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Silicon−Hydrogen Bond Activation and Formation of Silane Complexes Using a Cationic Rhodium(III) Complex

Felicia L. Taw,[†] Robert G. Bergman,*[,‡] and Maurice Brookhart*[,†]

Department of Chemistry, University of North Carolina at Chapel Hill, CB #3290,
Chapel Hill, North Carolina 27599-3290, and Department of Chemistry,
University of California, and Division of Chemical Sciences,
Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

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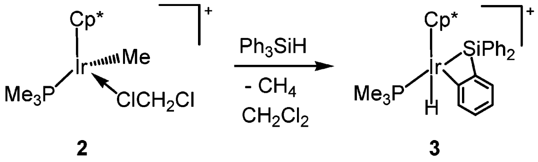
Addition of triphenylsilane, trimethylsilane, or triethylsilane to $[Cp^*(PMe_3)Rh(Me)(CH_2Cl_2)]BAr'_4$ (**4**), a cationic Rh(III) complex, resulted in Si−H bond activation and release of methane below −80 °C. The rare, nonclassical silane complexes $[Cp^*(PMe_3)Rh((C_6H_4)(\eta^2\text{-}HSiPh_2))]BAr'_4$ (**6**), $[Cp^*(PMe_3)Rh(SiMe_3)(\eta^2\text{-}HSiMe_3)]BAr'_4$ (**9**), and $[Cp^*(PMe_3)Rh(SiEt_3)(\eta^2\text{-}HSiEt_3)]BAr'_4$ (**11**) have been generated and characterized by NMR spectroscopy. Of note was the presence of ^{29}Si satellites of the hydride resonances of each of these compounds and large $^1J_{Si-H}$ coupling constants (56−84 Hz), diagnostic of the presence of η^2-silane ligands.

Introduction

The activation of an Si−H bond is one of the key steps in hydrosilation and other catalytic reactions.[1] Nearly all of the transition metals have been shown to undergo reactions with silanes, by either activating an Si−H bond via oxidative addition to form hydrido silyl complexes or coordinating the silane in an η^2 fashion to form σ complexes.[2] Numerous examples of neutral transition-metal η^2-silane complexes can be found in the literature, but cationic analogues are quite rare. Only a few examples of stable cationic silane complexes have been reported.[3] The paucity of these types of compounds has been attributed to their propensity to undergo heterolytic cleavage of the Si−H bond.[4]

While there are copious examples of classical rhodium hydrido silyl complexes, nonclassical rhodium silane compounds are rare.[2b] In an early report of such a system, Perutz and co-workers characterized $CpRh(SiMe_3)_2(\eta^2\text{-}HSiEt_3)$ (**1**) as an η^2-silane complex based on a J_{Si-H} coupling constant of 24.3 Hz.[5] Typically, nonclassical silane complexes exhibit J_{Si-H} coupling constants of 20 Hz to an upper limit of 200 Hz, in contrast to classical silyl hydride complexes, which generally exhibit J_{Si-H} values of <10 Hz.[2e] As further support for the structural assignment of **1**, a value of 17.9 Hz was measured for J_{Rh-Si} for the $SiEt_3$ moiety versus a value of 26.6 Hz for J_{Rh-Si} of the $SiMe_3$ ligands, indicating a stronger Rh−Si interaction with the trimethylsilyl groups.[5]

Scheme 1



Bergman and co-workers have reported the Si−H activation of triphenylsilane using $[Cp^*(PMe_3)Ir(Me)(CH_2Cl_2)]BAr'_4$ (**2**; Ar′ = 3,5-$(CF_3)_2C_6H_3$).[6] Treatment of a dichloromethane solution of **2** with triphenylsilane resulted in formation of a four-membered Ir(V) metallacycle (**3**), via Si−H activation, release of methane, and subsequent intramolecular C−H activation of an aryl ring (Scheme 1). Assignment of complex **3** as an Ir(V) species was based upon NMR data and X-ray crystal structure studies.

Herein, we report the Si−H bond activation of triaryl- and trialkylsilanes using the previously reported complex $[Cp^*(PMe_3)Rh(Me)(CH_2Cl_2)]BAr'_4$ (**4**).[7] The products of these reactions, cationic Rh silyl and silane complexes, have been characterized by NMR spectros-

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[†] University of North Carolina at Chapel Hill.

[‡] University of California and Lawrence Berkeley National Laboratory.

(1) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysts: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1992.

(2) For recent reviews, see: (a) Lin, Z. *Chem. Soc. Rev.* **2002**, *31*, 239. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175 (and references therein). (c) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068. (d) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21. (e) Schubert, U. *Adv. Organomet. Chem.* **1990**, 30, 151.

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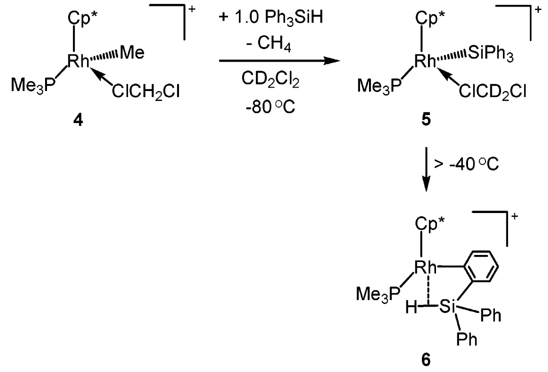
Scheme 2



copy and have been shown to adopt formal +3 oxidation states at rhodium, in contrast to the Ir(V) system (complex **3**) shown in Scheme 1.

