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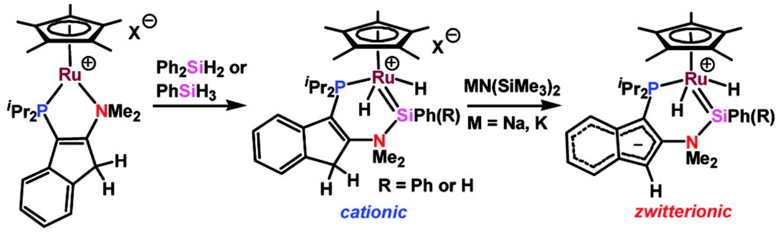

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# Silylene Extrusion from Organosilanes via Double Geminal Si−H Bond Activation by a Cp*Ru($\kappa^2$-*P*,*N*)$^+$ Complex: Observation of a Key Stoichiometric Step in the Glaser−Tilley Alkene Hydrosilylation Mechanism

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***Abstract:*** Treatment of Cp*RuCl($\kappa^2$-*P*,*N*-**2b**) (**2b** = 2-*N*Me$_2$-3-*P*$^i$Pr$_2$-indene) with TlSO$_3$CF$_3$ produced the cyclometalated complex [**4**]$^+$SO$_3$CF$_3^-$ in 94% isolated yield. Exposure of [**4**]$^+$X$^-$ (X = B(C$_6$F$_5$)$_4$ or SO$_3$CF$_3$) to Ph$_2$SiH$_2$ (10 equiv) or PhSiH$_3$ afforded the corresponding [Cp*($\mu$-*P*,*N*-**2b**)(H)$_2$Ru=SiRPh]$^+$X$^-$ complexes, [**5**]$^+$X$^-$ (R = Ph; X = B(C$_6$F$_5$)$_4$, 82%; X = SO$_3$CF$_3$, 39%) and [**6**]$^+$X$^-$ (R = H; X = B(C$_6$F$_5$)$_4$, 94%; X = SO$_3$CF$_3$, 95%). Notably, these transformations represent the first documented examples of Ru-mediated silylene extrusion via double geminal Si−H bond activation of an organosilane—a key step in the recently proposed Glaser−Tilley (G−T) alkene hydrosilylation mechanism. Treatment of [**5**]$^+$B(C$_6$F$_5$)$_4^-$ with KN(SiMe$_3$)$_2$ or [**6**]$^+$SO$_3$CF$_3^-$ with NaN(SiMe$_3$)$_2$ afforded the corresponding zwitterionic Cp*($\mu$-2-*N*Me$_2$-3-*P*$^i$Pr$_2$-indenide)(H)$_2$Ru=SiRPh complex in 69% (R = Ph, **7**) or 86% (R = H, **8**) isolated yield. Both [**6**]$^+$X$^-$ and **8** proved unreactive toward 1-hexene and styrene and provided negligible catalytic turnover in the attempted metal-mediated hydrosilylation of these substrates with PhSiH$_3$, thereby providing further empirical evidence for the required intermediacy of base-free Ru=Si species in the G−T mechanism. Isomerization of the P,N-indene ligand backbone in [**6**]$^+$X$^-$, giving rise to [Cp*($\mu$-1-*P*$^i$Pr$_2$-2-*N*Me$_2$-indene)(H)$_2$Ru=SiHPh]$^+$X$^-$ ([**9**]$^+$X$^-$), was observed. In the case of [**9**]$^+$SO$_3$CF$_3^-$, net intramolecular addition of the Ru=*Si*−*H* group across the styrene-like C=C unit within the ligand backbone to give **10** (96% isolated yield) was observed. Crystallographic characterization data are provided for [**4**]$^+$X$^-$, [**5**]$^+$X$^-$, [**6**]$^+$X$^-$, **8**, and **10**.

## Introduction

Transition metal silylene complexes featuring a formal M=Si linkage have been the subject of ongoing scrutiny over the past two decades, due in part to the key role that such reactive intermediates are proposed to play in a diversity of metal-mediated transformations,[1] including the direct process for the industrial synthesis of chlorosilanes from silicon and chlorocarbons.[2] Interest in such complexes intensified following a report by Glaser and Tilley in 2003,[3] in which experimental evidence for an unprecedented alkene hydrosilylation mechanism involving Ru=Si intermediates was provided. Key mechanistic steps in the proposed pathway for such hydrosilylations employing the metal silylene precatalyst [Cp*($^i$Pr$_3$P)(H)$_2$Ru=SiHPh·OEt$_2$]$^+$B(C$_6$F$_5$)$_4^-$ (**1**; Cp* = $\eta^5$-C$_5$Me$_5$) and the generic olefin R′CH=CH$_2$ include (Scheme 1): (i) double geminal Si−H bond activation of RSiH$_3$ by [Cp*($^i$Pr$_3$P)Ru]$^+$ (**1a**) to afford [Cp*($^i$Pr$_3$P)(H)$_2$Ru=SiHR]$^+$ (**1b**), for which the metallasilicenium ion **1b′** represents an important resonance contributor; (ii) direct, regioselective addition of the Ru=*Si*−*H* bond in **1b** to the alkene substrate to give [Cp*($^i$Pr$_3$P)(H)$_2$Ru=Si(CH$_2$CH$_2$R′)R]$^+$ (**1c**); (iii) H-migration from Ru to Si in **1c** to give [Cp*($^i$Pr$_3$P)(H)Ru−SiH(CH$_2$CH$_2$R′)R]$^+$ (**1d**); and (iv) Si−H reductive elimination of RSiH$_2$(CH$_2$CH$_2$R′) with concomitant regeneration of **1a**. In stark contrast to more traditional alkene hydrosilylation processes,[4] and in keeping with the proposed mechanism, only primary silanes were found to be compatible substrates when employing pre-catalyst **1**, whereas even trisubstituted alkenes underwent hydrosilylation to afford exclusively the corresponding *anti*-

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(1) For reviews, see: (a) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712. (b) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493. (c) Ogino, H. *Chem. Rec.* **2002**, *2*, 291. (d) Ogino, H.; Tobita, H. *Adv. Organomet. Chem.* **1998**, *42*, 223. (e) Zybill, C.; Handwerker, H.; Friedrich, H. *Adv. Organomet. Chem.* **1994**, *36*, 229. (f) Tilley, T. D. In *Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 24, p 1415.

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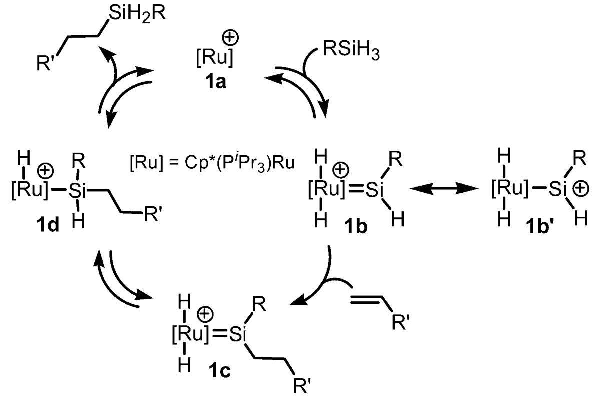
(4) For discussions of the Chalk−Harrod and the modified Chalk−Harrod mechanisms of alkene hydrosilylation, see: Sakaki, S.; Sumimoto, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* **2002**, *21*, 3788.

10.1021/ja0768800 CCC: $37.00

**Scheme 1.** Simplified View of the Glaser−Tilley Mechanism for Alkene Hydrosilylation



Markovnikov product in the absence of double-addition (i.e., $RSiH(CH_2CH_2R')_2$) or vinylsilane byproducts.[5]

Computational investigations[6] and stoichiometric reactivity studies have figured importantly in validating some of the key steps of the proposed Glaser−Tilley (G−T) hydrosilylation mechanism, as well as in providing insight into the role of charge distribution on the reactivity of the Si−H fragment in intermediates such as **1b**/**1b′**. The feasibility of the proposed direct addition of a Ru═*Si*−*H* bond to an olefinic substrate was demonstrated through the observed reaction of **1** with 1-hexene to afford $[Cp^*(^iPr_3P)(H)_2Ru{=}Si(hexyl)Ph]^+B(C_6F_5)_4^-$ (i.e., **1c** where R′ = $C_4H_9$).[3] Whereas the related Os complex $[Cp^*(^iPr_3P)(H)_2Os{=}SiH(trip)]^+B(C_6F_5)_4^-$ (trip = 2,4,6-$^iPr_3$−$C_6H_2$) reacts rapidly with alkenes in a similar manner,[3] the observation that the neutral silylene complex $Cp^*(^iPr_3P)(H)$-Os═SiH(trip) is unreactive under similar conditions underscores the influence of formal charge on such hydrosilylation processes, as well as the potential importance of resonance contributors such as **1b′** in the catalytic hydrosilylation chemistry derived from **1**.[7] However, despite the existence of structurally characterized Ru═Si species[8,9] and the demonstrated ability of a rather small number of mononuclear complexes of groups 6−9 to mediate silylene extrusion from organosilanes via thermally promoted Si−H oxidative addition/α-H migration pathways,[10] the direct formation of Ru═Si species via double geminal Si−H bond activation of a silane (as required by the G−T mechanism) has not been documented previously in the literature. Herein we report on the observation of such stoichiometric double geminal Si−H bond activation chemistry involving $Ph_2SiH_2$ or $PhSiH_3$ by $[Cp^*Ru(\kappa^2\text{-}P,N)]^+X^-$ species to afford crystallographically characterized products in which the initially $\kappa^2$-*P*,*N* ligand spans the Ru═Si fragment. The reactivity properties of the derived base-stabilized cationic Ru═Si complexes are also documented, including the observation of intramolecular alkene insertion into a Ru═*Si*−*H* fragment, and the formation of the first formally zwitterionic (neutral) Ru═Si species.

