Synthesis, Structure, and Reactivity of Neutral Hydrogen-Substituted Ruthenium Silylene and Germylene Complexes

Paul G. Hayes,[†] Rory Waterman,[‡] Paul B. Glaser,[§] and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, California 94720-1460. [†]Current address: Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge, Alberta, Canada, T1K 3M4. [‡]Current address: Department of Chemistry, University of Vermont, Burlington, Vermont 05405. [§]Current address: General Electric Global Research, Niskayuna, NY 12309.

Reaction of Cp*(^{i}Pr$_2$MeP)RuCl (**1**) with 0.5 equiv of Mg(CH$_2$Ph)$_2$(THF)$_2$ afforded the benzyl complex Cp*(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph) (**2**). Complex **2** readily reacted with primary silanes H$_3$SiR (R = trip, dmp, Mes^F; trip = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$, dmp = 2,6-Mes$_2$-C$_6$H$_3$, Mes^F = 2,4,6-(CF$_3$)$_3$-C$_6$H$_2$) to liberate toluene and afford hydrogen-substituted silylene complexes Cp*(^{i}Pr$_2$MeP)(H)Ru=SiH(R) [R = trip, **3**; dmp, **4**; Mes^F, **5**]. Complexes **3**−**5** exhibit characteristic SiH ^{1}H NMR resonances downfield of 8 ppm and very small $^2J_{SiH}$ coupling constants (8−10 Hz). The solid state structures of complexes **3** and **5** feature short Ru−Si distances of 2.205(1) and 2.1806(9) Å, respectively, and planar silicon centers. In addition, the silylene complex Cp*(^{i}Pr$_2$MeP)(H)Ru=SiPh(trip) (**6**) and the unusual, chlorine-substituted species Cp*(^{i}Pr$_2$MeP)(H)Ru=SiCl(R) [R = trip, **7**; dmp, **8**] were prepared. Hydrogen-substituted ruthenium germylene complex Cp*(^{i}Pr$_2$MeP)(H)Ru=GeH(trip) (**9**) was prepared similarly by reaction of **2** with tripGeH$_3$. Complex **9** is the first structurally characterized ruthernium germylene complex and has a remarkably short Ru−Ge distance of 2.2821(6) Å. Complex **9** adds H$_2$O across its Ru=Ge bond to give Cp*(^{i}Pr$_2$MeP)(H)$_2$RuGeH(OH)(trip) (**10**).

Introduction

Transition metal silylene complexes (L$_n$M=SiRR′) that formally possess a metal−silicon double bond represent unsaturated silicon compounds featuring chemical and physical properties of fundamental interest.[1] These complexes offer interesting comparisons to the better known carbene complexes and have been proposed to play important roles as intermediates in a variety of catalytic reactions such as the synthesis of methylchlorosilanes by the Direct Process,[2] the redistribution of substituents at silicon,[3] and the transfer of silylene fragments to an unsaturated carbon−carbon bond.[4] It was not until recently, however, that direct evidence for participation of a metal silylene complex in a catalytic transformation was obtained. This catalysis involves the hydrogen-substituted ruthenium complex [Cp*(^{i}Pr$_3$P)(H)$_2$-Ru=SiHPh·Et$_2$O][B(C$_6$F$_5$)$_4$], which efficiently catalyzes the hydrosilylation of alkenes.[5] Key characteristics of this reaction include the requirement for primary silane substrates, a compatibility with highly substituted alkenes, exclusive anti-Markovnikov regiochemistry, and *cis* stereochemistry for the Si−H addition. These features are inconsistent with the well-known Chalk−Harrod[6] and Lewis acid[7] mechanisms for alkene hydrosilylation, and mechanistic[5,8] and theoretical[9] investigations are consistent with a catalytic cycle that features the direct addition of an Si−H bond to the alkene. In this cycle, a silylene unit is transferred from RSiH$_3$ to the metal center (silylene extrusion) via two Si−H bond activations, an Si−H oxidative addition followed by an α-hydrogen migration to afford

*To whom correspondence may be addressed. Tel: 510-642-8939. E-mail: tdtilley@berkeley.edu.

(1) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712–719.

(2) (a) Lewis, K. M., Rethwisch, D. G., Eds. *Catalyzed Direct Reactions of Silicon*; Elsevier: Amsterdam, 1993. (b) Pachaly, B.; Weis, J. In *Organosilicon Chemistry III: From Molecules to Materials, Munich Silicon Days*; 1996; Wiley & Sons: New York, 1998; p 478. (c) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000; p 381. (d) Lewis, L. N. In *Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; Pt 2, p 1581.

(3) (a) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213–255. (b) Kumada, M. J. *J. Organomet. Chem.* **1975**, *100*, 127–138.

(4) Some recent examples include: (a) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949–957. (b) Palmer, W. S.; Woerpel, K. A. *Organometallics* **2001**, *20*, 3691–3697. (c) Cirakovic, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370–9371.