Results and Discussion

Activation of Triphenylsilane. When 1 equiv of triphenylsilane was added to a CD_2Cl_2 solution of Rh methyl complex **4**, Si−H activation and release of methane occurred. Monitoring this reaction by low-temperature NMR spectroscopy revealed that activation of the silane transpired below −80 °C, to give $[Cp^*(PMe_3)Rh(SiPh_3)(CD_2Cl_2)]BAr'_4$ (**5**; Scheme 2), which was the only observed species in the range of −80 to −40 °C.[8] Upon warming to −30 °C, a new product appeared which we have formulated as a Rh aryl silane complex, $[Cp^*(PMe_3)Rh((C_6H_4)(\eta^2\text{-}HSiPh_2))]BAr'_4$ (**6**; Scheme 2).

At room temperature, complex **6** is formed in ∼90% yield ($t_{1/2}$ of ∼15 min), as assessed by integrating its ^{1}H NMR resonances against the invariant BAr'_4 peaks. The ^{1}H NMR spectrum of **6** revealed a hydride resonance at δ −8.95 ppm, which appeared as a doublet of doublets due to coupling to both ^{103}Rh and ^{31}P nuclei ($^2J_{P-H}$ = 11.5 Hz, $^1J_{Rh-H}$ = 27.8 Hz; Figure 1). In addition, ^{29}Si satellites were detected, which provided a $^1J_{Si-H}$ value of 84 Hz. This value is typical of η^2-silane complexes[2e] and strongly suggests a σ(Si−H) interaction with Rh(III) in **6**, as shown in Scheme 2. Integration of these satellite signals (4.8% relative to the parent doublet of doublets) supports their assignment as ^{29}Si (4.7% natural abundance) satellites.[9] In addition to the ^{1}H NMR data, a $^{13}C\{^1H\}$ NMR spectrum of **6** revealed a doublet of doublets at δ 154.0 ppm ($^2J_{P-C}$ = 18.3 Hz, $^1J_{Rh-C}$ = 28.1 Hz), which is diagnostic of the ipso carbon of an aryl ring that is bound directly to rhodium.

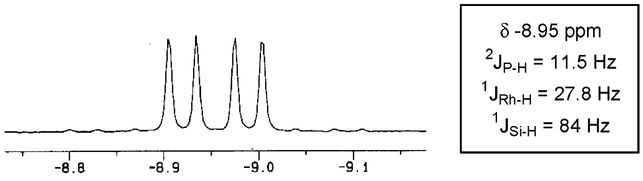


Figure 1. Hydride region of a ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 25 °C) of **6**.

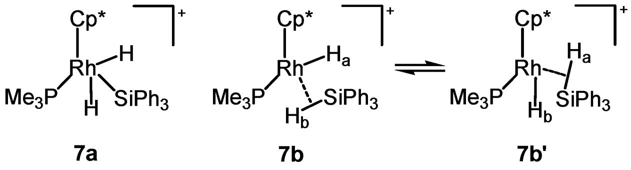
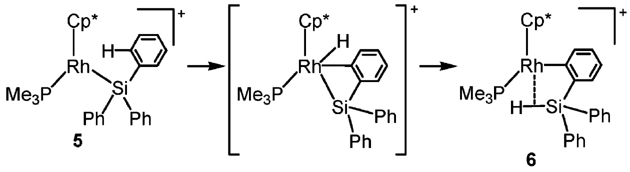


Figure 2. Possible structures for "$[Cp^*(PMe_3)Rh(H)_2(SiPh_3)]^+$" (**7**).

Scheme 3



The behavior of **4** with triphenylsilane provides an interesting contrast to that of Bergman's iridium analogue **2**. As with **2**, activation of a C−H bond at an ortho site of one of the aryl rings occurs, but in the ultimate product **6** the formal +3 oxidation state is retained by formation of a σ complex. A possible mechanistic pathway for conversion of **5** to **6** is shown in Scheme 3 and entails oxidative addition of the C−H aryl bond to form a Rh(V) intermediate followed by reductive elimination of the silyl hydride to form an η^2-Si−H bond (Scheme 3). An alternative mechanism which cannot be excluded is the metathesis of C−H and Rh−Si bonds via a four-center transition state.

Addition of excess triphenylsilane (5.0 equiv) to a CD_2Cl_2 solution of rhodium methyl complex **4** at room temperature again resulted in Si−H activation and release of methane. However, in this case a new product was observed, which can be formulated as $[Cp^*(PMe_3)Rh(H)_2(SiPh_3)]BAr'_4$ on the basis of its ^{1}H NMR spectrum. The hydride region exhibited a signal at δ −10.04 ppm ($^2J_{P-H}$ = 18.0 Hz, $^1J_{Rh-H}$ = 26.8 Hz), which was integrated to two hydrogens relative to the Cp* and PMe_3 ligands. Since the two hydrides appear equivalent by NMR and no ^{29}Si satellites were detected, this product may be characterized as either a classical Rh(V) dihydridosilyl complex, $[Cp^*(PMe_3)Rh(H)_2(SiPh_3)]BAr'_4$ (**7a**), or a nonclassical fluxional Rh(III) hydrido silane complex, $[Cp^*(PMe_3)Rh(H)(\eta^2\text{-}HSiPh_3)]BAr'_4$ (**7b**/**7b′**; Figure 2).