## Results and Discussion

One aspect of our research program focuses on the development of new, coordinatively unsaturated metal complexes derived from 1-$P^iPr_2$-2-$NMe_2$-indene (**2a**), 2-$NMe_2$-3-$P^iPr_2$-indene (**2b**), 2-$NMe_2$-3-$P^iPr_2$-indenide (**2c**), and related ligands, for use in mediating substrate E−H bond activation chemistry (E = main group element).[11] In this context, we have reported previously on our efforts to prepare $[Cp^*Ru(\kappa^2\text{-}P,N\text{-}\mathbf{2b})]^+B(C_6F_5)_4^-$ ($[\mathbf{3}]^+B(C_6F_5)_4^-$) via treatment of $Cp^*RuCl(\kappa^2\text{-}P,N\text{-}\mathbf{2b})$ with $Li(Et_2O)_{2.5}B(C_6F_5)_4$.[11e] Whereas the cyclometalated species $[\mathbf{4}]^+B(C_6F_5)_4^-$ was identified as the Ru-containing product obtained from this reaction on the basis of single-crystal X-ray diffraction data, variable-temperature NMR data revealed that the apparent cyclometalation of $[\mathbf{3}]^+B(C_6F_5)_4^-$ to give $[\mathbf{4}]^+B(C_6F_5)_4^-$ is reversible (Scheme 2).[11e] We have discovered subsequently that $Cp^*RuCl(\kappa^2\text{-}P,N\text{-}\mathbf{2b})$ also reacts cleanly with $TlSO_3CF_3$ to afford $[\mathbf{4}]^+SO_3CF_3^-$ in 94% isolated yield. An ORTEP[12] diagram of $[\mathbf{4}]^+SO_3CF_3^-$ is provided in Figure 1, while X-ray experimental data and selected metrical parameters for each of the crystallographically characterized complexes reported herein are collected in Tables 1, 2, and 3. The structural features found in $[\mathbf{4}]^+SO_3CF_3^-$ mirror those of $[\mathbf{4}]^+B(C_6F_5)_4^-$,[11e] as well as some other crystallographically characterized azaruthenacyclopropanes.[13]

**Base-Stabilized Ru═Si Complexes Formed via Double Si−H Bond Activation.** Given the apparent ability of $[\mathbf{4}]^+X^-$ (X = $B(C_6F_5)_4$ or $SO_3CF_3$) to reversibly activate C−H bonds in an intramolecular fashion, we became interested in exploiting these complexes as masked sources of $[\mathbf{3}]^+X^-$ in the pursuit of new metal-mediated intermolecular E−H bond activation chemistry. Treatment of $[\mathbf{4}]^+B(C_6F_5)_4^-$ with $Ph_2SiH_2$ (10 equiv) afforded after 48 h a single phosphorus-containing product ($[\mathbf{5}]^+B(C_6F_5)_4^-$; Scheme 2), which in turn was obtained in 82% isolated yield. Both $^1H$ and $^{13}C$ NMR data for $[\mathbf{5}]^+B(C_6F_5)_4^-$

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(9) For crystallographically characterized “base-stabilized” Ru═Si complexes, see: (a) Choo, T. N.; Kwok, W.-H.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2002**, *645*, 235. (b) Tobita, H.; Kurita, H.; Ogino, H. *Organometallics* **1998**, *17*, 2850. (c) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 11236. (d) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673. (e) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (f) Reference 8d herein.

(10) (a) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428. (b) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 4375. (c) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799. (d) Gusev, D. G.; Fontaine, F.-G.; Lough, A. J.; Zargarian, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 216. (e) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357. (f) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4065. (g) Mork, B. V.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 9702. (h) Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511. (i) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816. (j) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (k) Reference 7 herein.

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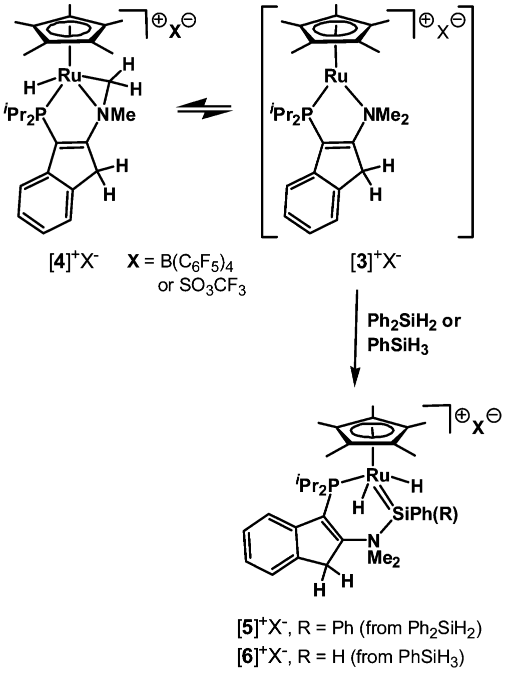
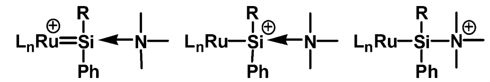
***Scheme 2.*** Silylene Extrusion from $Ph_2SiH_2$ or $PhSiH_3$ to Afford the Base-Stabilized Ru═Si Species $[\mathbf{5}]^+X^-$ and $[\mathbf{6}]^+X^-$



supported a preliminary assessment of this complex as containing a $C_s$-symmetric $Cp^*(PR_3)Ru(H)_2$ moiety. While a more complex mixture of products was generated when employing $[\mathbf{4}]^+SO_3CF_3^-$ under similar conditions ($^{31}P$ NMR), the analogous salt $[\mathbf{5}]^+SO_3CF_3^-$ was isolated from the reaction mixture in 39% isolated yield. The assignment of $[\mathbf{5}]^+X^-$ as base-stabilized $[Cp^*(\mu\text{-}P,N\text{-}\mathbf{2b})(H)_2Ru{=}SiPh_2]^+X^-$ complexes, presumably arising from initial Si−H oxidative addition to $[\mathbf{3}]^+X^-$ followed by some combination of α-H transfer from Si to Ru and migration of the N-donor fragment from Ru to Si,[14] was achieved through the crystallographic characterization of $[\mathbf{5}]^+SO_3CF_3^-$. An ORTEP[12] diagram of $[\mathbf{5}]^+SO_3CF_3^-$ is provided in Figure 1. The relatively short Ru═Si (2.2811(9) Å) and long Si−N (1.988(3) Å) linkages in $[\mathbf{5}]^+SO_3CF_3^-$,[15,16] when compared to related distances found in $[Cp^*(Me_3P)_2Ru{=}SiPh_2{\cdot}NCMe]^+BPh_4^-$ (2.328(2) Å and 1.932(8) Å, respectively),[9d,e] may point to heightened silylene character in $[\mathbf{5}]^+SO_3CF_3^-$ relative to this acetonitrile adduct. Nonetheless, the significant pyramidalization at Si (342.7° in $[\mathbf{5}]^+SO_3CF_3^-$) and the relatively low-frequency $^{29}Si$ NMR chemical shift associated with $[\mathbf{5}]^+B(C_6F_5)_4^-$ ($\delta$ $^{29}Si$ = 107 ppm) clearly distinguish such salts from related base-free silylene complexes including $[Cp^*(^iPr_3P)(H)_2Ru{=}Si(hexyl)Ph]^+B(C_6F_5)_4^-$ ($\delta$ $^{29}Si$ = 252)[3a] and $[Cp^*(Me_3P)_2Ru{=}SiR_2]^+B(C_6F_5)_4^-$ ($\delta$ $^{29}Si$ = 311, R = Me; $\delta$ $^{29}Si$ = 299, R = Ph).[8d,e,17] In this regard, the bonding in $[\mathbf{5}]^+X^-$ is perhaps best represented by a hybrid of resonance contributors that feature formal positive charges on Ru, Si, or N (Chart 1). Notably, the crystallographically determined Ru−*H* positions in $[\mathbf{5}]^+SO_3CF_3^-$, when considered along with the very small $^2J_{SiH}$ values measured for $[\mathbf{5}]^+B(C_6F_5)_4^-$ (<10 Hz), suggest that any interaction between the $Ru(H)_2$ ligands and Si in $[\mathbf{5}]^+X^-$ takes the form of a highly unsymmetrical Ru−H···Si bridging motif.[18]

***Chart 1.*** Three Simplified Representations of the Bonding within the Ru−Si−N Fragments of $[\mathbf{5}]^+X^-$ (R = Ph) and $[\mathbf{6}]^+X^-$ (R = H).



Having documented the first Ru-mediated silylene extrusion process in the apparent reaction of $[\mathbf{3}]^+X^-$ with $Ph_2SiH_2$ leading to $[\mathbf{5}]^+X^-$, we turned our attention to reactions employing $PhSiH_3$ in an effort to observe double geminal Si−H activation chemistry that is of direct relevance to the proposed G−T hydrosilylation mechanism. Gratifyingly, upon exposure to one equivalent of $PhSiH_3$, each of $[\mathbf{4}]^+X^-$ were transformed cleanly over the course of 30 min into the corresponding $[Cp^*(\mu\text{-}P,N\text{-}\mathbf{2b})(H)_2Ru{=}SiHPh]^+X^-$ complex ($[\mathbf{6}]^+X^-$) in 94% (X = $B(C_6F_5)_4$) or 95% (X = $SO_3CF_3$) isolated yield (Scheme 2). The $^1H$ and $^{13}C$ NMR spectra of $[\mathbf{6}]^+X^-$ are entirely consistent with the $C_1$-symmetric nature of these complexes, including the observation of diagnostic resonances for the magnetically nonequivalent Ru−*H* ligands and the Si−*H* group. An ORTEP[12] diagram of $[\mathbf{6}]^+SO_3CF_3^-$ is provided in Figure 1 and represents the first crystallographically characterized Ru═SiHR complex.[19] The overall structural features found in $[\mathbf{6}]^+SO_3CF_3^-$ mirror those observed in $[\mathbf{5}]^+SO_3CF_3^-$, with the exception of a slight contraction of the Ru═Si (2.262(2) Å) and Si−N (1.955(4) Å) linkages in the former relative to the latter. Interestingly, despite the base-stabilized nature of the silylene fragment in $[\mathbf{6}]^+SO_3CF_3^-$, the observed Ru═Si distance is only marginally longer than that of the base-free silylene complex $[Cp^*(Me_3P)_2Ru{=}SiMe_2]^+B(C_6F_5)_4^-$.[17] In keeping with $[\mathbf{5}]^+X^-$, the lack of discernible $^2J_{SiH}$ coupling for $[\mathbf{6}]^+X^-$ suggests little or no interaction between the $Ru(H)_2$ ligands and Si in $[\mathbf{6}]^+X^-$.[18] The migration of an ancillary ligand P-donor fragment from M to Si in the formation of base-stabilized M═SiH(X) species from excess $PhSiH_3$ has been reported (M = Os, X = H;[10d] M = Co, X = $NR_2$[19a]). However, while each of these transformations resulted in the degradation of the initially coordinated ancillary ligand, the structural integrity of ligand **2b** was retained upon formation of $[\mathbf{6}]^+X^-$. Although indirect evidence for reversible α-H migration leading to the formation of M═Si species has been published,[1a] the absence of observable chemical exchange ($^1H$ EXSY) involving the Ru−*H* and Si−*H* groups within $[\mathbf{6}]^+X^-$ or **8** (vide infra) suggests that α-H migration from Si to Ru in these complexes, if reversible, must occur with associated rates that are slow relative to the dynamic exchange NMR time scale.[20]

**Zwitterionic, Base-Stabilized Ru═Si Complexes.** We have demonstrated previously for some $[(\kappa^2\text{-}P,N\text{-}\mathbf{2b})ML_n]^+X^-$ com-

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(14) Alternative reaction pathways leading to $[\mathbf{5}]^+X^-$ involving initial Si−H oxidative addition to $[\mathbf{4}]^+X^-$, and/or featuring σ-bond metathesis steps, can also be envisioned.