(5) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640–13641.

(6) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16–21. (b) Seitz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed.* **1988**, *27*, 289–291. (c) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90–98. (d) Sakaki, S.; Sumimato, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* **2002**, *21*, 3788–3802.

(7) (a) Rubin, M.; Schwier, T.; Gevorgyan, N. *J. Org. Chem.* **2002**, *67*, 1936–1940. (b) Song, Y. S.; Yoo, B. R.; Lee, G. H.; Jung, I. N. *Organometallics* **1999**, *18*, 3109–3115. (c) Lambert, J. B.; Zhao, Y.; Wu, H. W. *J. Org. Chem.* **1999**, *64*, 2729–2736. (d) Schmeltzer, J. M.; Porter, L. A.; Stewart, M. P.; Buriak, J. M. *Langmuir* **2002**, *18*, 2971–2974.

(8) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 428–429.

(9) (a) Beddie, C.; Hall, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 13564–13565. (b) Beddie, C.; Hall, M. B. *J. Phys. Chem. A* **2006**, *110*, 1416. (c) Böhme, U. *J. Organomet. Chem.* **2006**, *691*, 4400–4410.

<div align="center">**Scheme 1**</div>
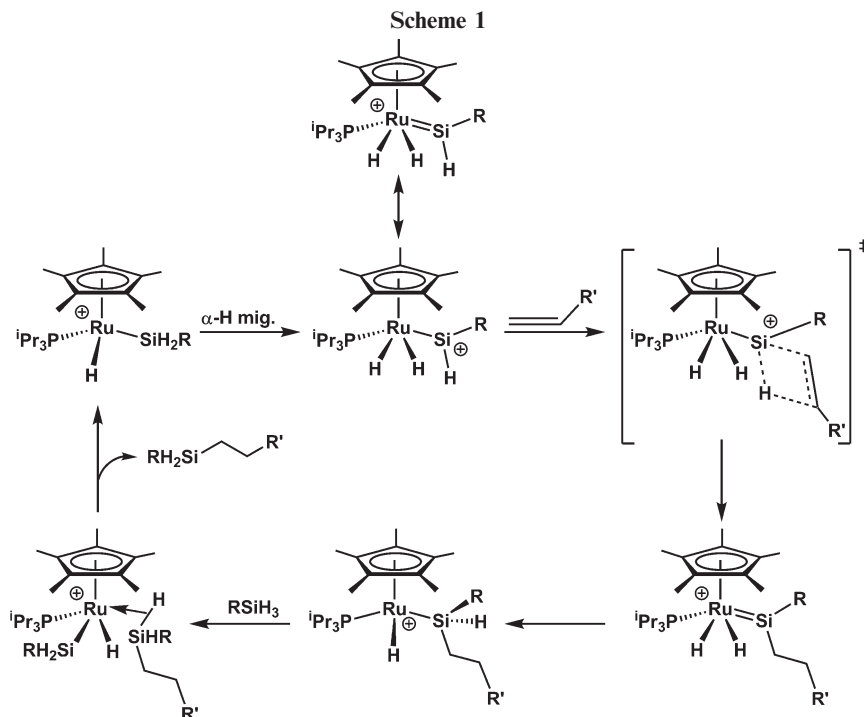
[Cp*(^{i}Pr$_3$P)(H)$_2$Ru=SiHR][B(C$_6$F$_5$)$_4$]. Direct addition of the sp^2 Si−H bond to an alkene (e.g., CH$_2$=CHR′) then gives a disubstituted silylene complex, [Cp*(^{i}Pr$_3$P)(H)$_2$-Ru=Si(CH$_2$CH$_2$R′)(R)][B(C$_6$F$_5$)$_4$]. Migration of hydrogen from the metal center to silicon and reductive elimination of the new silane molecule complete the catalytic cycle (Scheme 1).[5,8−10]

Although the related osmium complex [Cp*(^{i}Pr$_3$P)(H)$_2$-Os=SiH(trip)][B(C$_6$F$_5$)$_4$] (trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) is not catalytically active toward the hydrosilylation of alkenes, stoichiometric alkene insertion into the Si−H bond is exceedingly rapid, even at −78 °C.[5] Interestingly, neutral analogues of this osmium silylene complex, conveniently prepared via reaction of Cp*(^{i}Pr$_3$P)OsCH$_2$Ph with primary silanes, do not react with alkenes even at elevated temperatures.[8] Computational studies indicate that the much lower reactivity of these Cp*(^{i}Pr$_3$P)(H)Os=SiH(R) complexes toward alkenes is related to their higher degree of covalent double-bond character and a small localization of positive charge onto silicon (second resonance structure of Chart 1).[8] Nonetheless, neutral, hydrogen-substituted silylene complexes are expected to display a rich reaction chemistry that is distinct from that of cationic analogues.[5,8,11] In an attempt