Although no satellite peaks due to coupling to ^{29}Si were observed for the hydride resonance at −10.04 ppm, structure **7b**/**7b′** is not necessarily precluded. Due to rapid site exchange, the observed splitting by ^{29}Si would be an average of $J_{Si-H(terminal)}$ with $J_{Si-H(\eta^2)}$ (e.g., J_{Si-H_a} in **7b** with J_{Si-H_a} in **7b′**). Since $J_{Si-H(terminal)}$ will be ca. 0 Hz, the observed splitting by ^{29}Si would be half the value of $J_{Si-H(\eta^2)}$. Thus, values of $^1J_{Si-H(\eta^2)}$ in the range of 20−30 Hz (consequently, $J_{observed} \approx$ 10−15 Hz) would bring the satellites into the wings of the broad hydride resonance ($\nu_{1/2} \approx$ 50 Hz) and render them difficult to detect.

Addition of 1 equiv of acetonitrile to a CD_2Cl_2 solution of complex **7** at room temperature resulted in immediate loss of silane and generation of $[Cp^*(PMe_3)Rh(H)(NCMe)]BAr'_4$ (**8**), a complex which we have prepared by an independent route (see Experimental Section). Presumably, **7b**/**7b′** must be an energetically accessible species to allow facile displacement of a silane by the nitrile, which leads to rapid formation of **8**.

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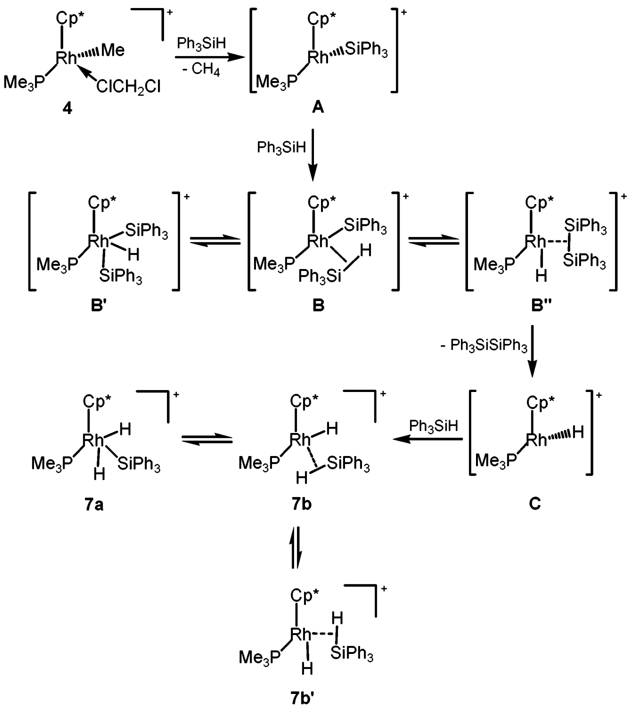
[8] See Experimental Section for ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR data for complex **5**.

[9] Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, Germany, 1993.

Scheme 4



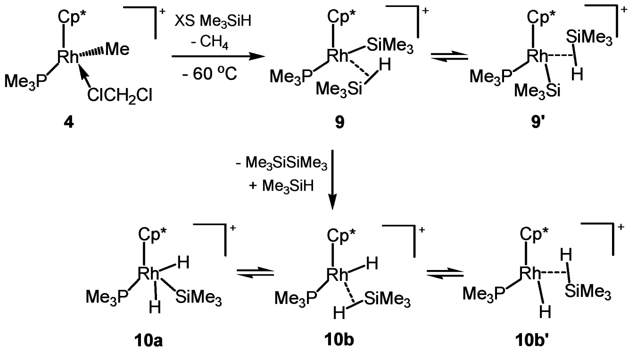
A proposed mechanism for the formation of complex **7** is shown in Scheme 4. Initial Si−H activation of 1 equiv of silane and release of methane forms the transient Rh silyl complex **A**. Excess silane present in the reaction mixture allows the cationic Rh silyl species to be trapped by a second 1 equiv of silane, resulting in a species formulated as $[Cp^*(PMe_3)Rh(H)(SiPh_3)_2]^+$ (**B** or **B′**; not observed by NMR spectroscopy).[10] To produce **7**, elimination of $(Ph_3Si)_2$ must occur, presumably via **B″**, to generate the transient Rh hydrido cation **C**, which is trapped by a third 1 equiv of silane to form **7a** or **7b**/**7b′**.

A similar mechanism was invoked to explain the conversion of a rhodium hydrido disilyl species to a dihydrido silyl complex by Slough and co-workers.[11] Reductive elimination of hexaethyldisilane, $(Et_3Si)_2$, from $(Ph_3P)_2Rh(H)(SiEt_3)_2$ and subsequent oxidative addition of triethylsilane resulted in production of $(Ph_3P)_2Rh(H)_2(SiEt_3)$. Additionally, the reaction in which elimination of H_2 from the dihydrido silyl complex and oxidative addition of triethylsilane to re-form the hydrido disilyl complex was also reported.

