measurements were made at a resolution of 4.0 cm^{-1}.

($PNP^{Ph}H$)$RuCl_2$ (1). A Teflon-stopped flask was charged with $PNP^{Ph}H$ (1.00 g, 1.77 mmol) and $[(COD)RuCl_2]_n$ (0.495 g, 1.77 mmol) followed by 25 mL of toluene. The reaction was heated at 110° for 24 h. The orange precipitate was collected by filtration and dried under vacuum to give **1** as an orange solid (1.10 g, 85% yield). ^{1}H NMR (CD_2Cl_2, 500.0 MHz): δ9.51 (s, 1H, N*H*), 8.16 (d, J_{HH} = 8.2, 2H, Ar*H*), 7.44 (br s, 4H, Ar*H*), 7.37 (d, J_{HH} = 8.2, 2H, Ar*H*), 7.19 (t, J_{HH} = 7.6, 2H, Ar*H*), 7.04 (br s, 2H, Ar*H*), 7.00 – 6.95 (ov m, 6H, Ar*H*), 6.84 (br s, 4H, Ar*H*), 6.66 (t, J_{HH} = 7.6, 4H, Ar*H*), 2.24 (s, 6H, ArCH_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125.9 MHz): δ 154.9, 136.7, 135.3, 132.4, 131.8, 130.6, 128.9, 127.9, 127.2, 126.7, 20.5. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.9 MHz): δ 65.6. IR (cm^{-1}): ν(N-H) 3015. Anal. Calcd. for $C_{38}H_{33}NCl_2P_2Ru$: C, 61.88; H, 4.51; N, 1.90. Found: C, 62.27; H, 4.72; N, 1.88.

($PNP^{Ph}H$)$Ru(OTf)_2$ (2). A flask covered with aluminum foil was charged with **1** (0.100 g, 0.136 mmol) and AgOTf (0.100 g, 2.64 mmol) followed by 10 mL of C_6H_6. The reaction was stirred at room temperature for 5 h, then the green-brown solution was filtered through Celite and evaporated to dryness. The resulting yellow residue was recrystallized from C_6H_6 at room temperature to give **2** as a yellow solid (0.090 g, 65% yield).^{1}H NMR (C_6D_6, 600.0 MHz): δ 11.72 (s, 1H, N*H*), 8.32 (d, J_{HH} = 8.2, 2H, Ar*H*), 7.47 (q, J_{HH} = 7.0, 4H, Ar*H*), 7.34 (t, J_{HH} = 7.4, 4H, Ar*H*), 7.08 – 7.00 (ov m, 8H, Ar*H*), 6.92 – 6.91 (ov m, 6H, Ar*H*), 6.74 (br s, 2H, Ar*H*), 1.68 (s, 6H, ArCH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 150.9 MHz): δ 139.8, 134.5, 133.5, 132.3, 131.6, 131.4, 130.9, 129.6, 129.2, 19.9. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz): δ 48.1. IR (cm^{-1}): ν(N-H) 3374. Anal. Calcd. for $C_{40}H_{33}NF_6O_6P_2S_2Ru$: C, 49.79; H, 3.45; N, 1.45. Found: C, 50.07; H, 3.36; N, 1.18.

[(PNP^{Ph})RuH_3]$_2$ (3). A flask was charged with **1** (0.100 g, 0.136 mmol) and $NaBH_4$ (0.100 g, 2.64 mmol) followed by 25 mL of THF. The reaction was stirred at 80° for 3 h, then the brown solution was reduced *in vacuo* and the resulting dark brown residue was dissolved in 10 mL of C_6H_6. The brown solution was filtered through Celite and the volatile material was removed under vacuum to give **3** as a red-brown solid (0.088 g, 96% yield). ^{1}H NMR (C_6D_6, 400.0 MHz): δ 7.93 – 7.88 (ov m, 4H, Ar*H*), 7.77 (dt, J_{HH} = 8.4, J_{HP} = 2.4, 2H, Ar*H*), 7.84 – 7.45 (ov m, 6H, Ar*H*), 7.33 – 7.26 (ov m, 6H, Ar*H*), 7.20 (ov m, 6H, Ar*H*), 7.15 (d, J_{HH} = 8.4 Hz, 2H, Ar*H*), 2.27 (s, 6H, ArCH_3), -12.08 (s, 1H, Ru-*H*), -13.17 (s, 1H, Ru-*H*), -15.55 (s, 1H, Ru-*H*). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125.9 MHz): δ 161.9 (t, J_{PC} = 8.8), 137.0, 136.7 (t, J_{PC} = 22.9), 136.3 (t, J_{PC} = 3.0), 135.9 (t, J_{PC} = 7.4), 135.5 (t, J_{PC} = 21.7), 135.1 (t, J_{PC} = 5.5), 131.9, 131.8, 130.8, 130.1, 130.0 (t, J_{PC} = 5.0), 129.4 (t, J_{PC} = 4.7), 124.0 (t, J_{PC} = 4.9), 21.9. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 161.9 MHz): δ 56.1. Anal. Calcd. for $C_{76}H_{70}N_2P_4Ru_2$: C, 68.25; H, 5.28; N, 2.09. Found: C, 69.16; H, 5.49; N, 1.89.