<div align="center">**Chart 1**</div>
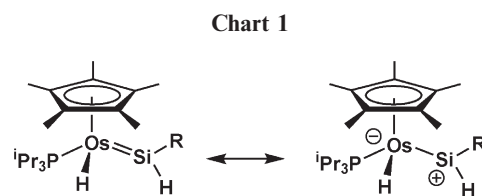
to further probe structure, bonding, and reactivity of M=SiH(R) and related M=GeH(R) neutral complexes, a series of ruthenium complexes have been prepared via extrusion reactions promoted by the benzyl complex Cp*-(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph) (**2**).
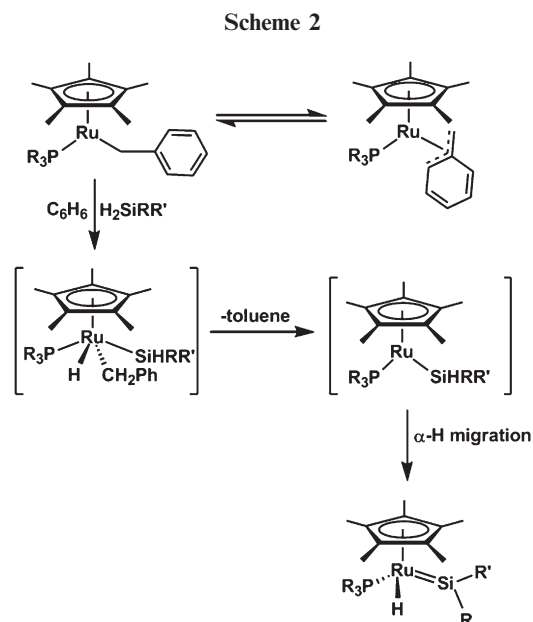
Results and Discussion

Synthesis of the Ruthenium Benzyl Complex Cp*-(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph) (2). The initial objective of this study was to develop a general silane activation process leading to silylene-hydride complexes. In this regard, allyl[11h] and benzyl complexes[8,11g] may serve as convenient starting materials because facile η^3-to-η^1 transformations of the ligand provide an empty coordination site that may be used for activation of an Si−H bond. Subsequent C−H reductive elimination then produces an unsaturated M-SiHRR′ intermediate, which can undergo α-migration to provide the final silylene complex. This process was envisioned as a general route to neutral ruthenium silylene complexes (Scheme 2).

Unlike the osmium analogue Cp*(^{i}Pr$_3$P)OsBr, reaction of Cp*(^{i}Pr$_3$P)RuCl with standard benzylating reagents (including Mg(CH$_2$Ph)$_2$(THF)$_2$, PhCH$_2$MgCl, and KCH$_2$Ph) did not afford the desired benzyl complex Cp*(^{i}Pr$_3$P)RuCH$_2$Ph. Upon combining the reactants in benzene-d_6 solution, there was an immediate change in color from dark purple to orange with concomitant disappearance of ^{1}H and ^{31}P NMR signals attributed to the starting materials. The observation of 1 equiv of toluene as a product suggests that Cp*(^{i}Pr$_3$P)RuCH$_2$Ph is generated in these reactions, but it decomposes rapidly under

(10) Brunner, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2749–2750.

(11) (a) Sakaba, H.; Hirata, T.; Kabuto, C.; Kabuto, K. *Organometallics* **2006**, *25*, 5145–5150. (b) Watanabe, T.; Hashimoto, H.; Tobita, H. *J. Am. Chem. Soc.* **2007**, *129*, 11338–11339. (c) Watanabe, T.; Hashimoto, H.; Tobita, H. *J. Am. Chem. Soc.* **2006**, *128*, 2176–2177. (d) Ochiai, M.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8192–8194. (e) Simmons, R. S.; Gallucci, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2002**, *654*, 224–228. (f) Watanabe, T.; Hashimoto, H.; Tobita, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 218–221. (g) Mork, B. V.; Tilley, T. D.; Schultz, A. J.; Cowan, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 10428–10440. (h) Feldman, J. D.; Peters, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2002**, *21*, 4065–4075. (i) Glaser, P. B.; Tilley, T. D. *Organometallics* **2004**, *23*, 5799–5812. (j) Rankin, M. A.; MacLean, D. F.; Schatte, G.; McDonald, R.; Stradiotto, M. *J. Am. Chem. Soc.* **2007**, *129*, 15855–15864. (k) Ochiai, M.; Hashimoto, H.; Tobita, H. *Dalton Trans.* **2009**, 1812–1814. (l) Hashimoto, H.; Ochiai, M.; Tobita, H. *J. Organomet. Chem.* **2007**, *692*, 36–43.
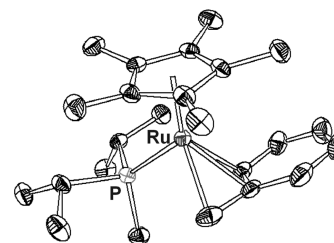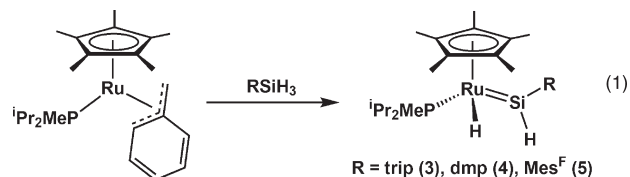
Scheme 2