Complexes **6** and **7** have resisted all efforts at isolation. This is not entirely surprising, as *no* examples of isolated rhodium η^2-silane complexes have been reported. Removal of volatile materials in vacuo from solutions of these compounds resulted in decomposition to unidentified products. Standard crystallization attempts using a variety of solvents were also unsuccessful.

Activation of Trimethylsilane. Addition of 1 equiv of trimethylsilane to a CD_2Cl_2 solution of Rh methyl complex **4** led to rapid formation of unidentified decomposition products, even at −80 °C. Repeating this experiment using excess (3−5 equiv) trimethylsilane allowed observation of an η^2-silane complex, $[Cp^*(PMe_3)Rh(SiMe_3)(\eta^2\text{-}HSiMe_3)]BAr'_4$ (**9**/**9′**), in the ^1H NMR spectrum at −60 °C (Scheme 5). The hydride resonance for **9**/**9′** exhibited ^{29}Si satellites (δ −12.02 ppm; $^2J_{P-H} = 7.5$ Hz, $^1J_{Rh-H} = 36.6$ Hz, $^1J_{Si-H(observed)} = 28.5$ Hz), lending support to assignment as a silyl η^2-silane complex. The Si−H coupling constant associated with the η^2 Si−H interaction was calculated from the observed Si−H coupling constant: $^1J_{Si-H(\eta^2)} = 2 \times {}^1J_{Si-H(observed)} = 2 \times 28.5\text{ Hz} = 57\text{ Hz}$. Consistent with the rapidly fluxional nature of **9** is the observation in the ^1H NMR spectrum of a single resonance at 0.50 ppm for the $SiMe_3$ groups. Over time, another product grew in, which was formulated as $[Cp^*(PMe_3)Rh(H)_2(SiMe_3)]BAr'_4$ (Scheme 5). As in the case with triphenylsilane, this complex may have the structure $[Cp^*(PMe_3)Rh(H)_2(SiMe_3)]BAr'_4$ (**10a**) or $[Cp^*(PMe_3)Rh(H)(\eta^2\text{-}HSiMe_3)]BAr'_4$ (**10b**/**10b′**). The hydride region of the ^1H NMR spectrum of **10** exhibited a resonance (δ −11.16 ppm; $^2J_{P-H} = 20.7$ Hz, $^1J_{Rh-H} = 27.9$ Hz) which was integrated to two equivalent protons. Once again, no ^{29}Si satellites were observed for the hydride peak, making assignment of the correct structure difficult.

Scheme 5



The iridium analogue of complex **10**, $[Cp^*(PMe_3)Ir(H)_2(SiMe_3)]^+[MeB(C_6F_5)_3]^-$, has been reported.[12] This complex was generated in situ by addition of 1 equiv of trimethylsilane to a solution of the cationic iridium hydrido complex $[Cp^*(PMe_3)Ir(H)(ClCD_2Cl)]^+[MeB(C_6F_5)_3]^-$. Assignment as an Ir(V) species was based upon NMR spectroscopic data.

By analogy to other rhodium/iridium systems in which the iridium compound prefers a formal +5 oxidation state and the rhodium compound prefers a lower +3 oxidation state, it is likely that η^2-silane complex **10b**/**10b′** is the correct structure. For example, iridium complex **3** was assigned as an Ir(V) species, while the Rh analogue **6** exhibited ^{29}Si satellites (with a large $^1J_{Si-H}$ coupling of 84 Hz) in the hydride region of the ^1H NMR spectrum, indicating a Rh(III) complex with an η^2-silane ligand. This trend is also mirrored with hydride ligands; an Ir(V) classical trihydride structure was established for $[Cp^*(PMe_3)Ir(H)_3]^+$,[13] while the analogous Rh(III) complex is the nonclassical hydride/dihydrogen complex $[Cp^*(PMe_3)Rh(H)(H_2)]^+$.[7]

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(10) This species ($[Cp^*(PMe_3)Rh(H)(SiPh_3)_2]^+$ (**B**, **B′**, or **B″**)) was not detected either at room temperature or when the experiment was repeated at low temperature (down to −70 °C) and the reaction mixture observed by variable-temperature NMR spectroscopy.

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(12) Golden, J. T.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 5837.

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Activation of Triethylsilane. As with trimethylsilane, addition of 1 equiv of triethylsilane to a CD_2Cl_2 solution of **4** led to rapid formation of unidentified decomposition products, even at −80 °C. Addition of 5.0 equiv of triethylsilane resulted in initial formation of a Rh silyl η^2-silane complex, $[Cp^*(PMe_3)Rh(SiEt_3)(\eta^2\text{-}HSiEt_3)]BAr'_4$ (**11**), observed in the ^1H NMR spectrum at −60 °C. Characterization of **11** as a σ complex is supported by the presence of ^{29}Si satellites of the hydride resonance (δ −12.39 ppm; $^2J_{P-H} = 6.8$ Hz, $^1J_{Rh-H} = 36.0$ Hz, $^1J_{Si-H(observed)} = 27.8$ Hz, $^1J_{Si-H(\eta^2)} = 56$ Hz).[14]