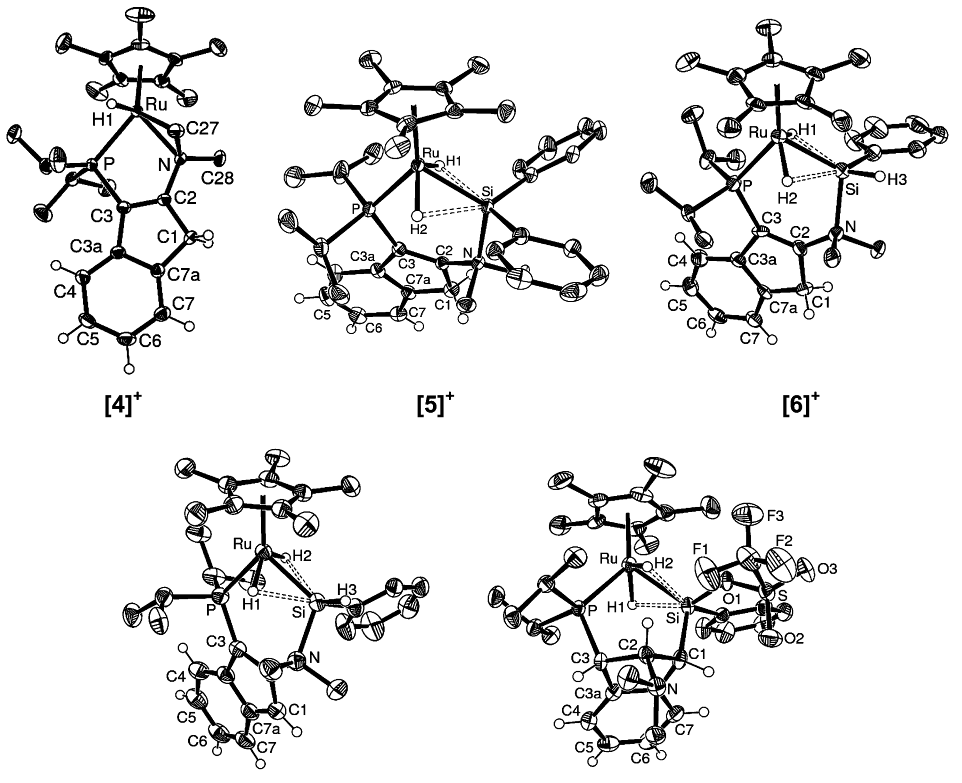
(15) Crystallographically characterized $(CO)_5Cr{=}Si(Ph)_n(o\text{-}C_6H_4CH_2NMe_2)_{2-n}$ ($n$ = 0 or 1) complexes in which a pendant $NMe_2$ group is coordinated to Si ($n$ = 0, Si−N 2.046(2) Å; $n$ = 1, Si−N 1.991(2) Å) have been reported: Handwerker, H.; Leis, C.; Probst, R.; Bissinger, P.; Grohmann, A.; Kiprof, P.; Herdtweck, E.; Blümel, J.; Auner, N.; Zybill, C. *Organometallics* **1993**, *12*, 2162.

(16) By comparison, the Ru−Si and Si−N distances observed in two related complexes featuring a $Cp^*Ru{-}SiR_2{-}NR'_2$ framework fall within the range of 2.4−2.5 Å and 1.7−1.8 Å, respectively: (a) Iwata, M.; Okazaki, M.; Tobita, H. *Organometallics* **2006**, *25*, 6115. (b) Reference 9c herein.

(17) Crystallographic data for $[Cp^*(Me_3P)_2Ru{=}SiMe_2]^+B(C_6F_5)_4^-$ (from references 8d,e herein): Ru═Si 2.238(3) Å; $\sum_{\text{angles at Si}}$ = 358.7°.

(18) (a) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, *2115.* (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

(19) Crystallographically characterized M═SiHR species are rare: (a) Ingleson, M.; Fan, H.; Pink, M.; Tomaszewski, J.; Caulton, K. G. *J. Am. Chem. Soc.* **2006**, *128*, 1804. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *J. Am. Chem. Soc.* **2006**, *128*, 2176. (c) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218. (d) References 7 and 10a,d cited herein.



$[\mathbf{4}]^+$ $[\mathbf{5}]^+$ $[\mathbf{6}]^+$

**8** **10**

***Figure 1.*** The crystallographically determined structures of $[\mathbf{4}]^+X^-$, $[\mathbf{5}]^+X^-$, $[\mathbf{6}]^+X^-$, **8**, and **10** shown with 50% displacement ellipsoids ($X = SO_3CF_3$). The triflate counterions and selected H-atoms have been omitted for clarity.

***Table 1.*** Crystallographic Data for $[\mathbf{4}]^+X^-$, $[\mathbf{5}]^+X^-$, and $[\mathbf{6}]^+X^-$

| | $[\mathbf{4}]^+SO_3CF_3^-$ | $[\mathbf{5}]^+SO_3CF_3^-$ | $[\mathbf{6}]^+SO_3CF_3^-$ |
|---|---|---|---|
| empirical formula | $C_{28}H_{41}F_3N_1O_3P_2Ru_1S_1$ | $C_{40}H_{53}F_3N_1O_3P_1Ru_2S_1Si_1$ | $C_{34}H_{49}F_3N_1O_3P_1Ru_1S_1Si_1$ |
| formula weight | 660.72 | 845.02 | 768.93 |
| crystal dimensions (mm$^3$) | 0.20 × 0.20 × 0.20 | 0.15 × 0.12 × 0.12 | 0.15 × 0.15 × 0.12 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 12.6180(3) | 10.8889(3) | 9.4515(3) |
| $b$ (Å) | 13.5390(3) | 19.4246(5) | 12.7981(3) |
| $c$ (Å) | 19.4530(4) | 19.3800(7) | 29.775(1) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 117.927(1) | 110.163(2) | 97.460(1) |
| $\gamma$ (deg) | 90 | 90 | 90 |
| $V$ (Å$^3$) | 2936.2(1) | 3847.9(2) | 3571.1(2) |
| Z | 4 | 4 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.495 | 1.459 | 1.430 |
| $\mu$ (mm$^{-1}$) | 0.709 | 0.588 | 0.626 |
| $2\theta$ limit (deg) | 55.02 | 52.74 | 43.92 |
| | $-15 \le h \le 16$ | $-13 \le h \le 13$ | $-9 \le h \le 9$ |
| | $-15 \le k \le 17$ | $-24 \le k \le 22$ | $-13 \le k \le 13$ |
| | $-25 \le l \le 25$ | $-24 \le l \le 24$ | $-31 \le l \le 31$ |
| total data collected | 24121 | 14004 | 14029 |
| independent reflections | 6729 | 7877 | 4348 |
| $R_{int}$ | 0.0338 | 0.0545 | 0.0604 |
| observed reflections | 5874 | 5980 | 3193 |
| data/restraints/parameters | 6729/0/357 | 7877/19/563 | 4348/0/429 |
| goodness-of-fit | 1.065 | 1.035 | 1.050 |
| $R_1$ [$F_o^2 \ge 2\sigma(F_o^2)$] | 0.0319 | 0.0442 | 0.0444 |
| $wR_2$ [$F_o^2 \ge -3\sigma(F_o^2)$] | 0.0749 | 0.0947 | 0.0982 |

plexes that treatment with base can result in the deprotonation of the indene backbone of **2b**, thereby affording structurally analogous neutral ($\kappa^2$-$P$,$N$-**2c**)ML$_n$ species.[11a,b,e] Such formally zwitterionic complexes are unusual in that the indenide unit in **2c** functions as an uncoordinated anionic charge reservoir to counterbalance the $\kappa^2$-$P$,$N$-coordinated cationic ML$_n$ fragment, rather than as a locale for metal binding.[21] In light of recent observations by Tilley and co-workers[7] that formal charge distribution can influence the reactivity of M=$Si$−$H$ fragments, and in the absence of reported zwitterionic Ru=Si species, we became interested in preparing zwitterionic relatives of $[\mathbf{5}]^+X^-$ and $[\mathbf{6}]^+X^-$. Treatment of $[\mathbf{5}]^+B(C_6F_5)_4^-$ with $KN(SiMe_3)_2$ or

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(20) H-atom site exchange in related L$_n$Ru($H$)(Si$H$Ph$_2$) species has been observed: Gusev, D. G.; Nadasdi, T. T.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6772.

***Table 2.*** Crystallographic Data for **8** and **10** (X = $SO_3CF_3$)

| | **8** | **10** |
|---|---|---|
| empirical formula | $C_{33}H_{48}N_1P_1Ru_1Si_1$ | $C_{34}H_{49}F_3N_1O_3P_1Ru_1S_1Si_1$ |
| formula weight | 618.85 | 768.93 |
| crystal dimensions ($mm^3$) | 0.72 × 0.55 × 0.50 | 0.20 × 0.20 × 0.15 |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 13.841(1) | 11.1810(2) |
| $b$ (Å) | 14.239(1) | 17.8260(4) |
| $c$ (Å) | 32.135(2) | 17.8990(4) |
| α (deg) | 90 | 90 |
| $\beta$ (deg) | 93.372(1) | 97.091(1) |
| $\gamma$ (deg) | 90 | 90 |
| $V$ (Å$^3$) | 6322.3(8) | 3540.2(1) |
| Z | 8 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.300 | 1.443 |
| $\mu$ (mm$^{-1}$) | 0.606 | 0.631 |
| $2\theta$ limit (deg) | 55.02 | 52.74 |
| | $-17 \leq h \leq 17$ | $-13 \leq h \leq 13$ |
| | $-18 \leq k \leq 18$ | $-22 \leq k \leq 20$ |
| | $-41 \leq l \leq 41$ | $-22 \leq l \leq 22$ |
| total data collected | 52274 | 13245 |
| independent reflections | 14500 | 7230 |
| $R_{int}$ | 0.0208 | 0.0414 |
| observed reflections | 12268 | 6014 |
| data/restraints/parameters | 14500/6/1048 | 7230/243/491 |
| goodness-of-fit | 1.113 | 1.293 |
| $R_1$ [$F_o^2 \geq 2\sigma(F_o^2)$] | 0.0310 | 0.0690 |
| $wR_2$ [$F_o^2 \geq -3\sigma(F_o^2)$] | 0.0806 | 0.1539 |