Figure 1. Molecular structure of complex **2** with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Ru–C(1) 2.156(4), Ru–C(11) 2.187(4), Ru–C(16) 2.330(4), Ru–P 2.222(4), Ru–C$_{centroid}$ 1.862(5), C(1)–C(11) 1.424(6), C(11)–C(12) 1.433(5), C(12)–C(13) 1.365(5), C(13)–C(14) 1.411(6), C(14)–C(15) 1.357(5), C(15)–C(16) 1.434(5), C(16)–C(11) 1.443(5), C(1)–Ru–P 89.42(11), C(11)–Ru–P 105.01 (11), C(16)–Ru–P 94.72(9), P–Ru–C$_{centroid}$ 126.6(8), C(1)–C(11)–C(16) 119.1(3), C(1)–Ru–C(16) 66.74(13), C(1)–Ru–C(11) 38.26(15).

the reaction conditions. Though the NMR spectra of the decomposition product did not provide a definitive formulation, predominant resonances at δ 52.9 in the ^{31}P NMR spectrum and a new Cp* signal at δ 2.02 in the ^{1}H NMR spectrum implied the generation of a relatively pure compound. The loss of symmetry for the ^{i}Pr methyl groups and the presence of a characteristic doublet at δ −11.9 in the ^{1}H NMR spectrum are consistent with two C–H activation events, leading to a metal hydride complex similar to Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH, which was prepared by deprotonation of {Cp*[^{i}Pr$_2$P(η^2-MeC=CH$_2$)]OsH$_2$}[B-(C$_6$F$_5$)$_4$] with KN(SiMe$_3$)$_2$.[11i] Unfortunately all attempts to isolate the ruthenium product led to intractable mixtures, and further characterization was not possible. Similarly, efforts to prepare silylene complexes by reaction of silanes such as tripSiH$_3$ and Mes^{F}SiH$_3$ with putative Cp*(^{i}Pr$_3$P)RuCH$_2$Ph, generated *in situ* at low temperatures, were unsuccessful.

On the basis of the results described above, it was thought that a more stable benzyl complex (i.e., one less prone to toluene elimination) might be obtained by use of a less sterically demanding phosphine ligand with fewer ^{i}Pr groups. Reaction of ^{i}Pr$_2$MeP with [Cp*RuCl]$_4$ in CH$_2$Cl$_2$ gave analytically pure, dark blue crystals of Cp*-(^{i}Pr$_2$MeP)RuCl (**1**) in 85% yield. Treatment of **1** with 0.5 equiv of Mg(CH$_2$Ph)$_2$(THF)$_2$ cleanly afforded the corresponding benzyl complex Cp*(^{i}Pr$_2$MeP)RuCH$_2$Ph (**2**) as analytically pure red crystals in 73% yield. Though complex **2** exhibits slight thermal sensitivity ($t_{1/2} \approx$ 24 h in benzene-d_6 solution at ambient temperature), it is indefinitely stable as a solid when stored under an inert atmosphere at −35 °C. The ^{1}H NMR spectrum of **2** exhibited distinct resonances at δ 6.89, 5.19, and 1.68, consistent with an η^3 structure that is static on the NMR time scale. X-ray quality single crystals of **2** were grown from cold hexanes solution. The solid state structure, shown in Figure 1, confirms the presence of an η^3-benzyl ligand with Ru–C bond distances of 2.156(4), 2.187(4), and 2.330(4) Å.

Synthesis of H-Substituted Ruthenium Silylene Complexes. Treatment of **2** with either PhSiH$_3$ or MesSiH$_3$ (Mes = 2,4,6-Me$_3$-C$_6$H$_2$) in benzene solution resulted in an immediate color change from red to orange, and complete consumption of the starting material was observed by ^{31}P and ^{1}H NMR spectroscopy. Though several different products were

observed, 1 equiv of toluene quantitatively formed. In the ^{1}H NMR spectrum of the intractable product mixtures, multiple hydride resonances and inequivalent ^{i}Pr and mesityl methyl groups suggest that intramolecular C–H activation, rather than the expected α-hydrogen migration from the putative silyl intermediate, Cp*(^{i}Pr$_2$MeP)RuSiH$_2$Ph, occurred.[12]