When the temperature was increased, a broadening of resonances associated with both free and bound silane was observed in the ^1H NMR spectrum. For example, at 10 °C, the hydride signal at δ −12.39 ppm as well as the $Et_3Si\text{-}H$ signal at δ 3.49 ppm have broadened into the baseline. When the temperature was lowered back to −60 °C, all resonances sharpened up again, with the exception of the methylene protons of bound silane, which are diastereotopic and exhibit a broad resonance throughout the entire temperature range. These effects can clearly be attributed to rapid intermolecular exchange of the bound silane in complex **11** with the excess free silane present in solution. In addition to this exchange of silane occurring, raising the temperature also resulted in the appearance of a species formulated as $[Cp^*(PMe_3)Rh(H)_2(SiEt_3)]BAr'_4$ (**12**). When the temperature was increased further to 20 °C, unidentified side products appeared and significant decomposition ensued. Complex **12** exhibited a hydride resonance in the ^1H NMR spectrum at δ −11.38 ppm ($^2J_{P-H} = 20.0$ Hz, $^1J_{Rh-H} = 27.2$ Hz), which was integrated to two equivalent protons. As in the previous examples, no ^{29}Si satellites were observed and thus definitive assignment as a Rh(III) or Rh(V) species was not possible.

Summary and Conclusions

We have shown that $[Cp^*(PMe_3)Rh(Me)(CH_2Cl_2)]BAr'_4$ (**4**), a cationic rhodium(III) complex, will activate the Si−H bonds of triaryl- and trialkylsilanes at low temperatures (below −80 °C).[15] Silane complexes $[Cp^*(PMe_3)Rh((C_6H_4)(\eta^2\text{-}HSiPh_2))]BAr'_4$ (**6**), $[Cp^*(PMe_3)Rh(SiMe_3)(\eta^2\text{-}HSiMe_3)]BAr'_4$ (**9**), and $[Cp^*(PMe_3)Rh(SiEt_3)(\eta^2\text{-}HSiEt_3)]BAr'_4$ (**11**) have been generated and characterized by NMR spectroscopy. Of note was the presence of ^{29}Si satellites of the hydride resonances of each of these compounds and large $^1J_{Si-H}$ coupling constants (56−84 Hz), signifying the presence of η^2-silane ligands. A series of complexes formulated as dihydrido silyl species (**7**, **10**, and **12**) have also been generated and characterized by NMR spectroscopy. It is likely that **7**, **10**, and **12** are all Rh(III) compounds. As discussed above, when rhodium complexes are compared with the analogous iridium complexes, the former tend to adopt formal +3 oxidation states, while the latter prefer +5 oxidation states. While $[Cp^*(PMe_3)Rh((C_6H_4)(\eta^2\text{-}HSiPh_2))]BAr'_4$ (**6**) and $[Cp^*(PMe_3)Rh(H)(H_2)]^+$ are both Rh(III) compounds,[7] the corresponding Ir compounds $[Cp^*(PMe_3)Ir(\eta^2\text{-}SiPh_2(C_6H_4))(H)]^+$ (**3**) and $[Cp^*(PMe_3)Ir(H)_3]^+$ are Ir(V) species.[6,13] By analogy, since $[Cp^*(PMe_3)Ir(H)_2(SiMe_3)]^+$ was reported to be an Ir(V) complex,[12] it is likely that the corresponding rhodium complexes **7**, **10**, and **12** are fluxional hydrido silane species $[Cp^*(PMe_3)Rh(H)(\eta^2\text{-}HSiR_3)]^+$ with a formal oxidation state of +3.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed using standard high-vacuum, Schlenk, or drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. ^1H and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C NMR signals of the deuterated solvents, respectively. ^{31}P NMR chemical shifts were referenced to an 85% H_3PO_4 sample used as an external standard, and ^{29}Si NMR chemical shifts were referenced to TMS used as an external standard. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

Materials. All solvents were deoxygenated and dried via passage over a column of activated alumina.[16] Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from CaH_2 and stored over 4 Å molecular sieves. Unless otherwise noted, all chemicals were purchased from Aldrich and used without further purification. The synthesis and full characterization of complex **4** has been previously reported.[7]

Spectral Data for BAr'^-_4. The ^1H and ^{13}C NMR resonances of the BAr'_4 ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) counteranion in CD_2Cl_2 were essentially invariant for all cationic complexes discussed here. Therefore, spectroscopic data for this anion are not repeated for each compound. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.73 (s, 8 H, H_o), 7.57 (s, 4 H, H_p). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 161.9 (q, $^1J_{C-B} = 49.8$ Hz, C_{ipso}), 135.0 (s, C_o), 129.0 (q, $^2J_{C-F} = 31.4$, C_m), 124.7 (q, $^1J_{C-F} = 272.6$ Hz, CF_3), 117.7 (s, C_p).