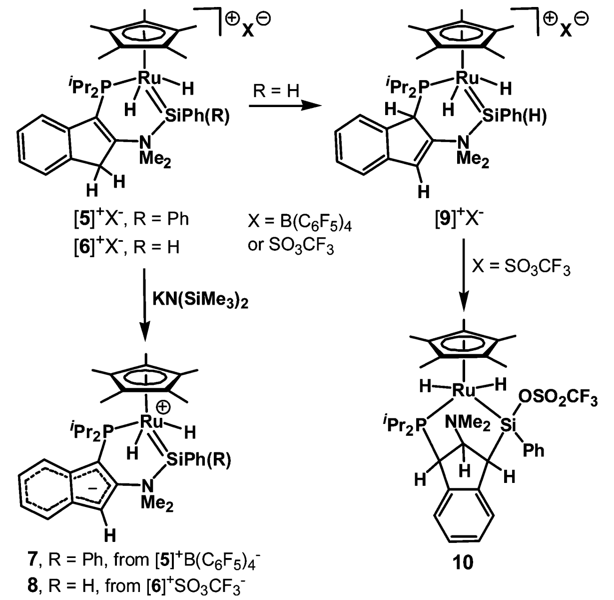
***Table 3.*** Selected Interatomic Distances (Å) and Angles (deg) for [**4**]$^+$X$^-$, [**5**]$^+$X$^-$, [**6**]$^+$X$^-$, **8**, and **10** (X = $SO_3CF_3$)

| | [**4**]$^{+c}$ | [**5**]$^{+d}$ | [**6**]$^{+d}$ | **8** | **10**$^e$ |
|---|---|---|---|---|---|
| Ru−P | 2.2974(6) | 2.2975(9) | 2.293(2) | 2.3193(5) | 2.304(2) |
| Ru−Si | – | 2.2811(9) | 2.262(2) | 2.2635(5) | 2.291(2) |
| Ru−H1 | 1.48(3) | 1.59(4) | 1.60(5) | 1.56(3) | 1.525 |
| Ru−H2 | – | 1.54(3) | 1.52(5) | 1.54(3) | 1.565 |
| Si−H3 | – | – | 1.52(5) | 1.41(2) | – |
| Si···N | – | 1.988(3) | 1.955(4) | 1.924(2) | – |
| Si···H1$^a$ | – | 2.13 | 2.13 | 2.16 | 2.12 |
| Si···H2$^a$ | – | 2.19 | 2.14 | 2.24 | 2.08 |
| P−C3 | 1.815(2) | 1.845(4) | 1.858(5) | 1.807(2) | 1.881(6) |
| N−C2 | 1.443(3) | 1.485(4) | 1.479(7) | 1.488(3) | 1.465(7) |
| C1−C2 | 1.506(3) | 1.509(5) | 1.501(7) | 1.381(3) | 1.547(8) |
| C2−C3 | 1.334(3) | 1.366(4) | 1.350(7) | 1.442(3) | 1.576(7) |
| C3−C3a | 1.484(3) | 1.499(5) | 1.502(7) | 1.453(3) | 1.519(8) |
| C3a−C4 | 1.390(3) | 1.401(5) | 1.398(8) | 1.411(3) | 1.410(8) |
| C4−C5 | 1.396(3) | 1.388(5) | 1.385(8) | 1.384(3) | 1.383(9) |
| C5−C6 | 1.382(4) | 1.382(6) | 1.379(8) | 1.400(4) | 1.374(10) |
| C6−C7 | 1.393(4) | 1.392(5) | 1.375(8) | 1.358(4) | 1.388(10) |
| C7−C7a | 1.384(3) | 1.387(5) | 1.381(7) | 1.415(3) | 1.400(8) |
| C1−C7a | 1.504(3) | 1.493(5) | 1.475(7) | 1.400(3) | 1.503(8) |
| C3a−C7a | 1.413(3) | 1.396(5) | 1.405(7) | 1.439(3) | 1.393(8) |
| ∑ angles at Si$^b$ | – | 342.7 | 341.2 | 339.9 | – |

$^a$ Measured in the final refined structure. $^b$ Sum of the Ru−Si−R angles (R = C or H). $^c$ Ru−N 2.142(2) Å; Ru−C27 2.069(2) Å; N−C27 1.435(3) Å; and N−C28 1.472(3) Å. $^d$ Shortest Si···$SO_3CF_3$ distance >5 Å. $^e$ Si−O1 1.77(1) Å and 1.88(2) Å for the two components of the disordered triflate group; Si−C1 1.892(6) Å.

[**6**]$^+SO_3CF_3^-$ with $NaN(SiMe_3)_2$ afforded cleanly ($^{31}$P NMR) the corresponding Cp*($\mu$-*P*,*N*-**2c**)(H)$_2$Ru═SiRPh complex, in the absence of observable products arising from deprotonation of a Ru−*H* group; these hydrocarbon-soluble zwitterionic silylenes were obtained in 69% (R = Ph, **7**) and 86% (R = H, **8**) isolated yield, respectively (Scheme 3). The connectivity within **7** and **8** that was assigned initially on the basis of NMR spectroscopic data was confirmed subsequently through the crystallographic characterization of **8**; an ORTEP[12] diagram of this complex is provided in Figure 1. With the exception of a slight elongation of the Ru−P distance in **8**, the connectivity within the Ru coordination sphere of this zwitterion is comparable to that of the precursory cationic complex [**6**]$^+SO_3CF_3^-$. However, the somewhat contracted Si−N distance in **8** (1.924(2) Å) versus that found in [**6**]$^+SO_3CF_3^-$ (1.955(4) Å) may reflect increased basicity of the N-donor fragment in the formally anionic ligand **2c** in **8**, relative to that of **2b** featured in [**6**]$^+SO_3CF_3^-$. In contrast to the pronounced bond length alternation that is observed within the indene backbone of [**6**]$^+SO_3CF_3^-$, the indenide unit in **8** exhibits a more delocalized structure in keeping with a Hückel aromatic (10$\pi$-electron) framework. However, in keeping with other crystallographically characterized complexes featuring $\kappa^2$-*P*,*N*-**2c**,[11] the short P−C3 and C1−C2 distances found in **8** suggest that a resonance contributor featuring a $^i$Pr$_2$P═C3 linkage and a formal anionic charge on phosphorus must also be considered when describing the electronic structure of this formally zwitterionic complex.[11,22]

***Scheme 3.*** Isomerization and Reactivity of the Base-Stabilized Ru═Si Complexes [**5**]$^+$X$^-$ and [**6**]$^+$X$^-$



**Reactivity of Base-Stabilized Ru═Si Complexes.** Having successfully prepared via double geminal Si−H bond activation the base-stabilized Ru−hydrosilylene cations [**6**]$^+$X$^-$ (X = $B(C_6F_5)_4$, $SO_3CF_3$), as well as the derived zwitterion **8**, we turned our attention to probing the reactivity of these species in the context of the proposed G−T hydrosilylation mechanism. In particular, we were interested in assessing how base-stabilization of the Ru═Si unit in such complexes, as well as the differing charge distribution in [**6**]$^+$X$^-$ versus **8**, might influence stoichiometric and catalytic reactivity with alkenes. In contrast to **1**,[3a] no reaction was observed ($^1$H and $^{31}$P NMR) between either [**6**]$^+$X$^-$ or **8** and 1-hexene or styrene ($C_6D_5Br$, 60 °C, 24 h). Moreover, negligible conversion was achieved in hydrosilylation reactions employing $PhSiH_3$ and either of these olefins in the presence of 5 mol % [**6**]$^+$X$^-$ or **8** ($C_6D_5Br$, 60

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[21] For discussions pertaining to the diverse coordination behavior of indenyl ligands, see: (a) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291. (b) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937. (c) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233−234*, 157. (d) Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219−221*, 311. (e) Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967.

[22] Izod, K. *Coord. Chem. Rev.* **2002**, *227*, 153.

°C, 48 h); under similar conditions, 0.5 mol % **1** affords >98% conversion.[3a] These observations, when considered alongside the established inability of Cp*($^i$Pr$_3$P)(H)$_2$Ru−SiHPh(X) (X = Cl, SO$_3$CF$_3$) to mediate such catalytic transformations,[3a] appear to provide indirect evidence for the required intermediacy of base-free Ru═Si species in alkene hydrosilylation catalysis mediated by M═Si complexes such as **1**.

In tracking the behavior of [**6**]$^+$B(C$_6$F$_5$)$_4$$^-$ in solution by use of NMR techniques, slow isomerization to [**9**]$^+$B(C$_6$F$_5$)$_4$$^-$ was noted. When employing Et$_2$O-$d_{10}$ as the solvent, this transformation was quantitative after 96 h, thereby allowing for the spectroscopic characterization of this complex in situ; no further reactivity was observed for [**9**]$^+$B(C$_6$F$_5$)$_4$$^-$. The isomerization of [**6**]$^+$SO$_3$CF$_3$$^-$ to [**9**]$^+$SO$_3$CF$_3$$^-$ was also observed in CH$_2$Cl$_2$, C$_6$D$_5$Br, or PhF; when employing CH$_2$Cl$_2$ as the solvent, >90% conversion was achieved after only 3 h ($^{29}$Si and $^{31}$P NMR). However, in continuing to monitor this solution over the course of 48 h, the clean conversion of this mixture of [**6**]$^+$SO$_3$CF$_3$$^-$ and [**9**]$^+$SO$_3$CF$_3$$^-$ to **10** was detected. Complex **10** was obtained in 96% isolated yield and was characterized spectroscopically. Whereas $^1$H NMR data supported the identity of **10** as a Cp*($\kappa^1$-*P*,N)Ru(H)$_2$ complex possessing $C_1$ symmetry, the absence of resonances attributable to an Si−H group or a vinylic indene C$_{sp2}$−H fragment suggested that **10** may result from the intramolecular addition of Si−H across the styrene-like C═C unit in a coordinatively unsaturated intermediate derived from [**9**]$^+$SO$_3$CF$_3$$^-$. This proposal was confirmed on the basis of data obtained from an X-ray diffraction study; an ORTEP[12] diagram of **10** is provided in Figure 1. Interestingly, the stoichiometric transformation of [**4**]$^+$SO$_3$CF$_3$$^-$ into [**6**]$^+$SO$_3$CF$_3$$^-$ and ultimately into **10** corresponds to the net triple Si−H bond activation of PhSiH$_3$, and is conceptually related to the stepwise conversion of **1a** into **1b**, and subsequently **1c** in the proposed G−T hydrosilylation mechanism (Scheme 1). The lack of such reactivity for [**9**]$^+$B(C$_6$F$_5$)$_4$$^-$ suggests that the conversion of [**9**]$^+$SO$_3$CF$_3$$^-$ into **10** is perhaps enabled by the coordinating ability of triflate. Furthermore, given the lack of inter- or intramolecular hydrosilylation chemistry observed for [**6**]$^+$SO$_3$CF$_3$$^-$, it is plausible that isomerization to [**9**]$^+$SO$_3$CF$_3$$^-$ promotes Si−N dissociation and/or provides more advantageous positioning of the Ru═*Si*−*H* unit for intramolecular addition to the alkene fragment.