In light of the results described above, silanes with more sterically demanding substituents were examined under the hypothesis that these substrates might lead to more stable ruthenium-silylene complexes. Addition of benzene solutions of **2** to sterically hindered primary silanes for periods of 5 min to 24 h cleanly generated the orange-red silylene complexes Cp*(^{i}Pr$_2$MeP)(H)Ru=SiH(R) (R = trip, **3**; dmp, **4**; trip = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$; dmp = 2,6-mesitylphenyl) in 43% and 79% yield, respectively (eq 1). Repeated attempts to observe the ^{29}Si NMR signal for complex **3** (including direct detection and 2-D HMBC experiments (ambient and variable temperature)) were unsuccessful. This may be due to rapid exchange of the RuH and SiH hydrogens, via the unsaturated species Cp*-(^{i}Pr$_2$MeP)RuSiH$_2$R, on the NMR time scale. Correspondingly, the diagnostic SiH and RuH resonances for complex **3**, which are observed at δ 9.41 and −13.5, respectively, are broad and featureless. The more bulky complex **4**, however, exhibits a well-defined ^{29}Si resonance at δ 204 and a sharp downfield SiH ^{1}H NMR resonance at δ 8.00 ($^3J_{HP}$ = 11.9 Hz, $^1J_{HSi}$ = 151 Hz). Similar to the osmium anologue,[8] ruthenium silylene complex **4** displayed a low $^2J_{SiH}$ value of 8.6 Hz, which implies significant metal–silicon double-bond character and minimal interaction between the ruthenium hydride and silicon atom. The upfield metal hydride resonance at δ −14.4 corroborates this assertion.

(1)

R = trip (3), dmp (4), Mes^F (5)

Crystals of **3** suitable for an X-ray diffraction study were grown from a concentrated hexanes solution cooled to −35 °C for 24 h. Complex **3** is isostructural with the osmium

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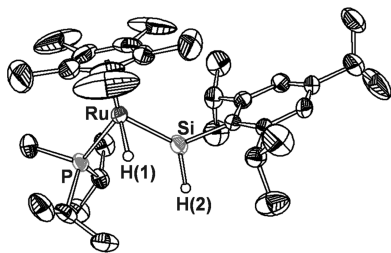(12) See Supporting Information for additional details.

Figure 2. Molecular structure of silylene complex **3** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity except for H(1) and H(2), which were located on Ru and Si, respectively. Selected distances (Å) and angles (deg): Ru−Si 2.205(1), Ru−C$_{centroid}$ 1.892(4), Si−C(61) 1.888(4), Ru−P 2.272(1), C(61)−Si−Ru 129.2(1), Ru−Si−H(2) 127.8(1), P−Ru−Si 93.38(4), C(61)−Si−H(2) 102.4(1), P−Ru−C$_{centroid}$ 132.1(2).

analogue,[8] featuring a short Ru=Si bond (Ru−Si = 2.205(1) Å). This compares well with the base-free silylene complexes [Cp*(Me$_3$P)$_2$Ru=SiMe$_2$][B(C$_6$F$_5$)$_4$] (Ru−Si = 2.238(3) Å)[13] and Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$] (Ru−Si = 2.220(2) Å)[11d] and base-stabilized primary silylene examples [Cp*(μ-P, N-L)(H)$_2$RuSiHPh][SO$_3$CF$_3$] (Ru−Si = 2.262(2) Å) and Cp*-(μ-P,N-L)(H)$_2$RuSiHPh (Ru−Si = 2.2635(5) Å; L = 2-NMe$_2$-3-P^{i}Pr$_2$-indenide), recently reported by Stradiotto and co-workers.[11j] Other notable features of the solid state structure include a planar silicon center (summation of angles at Si = 359.4°) and a H(1)−Ru−Si−H(2) dihedral angle of −48.8°, indicating an approximately *cis* geometry (Figure 2). Both H(1) on ruthenium and H(2) on silicon were located in the Fourier difference map and anisotropically refined.

Neutral silylene **3** is exceedingly thermally sensitive, and as a result, no reaction with alkenes, such as ethylene, 1-hexene, or ^{t}BuCH=CH$_2$, was observed prior to decomposition to a mixture of unidentified products (benzene-d_6 solution). In contrast, the steric bulk of the silicon substituent in **4** renders the complex indefinitely stable in aliphatic and aromatic solvents, although no reaction was observed upon heating toluene solutions of **4** and 1 equiv of various alkenes, such as ethylene, 1-hexene, or ^{t}BuCH=CH$_2$, to reflux for more than 96 h. Terphenyl substituents are common in the preparation of reactive main group species due to the kinetic stability imparted by this bulky fragment.[14] The inertness of **4** is presumably a reflection of the steric bulk of the dmp-substituted silylene functionality. This notion is supported by the observation that the synthesis of **4** requires approximately 50 times longer to reach completion than the synthesis of **3**.