$[Cp^*(PMe_3)Rh(H)(NCMe)]BAr'_4$ (8). Complex **8** was generated by addition of 1 equiv of acetonitrile to a dichloromethane solution of complex **7** at room temperature. Alternately, a Schlenk flask was charged with 43 mg (0.035 mmol) of **8b** (see below) and 5 mL of chlorobenzene. The contents of the flask were subjected to three freeze−pump−thaw cycles. The flask was back-filled with 1 atm of H_2, and the contents were stirred vigorously for 10 min at room temperature. All volatile materials were removed in vacuo to produce a yellow solid in >95% yield. When this reaction is monitored by NMR spectroscopy, quantitative yields are observed. This complex decomposed in dichloromethane but was stable in chlorobenzene. ^1H NMR (400 MHz, C_6D_5Cl, room temperature): δ 1.71 (s, 3 H, NCMe), 1.62 (s, 15 H, Cp*), 1.21 (d, $^2J_{P-H} = 10.7$ Hz, 9 H, PMe_3), −11.12 (dd, $^1J_{Rh-H} = 46.4$ Hz, $^2J_{P-H} = 18.8$ Hz, 1 H, hydride). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_5Cl, room temperature): δ 3.7 (d, $^1J_{Rh-P} = 136.4$ Hz, PMe_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Cl, room temperature): δ 123.1 (d, $^2J_{Rh-C} = 7.0$ Hz, N*C*Me), 100.6 (s, Cp*−Ar), 17.66 (d, $^1J_{P-C} = 33.3$ Hz, PMe_3), 10.03 (s, Cp*−Me), 2.33 (s, NC*Me*). Anal. Calcd for $C_{47}H_{40}NBF_{24}PRh$: C, 46.29; H, 3.31. Found: C, 46.11; H, 3.23.

$[Cp^*(PMe_3)Rh(Me)(NCMe)]BAr'_4$ (8b). A Schlenk flask was charged with 150 mg (0.12 mmol) of **4** and 5 mL of dichloromethane. Acetonitrile (1.0 equiv, 6.1 μL, 0.12 mmol)

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[14] As in the previous case, $^1J_{Si-H(\eta^2)} = 2 \times {}^1J_{Si-H(observed)}$. A value of 27.8 Hz was measured for $^1J_{Si-H(observed)}$; thus, $^1J_{Si-H(\eta^2)} = 56$ Hz.

[15] Similar experiments involving triisopropylsilane led to transient formation of the Si−H activation product $[Cp^*(PMe_3)Rh(Si^iPr_3)(CH_2Cl_2)]BAr'_4$ (**13**) at −40 °C. In contrast to the previously discussed examples, activation did not take place at temperatures below −40 °C and was likely hindered by the presence of bulky alkyl groups. Rapid decomposition of the reaction mixture occurred, and no other discernible Rh species were observed in solution.

[16] (a) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518. (b) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*(1), 64.

was added, and all volatile materials were removed in vacuo to produce a yellow-orange solid (138 mg, 0.11 mmol) in 95% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 2.27 (s, 3 H, NCMe), 1.63 (d, $^{4}J_{\mathrm{P-H}} = 2.8$ Hz, 15 H, Cp*), 1.37 (dd, $^{2}J_{\mathrm{P-H}} = 10.2$ Hz, $^{3}J_{\mathrm{Rh-H}} = 0.6$ Hz, 9 H, PMe_3), 0.52 (dd, $^{3}J_{\mathrm{P-H}} = 6.9$ Hz, $^{2}J_{\mathrm{Rh-H}} = 2.1$ Hz, 3 H, Rh−Me). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, room temperature): δ 5.2 (d, $^{1}J_{\mathrm{Rh-P}} = 151.1$ Hz, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, room temperature): δ 122.6 (d, $^{3}J_{\mathrm{P-C}} = 6.9$ Hz, N*C*Me), 117.9 (dd, $^{2}J_{\mathrm{P-C}} = 6.8$ Hz, $^{1}J_{\mathrm{Rh-C}} = 3.2$ Hz, Cp*−Ar), 14.82 (d, $^{1}J_{\mathrm{P-C}} = 31.9$ Hz, PMe_3), 9.24 (s, Cp*−Me), 3.89 (s, NC*C*H_3), −0.42 (dd, $^{2}J_{\mathrm{P-C}} = 22.7$ Hz, $^{1}J_{\mathrm{Rh-C}} = 13.5$ Hz, Rh−Me). Anal. Calcd for $C_{48}H_{42}NBF_{24}PRh$: C, 46.74; H, 3.43. Found: C, 46.51; H, 3.37.

Typical Procedures for Generation of Si−H Activation Products. The complexes listed below have been generated in situ and characterized by NMR spectroscopy. Typical procedures for preparing NMR-tube reactions for spectroscopic study are as follows: an NMR tube was charged with 20 mg (0.016 mmol) of **4**; ∼0.3 mL of CD_2Cl_2 was added to dissolve **4**, and the NMR tube was capped with a rubber septum; the tube was then placed in a −78 °C dry ice/acetone bath, and a CD_2Cl_2 solution (∼0.3 mL) of the appropriate silane was administered to the NMR tube contents via syringe. Attempts at isolation of products by removal of all volatiles in vacuo led to rapid decomposition of rhodium compounds. Standard recrystallization techniques also proved fruitless.

[Cp*(PMe$_3$)Rh(SiPh$_3$)(CD$_2$Cl$_2$)]BAr′$_4$ (5). This complex was generated by addition (at −78 °C) of 1.0 equiv of triphenylsilane to a CD_2Cl_2 solution of **4**. At −40 °C, complex **5** was the only observable rhodium species in solution. ^{1}H NMR (300 MHz, CD_2Cl_2, −40 °C): δ 7.53 (br m, 3 H, $SiPh_3$), 7.45 (br m, 6 H, $SiPh_3$), 7.34 (br m, 6 H, $SiPh_3$), 1.37 (d, $^{4}J_{\mathrm{P-H}} = 1.8$ Hz, 15 H, Cp*), 1.08 (d, $^{2}J_{\mathrm{P-H}} = 9.6$ Hz, 9 H, PMe_3). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −40 °C): δ −6.8 (d, $^{1}J_{\mathrm{Rh-P}} = 170.6$ Hz, PMe_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, −40 °C): δ 135.6 (s, $SiPh_3$), 131.0 (s, $SiPh_3$), 130.8 (s, $SiPh_3$), 129.5 (s, $SiPh_3$), 102.7 (s, Cp*−Ar), 17.93 (d, $^{1}J_{\mathrm{P-C}} = 31.5$ Hz, PMe_3), 9.96 (s, Cp*−Me).