(PNP^{Ph})RuH(H_2)(XylNC) (4). A solution of xylylisocyanide (0.018 g, 0.14 mmol) in 1 mL of toluene was added to a solution of **3** (0.092 g, 0.07 mmol) in 1 mL of toluene and the resulting solution was stirred for 20 h. The reaction mixture was filtered and dried under vacuum to give **4** as a brown solid (0.096 g, 87% yield). ^{1}H NMR (C_6D_6, 400.0 MHz): δ 8.15 (m, 4H, Ar*H*), 8.02 (m, 2H, Ar*H*), 7.83 (d, 2H, J_{HH} = 8.5 Hz, Ar*H*), 7.30 (m, 2H, Ar*H*), 7.06 (ov m, 6H, Ar*H*), 6.94 (m, 6H, Ar*H*), 6.74 (d, 2H, J_{HH} = 8.5 Hz, Ar*H*), 6.69 (m, 3H, Ar*H*), 1.94 (s, 6H, ArCH_3), 1.90 (s, 6H, ArCH_3), -4.38 (br s, 2H, Ru-H_2) , -8.80 (t, 1H, J_{HP} = 20.6 Hz, Ru-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.9 MHz): δ169.0, 136.6, 133.5, 131.8, 129.7, 129.1, 128.9, 124.6, 123.8, 123.0, 108.1, 19.9, 18.5. ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz): δ 55.6. IR (cm^{-1}): ν(Ru-H) 2040, 2010; ν(Ru-H_2) 1586. Anal. Calcd. for $C_{47}H_{44}N_2P_2Ru$: C, 70.57; H, 5.54; N, 3.50. Found: C, 69.59; H, 5.56; N, 3.57.

(PNP^{Ph})RuH(H_2)(PPh_3) (5). A solution of triphenylphosphine (0.037 g, 0.14 mmol) in 1 mL of toluene was added to a solution of **3** (0.092 g, 0.07 mmol) in 1 mL of toluene and the resulting solution was stirred for 24 h. The reaction mixture was filtered and dried under vacuum to give **5** as a brown solid (0.098 g, 76% yield). ^{1}H NMR (C_6D_6, 400.0 MHz): δ 7.86 (d, 2H, J_{HH} = 8.3 Hz, Ar*H*), 7.57 (m, 6H, Ar*H*), 7.50 (t, 6H, J_{HH} = 8.3 Hz, Ar*H*), 6.97 (m, 6H, Ar*H*), 6.90 (t, 10H, Ar*H*), 6.81 (t, 5H, J_{HH} = 7.0 Hz, Ar*H*), 6.69 (m, 6H, Ar*H*), 1.82 (s, 6H, ArCH_3), -4.59 (s, 2H, Ru-H_2), -9.73 (dt, 1H, J_{HP} = 21.7, 22.4 Hz, Ru-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.9 MHz): δ 160.7, 139.6, 139.3, 134.6, 134.5, 134.4, 133.7, 133.2, 133.0, 133.9, 131.1, 129.0, 128.4, 126.8, 126.7, 122.9, 67.4, 25.4. ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz): δ 71.13 (t, J_{PP} = 29.4 Hz), 55.3 (d, J_{PP} = 29.4 Hz). IR (cm^{-1}): ν(Ru-H) 1957, 1913; ν(Ru-H_2) 1579. Anal. Calcd. for $C_{56}H_{50}NP_3Ru$: C, 72.25; H, 5.41; N, 1.50. Found: C, 69.62; H, 5.61; N, 1.49. The low value observed for carbon may be due to incomplete combustion of the complex during analysis; alternatively, it may reflect a small amount of impurity that is not observed by NMR spectroscopy.

X-ray Structure Determination. The X-ray analysis of **3** was carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements were made on an APEX-II CCD area detector with a HELIOS multilayer mirrors monochromating device using Cu Kα radiation (λ = 1.54184 Å). Data was integrated and empirical absorption corrections were made using the APEX2 program package. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions.

Computational Details of 3*. All calculations were performed in the molecular graphics and computing facility of the College of Chemistry, University of California, Berkeley (NSF grant CHE-0233882). Calculations were performed using the Gaussian '03 suite of programs[27] at the B3LYP/LANL2DZ level of theory with LANL2DZdp ECP polarization functions for Ru.[28] Vibrational frequencies were calculated for all converged structures and confirm that these structures lie on a minimum. Graphical representations of the structures were generated using Mercury.

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