In an effort to obtain a more sterically accessible ruthenium silylene ligand, while retaining the thermal stability associated with **4**, the partially fluorinated silane H$_3$SiMes^F (Mes^F = 2,4,6-(CF$_3$)$_3$-C$_6$H$_2$)[15] was prepared. For this silane, the lack of accessible, benzylic C−H bonds was expected to prevent the metalation pathway believed to be operative for the mesityl-substituted silane. In addition, it seemed that the electron-withdrawing −Mes^F group might impart considerable electrophilicity to a silylene silicon center and thereby promote alkene insertions into the Si−H bond.
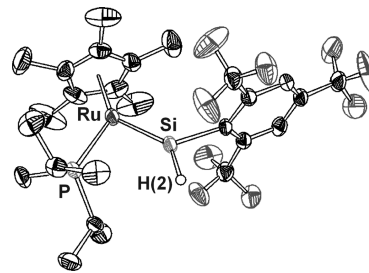

Figure 3. Molecular structure of silylene complex **5** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity except for H(2), which was located on Si. Selected distances (Å) and angles (deg): Ru−Si 2.1806(9), Ru−C$_{centroid}$ 1.886(3), Si−C(61) 1.947(3), Ru−P 2.2849(8), C(61)−Si−Ru 128.9(3), Ru−Si−H(2) 133.7(1), P−Ru−Si 90.99(3), C(61)−Si−H(2) 97.4(1), P−Ru−C$_{centroid}$ 132.3(2).

The rapid reaction of H$_3$SiMes^F with **2** proceeded to complete conversion to the corresponding silylene complex **5** within several minutes. Complex **5** can be isolated from alkane solvents as an analytically pure ruby red solid in 81% yield. As seen for **3** and **4**, the ^{1}H NMR spectrum of **5** exhibits a diagnostic multiplet attributed to RuH at δ −13.4. However, no resonance was observed for the silylene hydrogen or the ^{29}Si resonance, which is likely due to significant broadening of the signal caused by coupling to nine ^{19}F nuclei of the aryl substituent.[16]

The electron-withdrawing effect of the fluorinated substituent at silicon results in a small but statistically relevant contraction of the Ru−Si bond to 2.1806(9) Å. To the best of our knowledge, this represents the shortest Ru−Si distance yet reported. This short Ru−Si bond appears to reflect a higher bond order between ruthenium and silicon and reduced silicenium character for the silylene ligand (Figure 3). Consistent with this, a benzene-d_6 solution of complex **5** failed to react with 1 equiv of ethylene, 1-hexene, or ^{t}BuCH=CH$_2$ upon heating to reflux for 96 h.

Synthesis of Cl-Substituted Ruthenium Silylene Complexes. Complex **2** also participates in silylene extrusion processes with more sterically demanding, secondary silanes. For example, the asymmetrically substituted silylene Cp*-(^{i}Pr$_2$MeP)(H)Ru=SiPh(trip) (**6**) was readily isolated as an orange powder in 54% yield from reaction of benzene solutions of **2** with H$_2$SiPh(trip).

The results described above indicate that silane additions to **2** readily provide convenient, efficient pathways to ruthenium silylene complexes of the type Cp*(^{i}Pr$_2$MeP)-(H)Ru=SiRR'. To further investigate the generality of this method, attempts were made to obtain ruthenium silylene complexes with potentially reactive substituents. Along these lines, it is worth noting that a chloro-substituted silylene complex of molybdenum provided a route to the first silylyne complex, [Cp*(dmpe)HMo≡SiMes][B(C$_6$F$_5$)$_4$].[17] Reaction of 1 equiv of the chlorosilanes tripSiH$_2$Cl and dmpSiH$_2$Cl with complex **2** in toluene at room temperature afforded the corresponding silylene complexes Cp*(^{i}Pr$_2$MeP)(H)-Ru=SiCl(R) (R = trip (**7**), dmp (**8**)) as dark pink solids in

(13) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 5495–5496.

(14) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047–10064.

(15) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156–1163.

(16) Significant broadening and complex coupling patterns were also observed for the OsH and SiH resonances in the ^{1}H NMR spectrum of Cp*(^{i}Pr$_3$P)(H)Os=SiH(Mes^F): Unpublished results. Hayes, P. G.; Tilley, T. D.

(17) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357–360.

62% and 59% yield, respectively. Interestingly, replacement of hydrogen for chlorine at silicon does not cause a substantial shift in the ^{29}Si NMR resonances for **7** and **8**, which are observed at δ 222 and 205, respectively. Attempts to grow high-quality crystals have been unsuccessful; however, a single-crystal diffraction study on a poorly diffracting crystal of **7** provided a structure consistent with the formulation established spectroscopically.[18] Efforts to utilize the Cl group of complexes **7** and **8** for further derivatization reactions are currently in progress.