[Cp*(PMe$_3$)Rh((C$_6$H$_4$)(η^2-HSiPh$_2$))]BAr′$_4$ (6). Complex **6** was generated by addition (at room temperature) of 1.0 equiv of triphenylsilane to a CD_2Cl_2 solution of **4**. Within 3 h, **6** was formed in ∼90% yield, as determined by NMR spectroscopy (integration relative to invariant BAr′$_4$ peaks). The identities of small amounts of side products could not be determined, due to the low intensities of resonances exhibited in the NMR spectra. Alternately, when a solution of complex **5** was warmed to room temperature, **6** was formed. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 7.6 (br m, 2 H, Rh−Ar), 7.5 (br m, 10 H, Ph), 7.3 (br m, 2 H, Rh−Ar), 1.54 (d, $^{4}J_{\mathrm{P-H}} = 3.1$ Hz, 15 H, Cp*), 1.09 (d, $^{2}J_{\mathrm{P-H}} = 10.5$ Hz, 9 H, PMe_3), −8.95 (dd, $^{2}J_{\mathrm{P-H}} = 11.5$ Hz, $^{1}J_{\mathrm{Rh-H}} = 27.8$ Hz, $^{1}J_{\mathrm{Si-H}} = 84$ Hz, 1 H, Si−H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, room temperature): δ 4.6 (d, $^{1}J_{\mathrm{Rh-P}} = 141.6$ Hz, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, room temperature): δ 154.0 (dd, $^{2}J_{\mathrm{P-C}} = 18.3$ Hz, $^{1}J_{\mathrm{Rh-C}} = 28.1$ Hz, Rh−Ar(C_{ipso})), 136.5 (s, Ar), 135.5 (s, Ar), 135.2 (s, Ar), 134.7 (s, Ar), 133.8 (s, Ar), 133.7 (s, Ar), 133.4 (s, Ar), 133.1 (s, Ar), 132.6 (s, Ar), 131.9 (s, Ar), 131.5 (s, Ar), 131.3 (s, Ar), 131.2 (s, Ar), 129.6 (s, Ar), 129.3 (s, Ar), 128.5 (s, Ar), 125.6 (s, Ar), 104.1 (s, Cp*−Ar), 16.21 (d, $^{1}J_{\mathrm{P-C}} = 34.3$ Hz, PMe_3), 9.70 (s, Cp*−Me).

[Cp*(PMe$_3$)Rh(H)$_2$(SiPh$_3$)]BAr′$_4$ (7a) or [Cp*(PMe$_3$)Rh(H)(η^2-HSiPh$_3$)]BAr′$_4$ (7b/7b′). When 5.0 equiv of triphenylsilane was added to a CD_2Cl_2 solution of **4**, this complex was formed in ∼80% yield within 10 min at room temperature, as determined by NMR spectroscopy (integration relative to invariant BAr′$_4$ peaks). Complex **6** accounted for 10% of the reaction mixture, and the remaining 10% was comprised of unidentified side products. ^{1}H NMR (400 MHz, CD_2Cl_2, room temperature): δ 7.6 (br m, difficult to integrate—overlaps with free Ph_3SiH, $SiPh_3$), 7.4 (br m, difficult to integrate—overlaps with free Ph_3SiH, $SiPh_3$), 1.65 (d, $^{4}J_{\mathrm{P-H}} = 2.9$ Hz, 15 H, Cp*), 1.24 (d, $^{2}J_{\mathrm{P-H}} = 11.2$ Hz, 9 H, PMe_3), −10.04 (dd, $^{2}J_{\mathrm{P-H}} = 18.0$ Hz, $^{1}J_{\mathrm{Rh-H}} = 26.8$ Hz, 2 H, H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, room temperature): δ 4.4 (d, $^{1}J_{\mathrm{Rh-P}} = 107.7$ Hz, PMe_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, room temperature): δ 136.3 (s, $SiPh_3$), 133.5 (s, $SiPh_3$), 131.2 (s, $SiPh_3$), 129.4 (s, $SiPh_3$), 106.6 (s, Cp*−Ar), 20.00 (d, $^{1}J_{\mathrm{P-C}} = 36.9$ Hz, PMe_3), 10.01 (s, Cp*−Me).