## Summary and Conclusions

We have demonstrated herein that reactive, coordinatively unsaturated intermediates of the type [Cp*Ru($\kappa^2$-2-*N*Me$_2$-3-*P*$^i$Pr$_2$-indene)]$^+$X$^-$ ([**3**]$^+$X$^-$; X = B(C$_6$F$_5$)$_4$ or SO$_3$CF$_3$) are capable of extruding silylene fragments from Ph$_2$SiH$_2$ and PhSiH$_3$ in a stoichiometric fashion by way of double geminal Si−H bond activation, thereby affording complexes of the type [Cp*($\mu$-*P*,*N*)(H)$_2$Ru═SiRPh]$^+$X$^-$ ([**5**]$^+$X$^-$, R = Ph; [**6**]$^+$X$^-$, R = H). These transformations represent the first documented examples of the direct formation of Ru═Si species via double geminal Si−H bond activation of an organosilane. The observation of such reactivity involving PhSiH$_3$ leading to [**6**]$^+$X$^-$ is noteworthy, in that it provides persuasive empirical support for a key step in the proposed Glaser−Tilley hydrosilylation mechanism employing [Cp*($^i$Pr$_3$P)(H)$_2$Ru═SiHPh·OEt$_2$]$^+$B(C$_6$F$_5$)$_4$$^-$ (**1**) as a precatalyst (i.e., the conversion of **1a** to **1b**/**1b′** in Scheme 1).[3] Although mechanistic details regarding the formation of the base-stabilized Ru═Si species [**5**]$^+$X$^-$ and [**6**]$^+$X$^-$ are not currently known, the ancillary ligand **2b** in [**3**]$^+$X$^-$ can be viewed as providing access to an operational equivalent of the 14-electron complex [Cp*Ru($\kappa^1$-2-NMe$_2$-3-*P*$^i$Pr$_2$-indene)]$^+$X$^-$ (analogous to **1a**), as well as offering stabilization to the Ru═Si fragment generated following double geminal Si−H bond activation of Ph$_2$SiH$_2$ or PhSiH$_3$. Treatment of these new [Cp*($\mu$-*P*,*N*)(H)$_2$Ru═SiRPh]$^+$X$^-$ salts with base led to the formation of novel zwitterionic complexes of the type Cp*($\mu$-*P*,*N*)(H)$_2$Ru═SiRPh (**7**, R = Ph; **8**, R = H) that feature a formally anionic P,N-indenide ligand. In contrast to **1**, both [**6**]$^+$X$^-$ and **8** proved unreactive toward 1-hexene and styrene and provided negligible catalytic turnover in the attempted metal-mediated hydrosilylation of these substrates with PhSiH$_3$, thereby providing further experimental evidence for the required intermediacy of base-free Ru═Si species in catalytic alkene hydrosilylation chemistry mediated by complexes such as **1**. However, isomerization of the P,N-indene ligand backbone in [**6**]$^+$SO$_3$CF$_3$$^-$ ultimately resulted in the formation of **10**—the apparent product of intramolecular hydrosilylation involving the addition of a Ru═*Si*−*H* group across a C═C fragment within the indene ligand backbone. Encouraged by the demonstrated propensity of intermediates such as [**3**]$^+$X$^-$ for intermolecular double geminal Si−H bond activation, we are currently exploring the reactivity of this and other coordinatively unsaturated metal complexes supported by P,N-indene or indenide ligands with a range of E−H-containing substrates, in an effort to identify new metal-mediated E−H bond activation chemistry.

## Experimental Section

**General Considerations.** All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven-dried (130 °C) for 5 d and then evacuated for 24 h prior to use. The non-deuterated solvents dichloromethane, THF, diethyl ether, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system provided by mBraun Inc. Dichloromethane, THF, and diethyl ether were purified over two alumina-packed columns, while benzene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. C$_6$D$_6$, CD$_2$Cl$_2$, and PhF (Aldrich), as well as C$_6$D$_5$Br and Et$_2$O-$d_{10}$ (Cambridge Isotope Laboratories) were degassed by using a minimum of three repeated freeze−pump−thaw cycles and then were dried over 4 Å molecular sieves for 24 h prior to use. PhSiH$_3$ (Strem) was degassed by using three repeated freeze−pump−thaw cycles, and Ph$_2$SiH$_2$ (Gelest, shipped under argon) was not degassed; both of these silanes were dried over 4 Å molecular sieves for 24 h prior to use. Complexes [**4**]$^+$B(C$_6$F$_5$)$_4$$^-$ and Cp*RuCl($\kappa^2$-2-*N*Me$_2$-3-*P*$^i$Pr$_2$-indene) were prepared by employing published procedures.[11e] All other commercial reagents were obtained from Aldrich and were used as received, with the exceptions of NaN(SiMe$_3$)$_2$, KN(SiMe$_3$)$_2$, and TlSO$_3$CF$_3$ (Strem) that were dried in vacuo for 24 h prior to use. Unless otherwise stated, NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1 ($^1$H) MHz, 125.8 ($^{13}$C) MHz, 99.4 ($^{29}$Si) MHz, and 202.5 ($^{31}$P) MHz with chemical shifts reported in parts per million downfield of SiMe$_4$ (for $^1$H, $^{13}$C, and $^{29}$Si), or 85% H$_3$PO$_4$ in D$_2$O (for $^{31}$P). In some cases slightly fewer than expected independent $^1$H or $^{13}$C NMR resonances were observed (despite prolonged data acquisition times), and $^{13}$C resonances associated with B(C$_6$F$_5$)$_4$$^-$ and SO$_3$CF$_3$$^-$ were not assigned. $^1$H and $^{13}$C NMR chemical shift assignments are given on the basis of data obtained from $^{13}$C-DEPT, $^1$H−$^1$H

COSY, $^1$H−$^{13}$C HSQC, and $^1$H−$^{13}$C HMBC NMR experiments. $^{29}$Si NMR chemical shift assignments are given on the basis of data obtained from $^1$H−$^{29}$Si HMQC ($^1$H-coupled experiments were employed in the determination of $^1J_{SiH}$ values) as well as $^1$H−$^{29}$Si HMBC (*J*-HMBC[23] experiments were employed in the determination of $^nJ_{SiH}$ values for $n > 1$) experiments. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. *Note*: With the exception of [**4**]$^+$SO$_3$CF$_3$$^-$ and **10**, all complexes reported herein were found to be thermally unstable, even when stored under dinitrogen within a glovebox; storage of these complexes at or below −35 °C is recommended.

**Synthesis of [4]$^+$SO$_3$CF$_3$$^-$.** To a glass vial containing a magnetically stirred suspension of Cp*RuCl($\kappa^2$-2-*N*Me$_2$-3-*P*$^i$Pr$_2$-indene) (0.50 g, 0.91 mmol) in THF (10 mL), was added all at once solid TlSO$_3$CF$_3$ (0.32 g, 0.91 mmol). The addition caused an immediate color change from red-orange to brown and was accompanied by the precipitation of an off-white solid. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 1 h. Analysis of $^{31}$P NMR data collected on an aliquot of this crude reaction mixture solution indicated the quantitative formation of [**4**]$^+$SO$_3$CF$_3$$^-$. The mixture was then filtered through Celite, yielding a yellow-brown solution. The separated off-white precipitate was washed with THF (2 × 3 mL) followed by CH$_2$Cl$_2$ (2 × 3 mL), and the filtrate from the washings was combined with the filtered reaction mixture solution. The solvents and other volatiles were then removed in vacuo, and the resulting oily, yellow-brown solid was washed with pentane (3 × 1.5 mL). The solid residue was then extracted with CH$_2$Cl$_2$ (6 mL) and filtered through Celite. After removal of the solvent in vacuo, the residue was washed with pentane (2 × 3 mL). The solid was then dried in vacuo to yield [**4**]$^+$SO$_3$CF$_3$$^-$ as an analytically pure, pale-brown solid (0.57 g, 0.86 mmol, 94%). Anal. Calcd for C$_{28}$H$_{41}$PNF$_3$SO$_3$Ru: C, 50.90; H, 6.26; N, 2.12. Found: C, 50.63; H, 5.89; N, 2.23. In solution, complex [**4**]$^+$SO$_3$CF$_3$$^-$ exhibits dynamic behavior analogous to that described previously for [**4**]$^+$B(C$_6$F$_5$)$_4$$^-$.[11e] $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.42 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.36 (m, 1H, C7-H or C4-H), 7.32−7.26 (m, 2H, C5-H and C6-H), 3.74 (s, 2H, C1(H)$_2$), 2.66 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 1.89 (s, 15H, C$_5$Me$_5$), 1.19−1.00 (m, 12H, P(CH*Me$_a$Me$_b$*)$_2$), 0.87 (broad s, 6H, NMe$_2$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 173.0 (m, C2), 145.2 (broad m, C3a or C7a), 138.8 (broad m, C7a or C3a), 127.9 (C5 or C6), 127.2 (C6 or C5), 125.8 (C4 or C7), 122.9 (C7 or C4), 100.7 (broad m, *C*$_5$Me$_5$), 52.3 (NMe$_2$), 35.6 (broad m, C1), 24.9 (d, $^1J_{PC}$ = 28.6 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 18.7−18.6 (m, P(CH*Me$_a$Me$_b$*)$_2$), 11.4 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 83.3. A single crystal of [**4**]$^+$SO$_3$CF$_3$$^-$ grown from a concentrated Et$_2$O solution at ambient temperature proved suitable for X-ray analysis.

**Synthesis of [5]$^+$B(C$_6$F$_5$)$_4$$^-$.** To a glass vial containing a magnetically stirred suspension of [**4**]$^+$B(C$_6$F$_5$)$_4$$^-$ (0.15 g, 0.12 mmol) in Et$_2$O (4 mL), was added Ph$_2$SiH$_2$ (222 $\mu$L, 1.2 mmol) all at once by way of an Eppendorf micropipet. The vial was then sealed with a PTFE-lined cap, and the mixture was stirred magnetically for 48 h. Analysis of $^{31}$P NMR data collected on this solution indicated the quantitative formation of [**5**]$^+$B(C$_6$F$_5$)$_4$$^-$. The solvent and other volatiles were then removed in vacuo, yielding an oily, brown-yellow solid. The solid was then washed with pentane (5 × 3 mL), and the product was dried in vacuo to yield [**5**]$^+$B(C$_6$F$_5$)$_4$$^-$ as an analytically pure, off-white powder (0.14 g, 0.098 mmol, 82%). Anal. Calcd for C$_{63}$H$_{53}$PNSiBF$_{20}$Ru: C, 55.03; H, 3.89; N, 1.02. Found: C, 55.30; H, 4.11; N, 1.01. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.93−7.89 (broad s, 2H, Si-aryl-Hs), 7.86 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.62−7.60 (m, 2H, Si-aryl-Hs), 7.57 (m, 1H, aryl-H), 7.54 (m, 1H, aryl-H), 7.52−7.50 (m, 4H, Si-aryl-Hs), 7.45−7.40 (m, 3H, 2 Si-aryl-Hs and aryl-H), 3.87 (s, 2H, C1(H)$_2$), 3.03 (m, 2H, P(C*H*Me$_a$Me$_b$)), 2.84 (s, 6H, NMe$_2$), 1.66 (s, 15H, C$_5$Me$_5$), 1.25 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 6.5 Hz, 6H, P(CH*Me$_a$*Me$_b$)$_2$), 1.02 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)$_2$), −10.24 (d, $^2J_{PH}$ = 32.0 Hz, 2H, Ru(H)$_2$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 161.9 (d, $^2J_{PC}$ = 4.9 Hz, C2), 142.5 (Si-aryl-C), 137.2 (m, C3a or C7a), 136.0 (m, 2 Si-aryl-*C*Hs), 135.5 (2 Si-aryl-*C*Hs), 135.3 (C7a or C3a), 134.2 (aryl-*C*H), 130.4 (2 Si-aryl-*C*Hs), 128.2 (2 Si-aryl-*C*Hs), 128.1 (2 Si-aryl-*C*Hs), 127.1 (m, aryl-*C*H), 124.0 (2 aryl-*C*Hs), 115.1 (d, $^1J_{PC}$ = 4.9 Hz, C3), 98.5 (*C*$_5$Me$_5$), 52.3 (broad m, NMe$_2$), 39.8 (d, $^3J_{PC}$ = 7.0 Hz, C1), 30.9 (d, $^1J_{PC}$ = 24.2 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 20.4 (P(CHMe$_a$*Me$_b$*)$_2$), 19.0 (P(CH*Me$_a$*Me$_b$)$_2$), 11.2 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 73.7; $^{29}$Si{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 106.7 ($^1$H−$^{29}$Si HMBC), $^2J_{SiH}$ = 3.0 Hz (*J*-HMBC).