Synthesis of H-Substituted Ruthenium Germylene Complexes. On the basis of the success of **2** as a suitable precursor for the synthesis of various silylene complexes, this strategy was investigated to prepare previously unknown, H-substituted germylene complexes. Thus, reaction of **2** with trip-GeH$_3$ in benzene gave the hydrogen-substituted germylene complex Cp*(^{i}Pr$_2$MeP)(H)Ru=GeH(trip) (**9**) as an analytically pure orange solid in 67% yield. The identity of complex **9** is supported by ^1H NMR resonances at δ 12.4 (GeH) and $-$12.8 (RuH), but the lack of a useful NMR-active nucleus (^{73}Ge: $I = ^9/_2$, 7.7%) renders it difficult to obtain conclusive solution state information regarding the nature of the ruthenium$-$germanium interaction. Fortunately, high-quality orange crystalline blocks were grown from cold pentane solutions of **9**. The most remarkable element of the solid state structure is the extremely short ruthenium$-$germanium bond length of 2.2821(6) Å (Figure 4). This is especially notable as **9** represents the first structurally characterized ruthenium germylene complex, and the ruthenium germanium distance is more than 0.1 Å shorter than any previously reported Ru$-$Ge bonds.[19] Both of the ruthenium- and germanium-bound hydrogen atoms were located in the Fourier difference map, and the germanium center is essentially planar (summation of angles at Ge = 359.1°), consistent with a Ru=Ge double bond.

In contrast to silylene complex **3**, germylene complex **9** is thermally stable with no evidence of decomposition indicated after 24 h in toluene-d_8 solution at 60 °C (by ^1H NMR spectroscopy). Preliminary experiments indicate that the related *tert*-butyl-substituted ruthenium germylene complex Cp*(^{i}Pr$_2$MeP)(H)Ru=GeH(^{t}Bu) is generated *in situ* by reaction of **2** with ^{t}BuGeH$_3$ in benzene-d_6.[12]

Germylene complex **9** is not reactive toward 1 equiv of common alkenes such as ethylene, 1-hexene, or ^{t}BuCH=CH$_2$ upon heating to reflux for 48 h. However, treatment of **9** with 1 equiv of oxygen-free H$_2$O in benzene-d_6 resulted in quantitative formation of Cp*(^{i}Pr$_2$MeP)-(H)$_2$Ru=GeH(OH)(trip) (**10**), as evidenced by ^1H NMR spectroscopy (eq 2). Most diagnostically, two resonances attributed to the ruthenium hydrides are observed at δ $-$11.1 and $-$11.6 and the GeH signal shifts upfield to δ 6.97. The OH resonance appears at δ 0.55. To lend credence to the
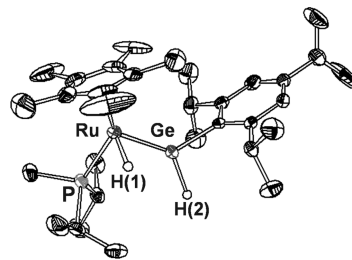

Figure 4. Molecular structure of germylene complex **9** with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity except for H(1) and H(2), which were located on Ru and Ge, respectively. Selected distances (Å) and angles (deg): Ru$-$Ge 2.2821(6), Ru$-$C$_{centroid}$ 1.885(5), Ge$-$C(61) 1.974(3), Ru$-$P 2.272(2), C(61)$-$Ge$-$Ru 129.3(1), Ru$-$Ge$-$H(2) 130.8, P$-$Ru$-$Ge 93.51(3), C(11)$-$Ge$-$H(2) 99.0(1), P$-$Ru$-$C$_{centroid}$ 129.7(2).

possibility that this reaction proceeds via concerted addition of an O$-$H bond across Ru=Ge, a labeling experiment utilizing D$_2$O was undertaken. In good agreement with this mechanism Cp*(^{i}Pr$_2$MeP)(H)(D)Ru$-$GeH(OD)(trip) (**10-d_2**) formed exclusively as indicated by complete disappearance of the OH resonance of **10** at δ 0.55 and a RuH signal that integrates as 1H at δ $-$11.1. No evidence for RuD/GeH exchange was observed after 6 h in benzene-d_6 solution at ambient temperature.
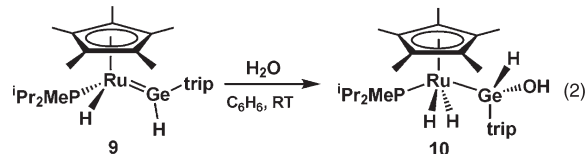
Concluding Remarks. A general route to neutral ruthenium silylene and germylene complexes, including rare hydrogen-substituted silylenes and previously unknown hydrogen-substituted germylene species, has been discovered. The ease of these syntheses should allow a number of informative spectroscopic and structural comparisons to be made for this class of complexes. This general synthesis, and the possibility for inclusion of a range of substituents at the silicon atom, should also enable a number of reactivity studies for complexes with Ru$-$Si and Ru$-$Ge multiple bonds.

Experimental Section

General Procedures. All manipulations involving air-sensitive compounds were conducted using standard Schlenk techniques under a purified N$_2$ atmosphere or in an MBraun Uni-Lab drybox. Solvents were distilled under N$_2$ from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents and vacuum-transferred prior to use.