[Cp*(PMe$_3$)Rh(SiMe$_3$)(η^2-HSiMe$_3$)]BAr′$_4$ (9/9′). Complex **9/9′** was generated by addition (at −78 °C) of 5.0 equiv of trimethylsilane to a CD_2Cl_2 solution of **4**. After ∼10 min at −60 °C, complex **9/9′** was the predominant species (∼90%) in solution. Small amounts of **10** (5%) and other unidentified side products (5%) were present. ^{1}H NMR (300 MHz, CD_2Cl_2, −60 °C): δ 1.74 (d, $^{4}J_{\mathrm{P-H}} = 2.6$ Hz, 15 H, Cp*), 1.39 (d, $^{2}J_{\mathrm{P-H}} = 9.8$ Hz, 9 H, PMe_3), 0.50 (s, 18 H, $SiMe_3$), −12.02 (dd, $^{2}J_{\mathrm{P-H}} = 7.5$ Hz, $^{1}J_{\mathrm{Rh-H}} = 36.6$ Hz, $^{1}J_{\mathrm{Si-H(observed)}} = 28.5$ Hz, $^{1}J_{\mathrm{Si-H}(\eta^2)} = 57$ Hz, 1 H, Si−H). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −60 °C): δ −10.8 (d, $^{1}J_{\mathrm{Rh-P}} = 155.5$ Hz, PMe_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, −60 °C): δ 105.3 (s, Cp*−Ar), 21.32 (d, $^{1}J_{\mathrm{P-C}} = 33.5$ Hz, PMe_3), 11.43 (s, Cp*−Me), 3.26 (s, $SiMe_3$).

[Cp*(PMe$_3$)Rh(H)$_2$(SiMe$_3$)]BAr′$_4$ (10a) or [Cp*(PMe$_3$)Rh(H)(η^2-HSiMe$_3$)]BAr′$_4$ (10b/10b′). When a CD_2Cl_2 solution of complex **9/9′** (generated as described above) was allowed to stand at −60 °C, this complex grew in slowly (as observed by NMR spectroscopy). After ∼1 h, **10** comprised ∼10% of the reaction mixture, with the rest composed of **9/9′** and unidentified side products. Upon warming to −20 °C, the amount of **10** increased to ∼50% of the reaction mixture. Complex **10** is not stable, and decomposition occurred over the course of several hours at 0 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, −20 °C): δ 1.94 (d, $^{4}J_{\mathrm{P-H}} = 3.1$ Hz, 15 H, Cp*), 1.58 (d, $^{2}J_{\mathrm{P-H}} = 11.2$ Hz, 9 H, PMe_3), 0.58 (s, 9 H, $SiMe_3$), −11.16 (dd, $^{2}J_{\mathrm{P-H}} = 20.7$ Hz, $^{1}J_{\mathrm{Rh-H}} = 27.9$ Hz, 2 H, H). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −20 °C): δ 4.2 (d, $^{1}J_{\mathrm{Rh-P}} = 109.9$ Hz, PMe_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, −20 °C): δ 103.4 (s, Cp*−Ar), 20.74 (d, $^{1}J_{\mathrm{P-C}} = 32.1$ Hz, PMe_3), 10.49 (s, Cp*−Me), 1.93 (s, $SiMe_3$).

[Cp*(PMe$_3$)Rh(SiEt$_3$)(η^2-HSiEt$_3$)]BAr′$_4$ (11). Complex **11** was generated by addition (at −78 °C) of 5.0 equiv of triethylsilane to a CD_2Cl_2 solution of **4**. When the temperature was raised to −60 °C, this complex was present in >90% yield, as determined by NMR spectroscopy. A ^{13}C{^{1}H} NMR spectrum could not be obtained, due to solubility problems. ^{1}H NMR (400 MHz, CD_2Cl_2, −60 °C): δ 1.71 (d, $^{4}J_{\mathrm{P-H}} = 1.9$ Hz, 15 H, Cp*), 1.37 (d, $^{2}J_{\mathrm{P-H}} = 9.6$ Hz, 9 H, PMe_3), 1.03 (br s, 12 H, methylene H's of Et), 0.89 (t, $^{3}J_{\mathrm{H-H}} = 7.9$ Hz, 18 H, methyl H's of Et), −12.39 (dd, $^{2}J_{\mathrm{P-H}} = 6.8$ Hz, $^{1}J_{\mathrm{Rh-H}} = 36.0$ Hz, $^{1}J_{\mathrm{Si-H(observed)}} = 27.8$ Hz, $^{1}J_{\mathrm{Si-H}(\eta^2)} = 56$ Hz, 1 H, Si−H). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −60 °C): δ −12.5 (d, $^{1}J_{\mathrm{Rh-P}} = 158.0$ Hz, PMe_3).

[Cp*(PMe$_3$)Rh(H)$_2$(SiEt$_3$)]BAr′$_4$ (12). When a CD_2Cl_2 solution of **11** (generated as described above) was warmed to −40 °C, some conversion to complex **12** occurred, as observed by NMR spectroscopy. However, the rate of formation was slow and significant amounts of unidentified side products were also formed. The amount of **12** in solution never exceeded ∼15%, and thus a satisfactory ^{13}C{^{1}H} NMR spectrum could not be obtained. ^{1}H NMR (400 MHz, CD_2Cl_2, −20 °C): δ 1.90 (d, $^{4}J_{\mathrm{P-H}} = 3.0$ Hz, 15 H, Cp*), 1.57 (d, $^{2}J_{\mathrm{P-H}} = 11.3$ Hz, 9 H, PMe_3) ($SiEt_3$ protons overlapped with those of free silane and was not observed), −11.38 (dd, $^{2}J_{\mathrm{P-H}} = 20.0$ Hz, $^{1}J_{\mathrm{Rh-H}} = 27.2$ Hz, 2 H, H). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, −20 °C): δ 3.6 (d, $^{1}J_{\mathrm{Rh-P}} = 111.8$ Hz, PMe_3).

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