**Synthesis of [5]$^+$SO$_3$CF$_3$$^-$.** To a glass vial containing a magnetically stirred solution of [**4**]$^+$SO$_3$CF$_3$$^-$ (0.37 g, 0.55 mmol) in PhF (8 mL), was added Ph$_2$SiH$_2$ (1.15 mL, 5.53 mmol) all at once by way of an Eppendorf micropipet. The vial was then sealed with a PTFE-lined cap and mixed manually by inversion several times. After 4 d, the mixture had lightened slightly from light brown to yellow-brown. Analysis of an aliquot of this solution by use of $^{31}$P NMR methods indicated the presence of several P-containing products. After returning the NMR tube contents to the reaction vial, the mixture was concentrated in vacuo to approximately 3 mL in order to induce crystallization. After 24 h, the colorless crystalline solid that had settled in the vial was isolated by transferring the supernatant solution to a new glass vial by using a Pasteur pipet; this solution was then concentrated in vacuo in order to induce further crystallization. After repeating this procedure, the isolated crops of crystals were then combined, dried in vacuo, and washed with PhF (3 × 1.5 mL), and then pentane (3 × 1.5 mL), to yield [**5**]$^+$SO$_3$CF$_3$$^-$ as a white solid (0.18 g, 0.22 mmol, 39%). Anal. Calcd for C$_{40}$H$_{53}$PNSiF$_3$SO$_3$Ru$_1$: C, 56.85; H, 6.33; N, 1.66. Found: C, 56.49; H, 6.27; N, 1.25. A single crystal of [**5**]$^+$SO$_3$CF$_3$$^-$ grown from an undisturbed PhF solution of the initially prepared reaction mixture stored at ambient temperature proved suitable for X-ray analysis. Complex [**5**]$^+$SO$_3$CF$_3$$^-$ was found to be either insoluble in or reactive with all common solvents; for example, THF, CH$_2$Cl$_2$, acetone, C$_6$D$_5$Br, PhF, and CH$_3$CN all proved unsatisfactory.

**Synthesis of [6]$^+$B(C$_6$F$_5$)$_4$$^-$.** To a glass vial containing a magnetically stirred suspension of [**4**]$^+$B(C$_6$F$_5$)$_4$$^-$ (0.15 g, 0.12 mmol) in Et$_2$O (4 mL) was added PhSiH$_3$ (15 $\mu$L, 0.12 mmol) all at once via an Eppendorf micropipet. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 30 min. During this time period, the suspension had become a yellow solution. Analysis of $^{31}$P NMR data collected on an aliquot of this solution indicated the quantitative formation of [**6**]$^+$B(C$_6$F$_5$)$_4$$^-$. The solvent and other volatiles were then removed in vacuo yielding an oily, yellow foam. This material was then washed with pentane (5 × 3 mL), and the product was dried in vacuo to yield [**6**]$^+$B(C$_6$F$_5$)$_4$$^-$ as an analytically pure, pale-yellow powder (0.16 g, 0.12 mmol, 94%). Anal. Calcd for C$_{57}$H$_{49}$PNSiBF$_{20}$Ru: C, 52.71; H, 3.80; N, 1.08. Found: C, 52.77; H, 3.58; N, 0.94. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 7.91 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.69 (d, $^3J_{HH}$ = 6.5 Hz, 2H, 2 Si-aryl-Hs), 7.49−7.35 (m, 6H, 3 aryl-Hs and 3 Si-aryl-Hs), 5.56 (apparent t, $J$ = 8.0 Hz, 1H, Si−H), 3.77−3.57 (m, 2H, C(*H$_a$*)(*H$_b$*)), 3.33 (s, 3H, NMe$_a$), 3.24 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.89 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.86 (s, 3H, NMe$_b$), 1.92 (s, 15H, C$_5$Me$_5$), 1.26−1.14 (m, 6H, P(CH*Me$_a$*Me$_b$) and P(CH*Me$_c$*Me$_d$)), 0.99 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.96 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), −9.91 (d, $^2J_{PH}$ = 34.4 Hz, 1H, Ru−H$_a$), −11.26 (apparent d of d, $J$ = 32.5 Hz, $J$ = 4.0 Hz, 1H, Ru−H$_b$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 160.4 (d, $^2J_{PC}$ = 5.3 Hz, C2), 139.7 (m, Si-aryl-C), 137.7 (m, C3a or C7a), 135.7 (m, C7a or C3a), 135.2 (2 Si-aryl-*C*Hs), 134.9 (d, $^1J_{PC}$ = 36.0 Hz, C3), 131.2 (Si-aryl-*C*H), 129.0 (2 Si-aryl-*C*Hs), 127.8 (C5 or C6), 127.7 (aryl-*C*H), 124.5 (aryl-*C*H), 124.3 (C4 or C7), 98.5 (*C*$_5$Me$_5$), 56.7 (NMe$_a$), 53.5 (NMe$_b$), 39.5 (d, $^3J_{PC}$ = 6.0 Hz, C1), 31.3 (d, $^1J_{PC}$ = 23.5 Hz, P(*C*HMe$_c$Me$_d$)), 30.6 (d, $^1J_{PC}$ = 26.4 Hz, P(*C*HMe$_a$Me$_b$)), 21.0 (P(CHMe$_c$*Me$_d$*)), 20.7−20.6 (m, (P(CHMe$_a$*Me$_b$*) and P(CH*Me$_c$*Me$_d$)), 19.3 (d, $^2J_{PC}$ = 7.0 Hz, P(CH*Me$_a$*Me$_b$)), 11.4 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 79.6; $^{29}$Si{$^1$H} NMR (CD$_2$Cl$_2$): $\delta$ 112.0 ($^1$H−$^{29}$Si HMBC/

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[23] *J*-HMBC: Meissner, A.; Sørensen, O. W. *Magn. Reson. Chem.* **2001**, *39*, 49.

HMQC), $^{1}J_{\mathrm{SiH}} = 191.4$ Hz ($^{1}$H-coupled $^{1}$H−$^{29}$Si HMQC), $^{2}J_{\mathrm{SiH}}$ not detected by $J$-HMBC.

**Synthesis of [6]$^+$SO$_3$CF$_3$$^-$.** To a glass vial containing a magnetically stirred suspension of [**4**]$^+$SO$_3$CF$_3$$^-$ (0.31 g, 0.47 mmol) in PhF (7 mL) was added PhSiH$_3$ (58 $\mu$L, 0.47 mmol) all at once via Eppendorf micropipet. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 30 min. During this time period, the suspension had lightened from a brown solution to one yellow in color. Analysis of $^{31}$P NMR data collected on an aliquot of this solution indicated the quantitative formation of [**6**]$^+$SO$_3$CF$_3$$^-$. The solvent and other volatiles were then removed in vacuo, yielding an oily, yellow solid. The solid was then washed with pentane (3 × 3 mL), and the product was dried in vacuo to yield [**6**]$^+$SO$_3$CF$_3$$^-$ as an analytically pure, fluffy, off-white solid (0.34 g, 0.45 mmol, 95%). Anal. Calcd for $C_{34}H_{49}PNSiF_3SO_3Ru$: C, 53.10; H, 6.42; N, 1.82. Found: C, 52.71; H, 6.65; N, 1.80. $^{1}$H NMR (C$_6$D$_5$Br): $\delta$ 7.57 (d, $^{3}J_{\mathrm{HH}} = 8.0$ Hz, 1H, C4-H or C7-H), 7.41−7.37 (m, 2H, 2 Si-aryl-Hs), 7.17−7.09 (m, 5H, 2 aryl-Hs and 3 Si-aryl-Hs), 7.01 (t, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 1H, C5-H or C6-H), 5.10 (apparent t, $J = 4.0$ Hz, 1H, Si−H), 4.21 (apparent d, $J = 24.5$ Hz, 1H, C($H_a$)(H$_b$)), 3.19−3.12 (m, 4H, C(H$_a$)($H_b$) and NMe$_a$), 2.78 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.67 (s, 3H, NMe$_b$), 2.47 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.50 (s, 15H, C$_5$Me$_5$), 0.81−0.73 (m, 6H, P(CH$Me_a$-Me$_b$) and P(CH$Me_c$Me$_d$)), 0.64 (d of d, $^{3}J_{\mathrm{PH}} = 15.5$ Hz, $^{3}J_{\mathrm{HH}} = 6.5$ Hz, 3H, P(CHMe$_a$$Me_b$)), 0.44 (d of d, $^{3}J_{\mathrm{PH}} = 17.0$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 3H, P(CHMe$_c$$Me_d$)), −10.38 (d, $^{2}J_{\mathrm{PH}} = 34.0$ Hz, 1H, Ru−H$_a$), −11.74 (apparent d of d, $J = 32.5$ Hz, $J = 3.0$ Hz, 1H, Ru−H$_b$); $^{13}$C{$^{1}$H} NMR (C$_6$D$_5$Br): $\delta$ 162.2 (d, $^{2}J_{\mathrm{PC}} = 5.1$ Hz, C2), 142.0 (C3a or C7a), 140.1 (Si-aryl-C), 138.5 (d, $J_{\mathrm{PC}} = 5.8$ Hz, C7a or C3a), 135.0 (2 Si-aryl-*C*Hs), 132.4 (d, $^{1}J_{\mathrm{PC}} = 38.2$ Hz, C3), 130.6 (Si-aryl-*C*H), 128.6 (2 Si-aryl-*C*Hs), 127.2 (C5 or C6), 127.0 (aryl-*C*H), 124.9 (aryl-*C*H), 123.4 (C4 or C7), 97.5 (*C*$_5$Me$_5$), 56.2 (NMe$_a$), 53.1 (NMe$_b$), 39.8 (d, $^{3}J_{\mathrm{PC}} = 6.0$ Hz, C1), 30.9 (d, $^{1}J_{\mathrm{PC}} = 23.7$ Hz, P(*C*HMe$_c$Me$_d$)), 30.0 (d, $^{1}J_{\mathrm{PC}} = 26.5$ Hz, P(*C*HMe$_a$Me$_b$)), 20.8 (d, $^{2}J_{\mathrm{PC}} = 9.4$ Hz, P(CH$Me_a$-Me$_b$) or P(CH$Me_c$Me$_d$)), 20.7 (P(CHMe$_c$$Me_d$)), 20.5 (P(CHMe$_a$$Me_b$)), 19.0 (d, $^{2}J_{\mathrm{PC}} = 6.8$ Hz, P(CH$Me_c$Me$_d$) or P(CH$Me_a$Me$_b$)), 11.4 (C$_5$*Me*$_5$); $^{31}$P{$^{1}$H} NMR (C$_6$D$_5$Br): $\delta$ 76.6; $^{29}$Si{$^{1}$H} NMR (C$_6$D$_5$Br): $\delta$ 107.2 ($^{1}$H−$^{29}$Si HMBC/HMQC), $^{1}J_{\mathrm{SiH}} = 195.0$ Hz ($^{1}$H-coupled $^{1}$H−$^{29}$Si HMQC), $^{2}J_{\mathrm{SiH}}$ not detected by $J$-HMBC. A single crystal of [**6**]$^+$SO$_3$CF$_3$$^-$ grown from a mixture of PhF and hexanes at ambient temperature proved suitable for X-ray analysis.

**Synthesis of 7**. To a glass vial containing a magnetically stirred oily suspension of [**5**]$^+$B(C$_6$F$_5$)$_4$$^-$ (0.19 g, 0.14 mmol) in C$_6$H$_6$ (5 mL) was added solid KN(SiMe$_3$)$_2$ (0.027 g, 0.15 mmol) all at once. The addition of base resulted in an immediate darkening of the mixture from yellow to brown. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 2 h. Analysis of $^{31}$P NMR data collected on this solution indicated the quantitative formation of **7**. The solution was then filtered through Celite, and the benzene solvent and other volatiles were removed in vacuo, yielding an oily, yellow solid. The solid was then washed with pentane (3 × 1.5 mL) and dried in vacuo. The residue was then treated with benzene (5 mL), and the resulting mixture was filtered through Celite. The filtrate was then stripped of benzene in vacuo, and the residual solid was subsequently washed with pentane (3 × 3 mL) and dried again in vacuo. This benzene extraction process was repeated twice more. Analysis of $^{19}$F NMR (C$_6$H$_6$) collected on a sample of the residual powder confirmed the absence of KB(C$_6$F$_5$)$_4$ or other F-containing species. After removal of volatiles in vacuo, **7** was isolated as an analytically pure, pale-yellow powder (0.067 g, 0.096 mmol, 69%). Anal. Calcd for $C_{39}H_{52}PNSiRu$: C, 67.40; H, 7.54; N, 2.02. Found: C, 67.14; H, 7.67; N, 1.68. $^{1}$H NMR (C$_6$D$_6$): $\delta$ 7.86 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 1H, C4-H), 7.76−7.74 (m, 2H, Si-aryl-Hs), 7.48 (d, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 1H, C7-H), 7.23−7.17 (m, 8H, Si-aryl-Hs), 6.78 (t, $^{3}J_{\mathrm{HH}} = 8.0$ Hz, 1H, C6-H), 6.72 (t, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 1H, C5-H), 6.17 (d, $J = 3.5$ Hz, 1H, C1-H), 2.64 (s, 6H, NMe$_2$), 1.44 (s, 15H, C$_5$Me$_5$), 1.13 (d of d, $^{3}J_{\mathrm{PH}} = 15.5$ Hz, $^{3}J_{\mathrm{HH}} = 6.0$ Hz, 6H, P(CH$Me_a$Me$_b$)$_2$), 1.07 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 0.97 (m, 6H, P(CHMe$_a$$Me_b$)$_2$), −10.45 (d, $^{2}J_{\mathrm{PH}} = 30.0$ Hz, 2H, Ru(H)$_2$); $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 149.6 (d, $^{2}J_{\mathrm{PC}} = 12.9$ Hz, C2), 135.7 (Si-aryl-C), 135.2 (m, Si-aryl-*C*H), 132.3 (C7a), 129.5 (Si-aryl-*C*H), 129.0 (m, C3a), 128.0 (overlapping Si-aryl-*C*Hs), 127.8 (Si-aryl-*C*H), 127.3 (overlapping Si-aryl-*C*Hs), 121.0 (C4), 120.1 (C7), 115.7 (C6), 114.7 (C5), 96.5 (*C*$_5$-Me$_5$), 92.9 (d, $^{3}J_{\mathrm{PC}} = 6.7$ Hz, C1), 85.0 (d, $^{1}J_{\mathrm{PC}} = 62.6$ Hz, C3), 50.2 (broad m, NMe$_2$), 21.5 (m, P(*C*HMe$_a$Me$_b$)$_2$), 20.2 (P(CHMe$_a$$Me_b$)$_2$), 19.2 (broad m, P(CH$Me_a$Me$_b$)$_2$), 11.0 (C$_5$*Me*$_5$); $^{31}$P{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 58.1; $^{29}$Si{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 96.3 ($^{1}$H−$^{29}$Si HMBC), $^{2}J_{\mathrm{SiH}} = 6.2$ Hz ($J$-HMBC).

**Synthesis of 8**. To a glass vial containing a magnetically stirred suspension of [**6**]$^+$SO$_3$CF$_3$$^-$ (0.20 g, 0.26 mmol) in PhF (8 mL) was added solid NaN(SiMe$_3$)$_2$ (0.050 g, 0.027 mmol) all at once. The addition of base resulted in an immediate darkening of the mixture from yellow to brown. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 1 h. Analysis of $^{31}$P NMR data collected on this solution indicated the quantitative formation of **8**. The solution was then filtered through Celite, and the PhF solvent and other volatiles were removed in vacuo, yielding an oily, yellow solid. The solid was then washed with pentane (3 × 1.5 mL) and dried in vacuo. The residue was then treated with benzene (5 mL), and the resulting mixture was filtered through Celite. The filtrate was then stripped of benzene in vacuo, and the residual solid was subsequently washed with pentane (3 × 3 mL). After removal of traces of pentane in vacuo, **8** was isolated as an analytically pure, off-white powder (0.14 g, 0.22 mmol, 86%). Anal. Calcd for $C_{33}H_{48}PNSiRu$: C, 64.04; H, 7.82; N, 2.26. Found: C, 63.93; H, 8.16; N, 2.17. $^{1}$H NMR (C$_6$D$_6$): $\delta$ 8.19 (d, $^{3}J_{\mathrm{HH}} = 8.5$ Hz, 1H, C4-H or C7-H), 7.95 (d, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 1H, C7-H or C4-H), 7.50−7.47 (m, 2H, Si-aryl-Hs), 7.36 (m, 1H, C5-H or C6-H), 7.30 (m, 1H, C6-H or C5-H), 7.06−7.03 (m, 3H, Si-aryl-Hs), 6.17 (d, $J = 4.5$ Hz, 1H, C1-H), 5.44 (apparent t, $J = 3.5$ Hz, 1H, Si−H), 3.68 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.92 (s, 3H, NMe$_a$), 2.56 (s, 3H, NMe$_b$), 2.31 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.70 (s, 15H, C$_5$Me$_5$), 1.29 (d of d, $^{3}J_{\mathrm{PH}} = 14.0$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 3H, P(CH$Me_c$Me$_d$)), 1.13 (d of d, $^{3}J_{\mathrm{PH}} = 16.5$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 3H, P(CHMe$_c$$Me_d$)), 1.02−0.95 (m, 6H, P(CH$Me_a$$Me_b$)), −9.86 (d, $^{2}J_{\mathrm{PH}} = 31.5$ Hz, 1H, Ru−H$_a$), −11.37 (apparent d of d, $J = 30.0$ Hz, $J = 3.0$ Hz, 1H, Ru−H$_b$); $^{13}$C{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 145.1 (d, $J_{\mathrm{PC}} = 13.7$ Hz, C2), 143.5 (Si-aryl-C), 134.7 (Si-aryl-CHs), 133.5 (d, $J_{\mathrm{PC}} = 2.9$ Hz, C3a or C7a), 130.6 (d, $J_{\mathrm{PC}} = 10.4$ Hz, C7a or C3a), 129.4 (Si-aryl-CH), 127.9 (Si-aryl-CHs), 121.7 (C4 or C7), 120.9 (C7 or C4), 117.4 (C5 or C6), 116.2 (C6 or C5), 95.8 (*C*$_5$Me$_5$), 94.2 (d, $^{3}J_{\mathrm{PC}} = 7.3$ Hz, C1), 81.4 (d, $^{1}J_{\mathrm{PC}} = 70.3$ Hz, C3), 59.1 (NMe$_a$), 52.9 (NMe$_b$), 33.6 (d, $^{1}J_{\mathrm{PC}} = 25.9$ Hz, P(*C*HMe$_c$Me$_d$)), 27.3 (d, $^{1}J_{\mathrm{PC}} = 32.5$ Hz, P(*C*HMe$_a$Me$_b$)), 21.0 (m, P(CH$Me_c$Me$_d$)), 20.4 (apparent s, P(CHMe$_c$$Me_d$) and P(CHMe$_a$$Me_b$)), 19.9 (d, $^{2}J_{\mathrm{PC}} = 6.7$ Hz, P(CH$Me_a$Me$_b$)), 11.4 (C$_5$*Me*$_5$); $^{31}$P{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 56.6; $^{29}$Si{$^{1}$H} NMR (C$_6$D$_6$): $\delta$ 97.7 ($^{1}$H−$^{29}$Si HMBC/HMQC), $^{1}J_{\mathrm{SiH}} = 179.0$ Hz ($^{1}$H-coupled $^{1}$H−$^{29}$Si HMQC), $^{2}J_{\mathrm{SiH}} = 3.6$ Hz ($J$-HMBC). A single crystal of **8** grown from a mixture of benzene and pentane at ambient temperature proved suitable for X-ray analysis.

**Synthesis of [9]$^+$B(C$_6$F$_5$)$_4$$^-$.** A sample of [**6**]$^+$B(C$_6$F$_5$)$_4$$^-$ (0.019 g) in 0.8 mL of Et$_2$O-$d_{10}$ was left undisturbed in an NMR tube in the glovebox for 96 h. Analysis of $^{31}$P NMR data collected on this solution indicated the quantitative formation of [**9**]$^+$B(C$_6$F$_5$)$_4$$^-$. $^{1}$H NMR (Et$_2$O-$d_{10}$): $\delta$ 7.79−7.76 (m, 2H, Si-aryl-Hs), 7.60 (d, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 1H, C4-H or C7-H), 7.51−7.46 (m, 3H, Si-aryl-Hs), 7.37−7.28 (m, 3H, aryl-Hs), 6.50 (s, 1H, C3-H), 5.63 (m, 1H, Si−H), 3.98 (d, $^{2}J_{\mathrm{PH}} = 10.5$ Hz, 1H, C1-H), 3.29 (s, 3H, NMe$_a$), 2.86 (s, 3H, NMe$_b$), 2.44 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.09 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.77 (s, 15H, C$_5$-Me$_5$), 1.62−1.54 (m, 6H, P(CH$Me_c$$Me_d$)), 0.99 (d of d, $^{3}J_{\mathrm{PH}} = 17.5$ Hz, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 3H, P(CH$Me_a$Me$_b$)), 0.33 (d of d, $^{3}J_{\mathrm{PH}} = 17.0$ Hz, $^{3}J_{\mathrm{HH}} = 6.5$ Hz, 3H, P(CHMe$_a$$Me_b$)), −10.60 (d, $^{2}J_{\mathrm{PH}} = 32.8$ Hz, 1H, Ru−H$_a$), −11.37 (apparent d of d, $J = 28.0$ Hz, $J = 5.5$ Hz, 1H, Ru−H$_b$); $^{13}$C{$^{1}$H} NMR (Et$_2$O-$d_{10}$): $\delta$ 152.8 (m, C2), 141.5 (m, C3a or C7a), 141.2 (m, C7a or C3a), 138.2 (m, Si-aryl-C), 136.7−136.6 (m, 2 Si-aryl-*C*Hs), 132.1 (Si-aryl-*C*H), 129.5 (m, 2 Si-aryl-*C*Hs), 128.7 (aryl-*C*H), 127.0 (aryl-*C*H), 126.8 (d, $^3J_{PC}$ = 5.4 Hz, C3), 126.4 (C4 or C7), 124.1 (aryl-*C*H), 98.2 (*C*$_5$Me$_5$), 53.7 (NMe$_b$), 52.4 (NMe$_a$), 48.1 (d, $^1J_{PC}$ = 15.1 Hz, C1), 30.9 (d, $^1J_{PC}$ = 17.6 Hz, P(*C*HMe$_c$Me$_d$)), 28.6 (d, $^1J_{PC}$ = 24.0 Hz, P(*C*HMe$_a$Me$_b$)), 20.4 (P(CH*Me*$_c$Me$_d$) or P(CHMe$_c$*Me*$_d$)), 19.8 (P(CHMe$_a$*Me*$_b$)), 19.7 (d, $^2J_{PC}$ = 7.0 Hz, P(CHMe$_c$*Me*$_d$) or P(CH*Me*$_c$Me$_d$)), 17.7 (d, $^2J_{PC}$ = 5.2 Hz, P(CH*Me*$_a$Me$_b$)), 11.4 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (Et$_2$O-*d*$_{10}$): δ 87.2; $^{29}$Si{$^1$H} NMR (Et$_2$O-*d*$_{10}$): δ 111.6 ($^1$H−$^{29}$Si HMBC/HMQC), $^1J_{SiH}$ = 192.0 Hz ($^1$H-coupled $^1$H−$^{29}$Si HMQC).

**Synthesis of 10.** To a glass vial charged with [**6**]$^+$SO$_3$CF$_3^-$ (0.080 g, 0.10 mmol) was added CH$_2$Cl$_2$ (4 mL). The resultant brown mixture was then sealed with a PTFE-lined cap. Analysis of $^{31}$P NMR data collected on this solution after 3 h indicated ∼90% isomerization of the starting material [**6**]$^+$SO$_3$CF$_3^-$ to [**9**]$^+$SO$_3$CF$_3^-$; this structural assignment was made by comparison to diagnostic $^1$H, $^{29}$Si, and $^{31}$P NMR data for [**9**]$^+$B(C$_6$F$_5$)$_4^-$. Selected NMR data for [**9**]$^+$SO$_3$CF$_3^-$: Diagnostic $^1$H NMR shifts (CD$_2$Cl$_2$): δ 6.49 (s, 1H, C3-H), 5.64 (m, 1H, Si-H), 4.00 (d, $^2J_{PH}$ = 10 Hz, 1H, C1-H); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): δ 87.2; $^{29}$Si{$^1$H} NMR (CD$_2$Cl$_2$): δ 108.4 ($^1$H−$^{29}$Si HMBC/HMQC), $^1J_{SiH}$ = 197.1 Hz ($^1$H-coupled $^1$H−$^{29}$Si HMQC). Analysis of $^{31}$P NMR data collected on this solution after 12 h revealed the presence of [**9**]$^+$SO$_3$CF$_3^-$ and a new P-containing product (**10**) (∼ 1:3 ratio). After a total of 48 h, only **10** was observed ($^{31}$P NMR). The vial contents were then filtered through Celite and were stripped of solvent and other volatile materials in vacuo. The residual solid was subsequently washed with pentane (3 × 3 mL). After removal of traces of pentane in vacuo, **10** was isolated as an analytically pure, pale-brown powder (0.077 g, 0.10 mmol, 96%). C$_{34}$H$_{49}$PNSiSO$_3$F$_3$Ru: C, 53.10; H, 6.42; N, 1.82. Found: C, 52.91; H, 6.55; N, 1.71. $^1$H NMR (CD$_2$Cl$_2$): δ 7.47 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Si-aryl-Hs), 7.39−7.32 (m, 3H, Si-aryl-Hs), 7.07 (m, 1H, C4-H or C7-H), 6.91 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5-H or C6-H), 6.77 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H or C5-H), 5.81 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H or C4-H), 3.88 (m, 1H, C2-H), 3.54 (d, $^2J_{PH}$ = 10.5 Hz, 1H, C3-H), 2.82 (s, 1H, C1-H), 2.29 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.11 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.01 (broad s, 6H, NMe$_2$), 1.75 (s, 15H, C$_5$Me$_5$), 1.52 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 1.44 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 1.11 (d of d, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.77 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$*Me*$_b$)), −11.58 (d, $^2J_{PH}$ = 26.5 Hz, 1H, Ru−H$_a$), −12.58 (d, $^2J_{PH}$ = 27.1 Hz, 1H, Ru−H$_b$); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): δ 145.8 (m, C3a or C7a), 140.9 (m, C7a or C3a), 138.7 (m, Si-aryl-C), 135.6 (2 Si-aryl-*C*Hs), 129.6 (Si-aryl-*C*H), 127.5 (2 Si-aryl-*C*Hs), 126.8 (C5 or C6), 125.7 (C4 and C7), 125.2 (C6 or C5), 96.8 (*C*$_5$Me$_5$), 75.7 (m, C2), 45.1 (d, $^1J_{PC}$ = 19.6 Hz, C3), 44.4 (C1), 42.4 (NMe$_2$), 27.2 (d, $^1J_{PC}$ = 20.1 Hz, P(*C*HMe$_c$Me$_d$)), 26.4 (d, $^1J_{PC}$ = 22.4 Hz, P(*C*HMe$_a$Me$_b$)), 22.8 (P(CHMe$_a$*Me*$_b$)), 21.6 (P(CH*Me*$_c$Me$_d$)), 19.1 (P(CH*Me*$_a$Me$_b$)), 18.5 (d, $^2J_{PC}$ = 5.0 Hz, P(CHMe$_c$*Me*$_d$)), 11.5 (C$_5$*Me*$_5$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): δ 87.6; $^{29}$Si{$^1$H} NMR (CD$_2$Cl$_2$): δ 91.4 ($^1$H−$^{29}$Si HMBC), $^2J_{SiH}$ not detected by *J*-HMBC. Slow diffusion of pentane into a CH$_2$Cl$_2$ solution of **10** at ambient temperature provided a single crystal suitable for X-ray analysis.

**Crystallographic Solution and Refinement Details for [4]$^+$X$^-$, [5]$^+$X$^-$, [6]$^+$X$^-$, and 10 (X = SO$_3$CF$_3$).** In each case, crystallographic data were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved using the COLLECT software (Nonius) and refined with the HKL DENZO and SCALEPACK software.[24] Data reduction and absorption correction (multiscan) were also performed with the HKL DENZO and SCALEPACK software. The structure was solved by using the direct methods package in SIR-97[25] and refined with SHELXL-97-2[26] by use of full-matrix least-squares procedures (on $F^2$) with $R_1$ based on $F_o^2 \geq 2\sigma(F_o^2)$ and $wR_2$ based on $F_o^2 \geq -3\sigma(F_o^2)$. With the exception of the Ru−*H* and Si−*H* (the positions of which were located in the difference map and refined, except for **10**) all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. In the solution and refinement of [**5**]$^+$X$^-$, one of the carbon atoms of an isopropyl group was modeled as being disordered over two positions, with site occupancy factors that refined to 0.64(1) and 0.36(1). The atoms of the triflate anion in [**5**]$^+$X$^-$ were modeled successfully as being fully disordered into two superimposed sets of positions, with group site occupancy factors that refined to 0.58(3) and 0.42(3). In the solution and refinement of **10**, the program XHYDEX[27] was used to predict the positions of the Ru−*H* atoms; these positions were fixed during the refinement process. The atoms of the triflate group in **10** were modeled successfully as being fully disordered into two superimposed sets of positions by use of the SIMU, DELU, and SAME constraints, with group site occupancy factors that refined to 0.567(4) and 0.433(4). Additional experimental details related to the crystallographic characterization of [**4**]$^+$X$^-$, [**5**]$^+$X$^-$, [**6**]$^+$X$^-$, and **10** are provided in the accompanying crystallographic information file.

**Crystallographic Solution and Refinement Details for 8.** Crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by using a Patterson search/structure expansion, and refined by using a full-matrix least-squares procedures (on $F^2$) with $R_1$ based on $F_o^2 \geq 2\sigma(F_o^2)$ and $wR_2$ based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-H atoms. With the exception of the Ru−*H* and Si−*H* (the positions of which were located in the difference map and refined) all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. In the course of the solution and refinement process, a model featuring two crystallographically independent molecules of **8** in the asymmetric unit was employed successfully. Since one of these molecules is fully disordered into two superimposed sets of positions (55:45 ratio), only details of the nondisordered crystallographically independent molecule are discussed in the text. Additional experimental details related to the crystallographic characterization of **8** are provided in the accompanying crystallographic information file.

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Tilley, in honor of his receiving the 2008 ACS-Stanley Kipping Award for Silicon Chemistry.

**Note Added in Proof.** A crystallographically characterized Ru═SiHR complex has recently been reported: Ochiai, M.; Hashimoto, H.; Tobita, H. *Angew. Chem. Int. Ed.* **2007**, *46*, 8192.

**Supporting Information Available:** Single-crystal X-ray diffraction data in CIF format for [**4**]$^+$X$^-$, [**5**]$^+$X$^-$, [**6**]$^+$X$^-$, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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