Silanes and germanes were prepared by LiAlH$_4$ reduction of the corresponding silyl or germyl chlorides in diethyl ether[15] and were fractionally distilled under N$_2$ or recrystallized from cold hexanes. Compounds [Cp*RuCl]$_4$,[20] ^{i}Pr$_2$MeP,[21] and Mg-(CH$_2$Ph)$_2$(THF)$_2$[22] were prepared as previously reported. All

(18) See Supporting Information for additional details.
(19) (a) Chan, L. Y. Y.; Graham, W. A. G. *Inorg. Chem.* **1975**, *14*, 1778–1781. (b) Ball, R.; Bennett, M. J. *Inorg. Chem.* **1972**, *11*, 1806–1811. (c) Adams, R. D.; Captain, B.; Zhu, L. *Inorg. Chem.* **2005**, *44*, 6623–6631. (d) Adams, R. D.; Captain, B.; Fu, W. *Inorg. Chem.* **2003**, *42*, 1328–1333. (e) Adams, R. D.; Boswell, E. M.; Captain, B.; Patel, M. A. *Inorg. Chem.* **2007**, *47*, 533–540. (f) Matsumoto, T.; Nakaya, Y.; Itakura, N.; Tatsumi, K. *J. Am. Chem. Soc.* **2008**, *130*, 2458–2459. (g) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X. *Organometallics* **2001**, *20*, 3829–3832. (h) Adams, R. D.; Captain, B.; Fu, W. *J. Organomet. Chem.* **2003**, *671*, 158–165. (i) Freeman, W. P.; Tilley, T. D.; Rheingold, A. L.; Ostrander, R. L. *Angew. Chem., Int. Ed.* **1993**, *32*, 1744–1745. (j) Howard, J. A. K.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1978**, 412–416. (k) Marciniec, B.; Ławicka, H.; Majchrzak, M.; Kubicki, M.; Kownacki, I. *Chem.—Eur. J.* **2006**, *12*, 244–250.

(20) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719.
(21) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074–5084.
(22) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209–225.

other materials were purchased from Gelest Co. or Aldrich Chemicals and purified according to standard procedures.

NMR spectra (^{1}H (500.1 MHz), ^{13}C{^{1}H} (124.7 MHz), ^{31}P-{^{1}H} (202.4 MHz), and ^{29}Si{^{1}H} (99.3 MHz)) were acquired on a Bruker DRX-500 spectrometer equipped with a 5 mm BBI probe. Unless otherwise specified, spectra were recorded at ambient temperature and were referenced to residual proteo signals in the deuterated solvent for ^{1}H, solvent peaks for ^{13}C, internal SiMe$_4$ for ^{29}Si, and external 85% H$_3$PO$_4$ for ^{31}P. Infrared spectra (Nujol mulls, KBr plates) were recorded using a Mattson FTIR spectrometer at a resolution of 2 cm^{-1}. X-ray diffraction data were collected on a Bruker Platform goniometer with a charged coupled device (CCD) detector (Smart Apex). Structures were solved using the SHELXTL (version 5.1) program library. All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library.[23] Elemental analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility.

Synthesis of Cp*(^{i}Pr$_2$MeP)RuCl (1). Complex **1** was prepared by modification of a literature preparation.[24] A 5 mL CH$_2$Cl$_2$ solution of ^{i}Pr$_2$MeP (0.42 g, 3.2 mmol) was added dropwise to a rapidly stirring 4 mL CH$_2$Cl$_2$ suspension of [Cp*RuCl]$_4$ (0.87 g, 0.80 mmol). The reaction mixture immediately became dark blue-purple, although trace orange color, attributed to local concentrations of Cp*(^{i}Pr$_2$MeP)$_2$RuCl, was observed during the first 30 s of mixing. The reaction mixture was stirred for an additional 15 min, at which point the solvent was removed under reduced pressure to give a dark blue powder, which was recrystallized from hexanes (3 mL) at −35 °C. Yield: 1.10 g, 0.27 mmol, 85%. ^{1}H NMR (benzene-d_6): δ 1.73 (sp, 2H, CHMe$_2$, J_{HH} = 7.2 Hz), 1.43 (s, 15H, C$_5$Me$_5$), 1.24 (d, 3H, PMe, $^2J_{HP}$ = 6.9), 1.04 (ov m, 12H, CHMe_2, J_{HH} = 7.2). All remaining spectral data matched literature values.[24]

Synthesis of Cp*(^{i}Pr$_2$MeP)Ru(η^3-CH$_2$Ph) (2). A 10 mL RB flask was charged with Cp*(^{i}Pr$_2$MeP)RuCl (0.074 g, 0.18 mmol) and toluene (4 mL). The resultant purple solution was cannula transferred into a separate 10 mL RB flask containing Mg-(CH$_2$Ph)$_2$(THF)$_2$ (0.032 g, 0.091 mmol). Within 1 min of rapid stirring the solution changed color to orange-red. The reaction mixture was stirred for an additional 10 min, at which point the solvent was removed *in vacuo* to afford an oily red solid. The residue was triturated with pentane (3 × 5 mL), and the resulting solution was filtered and concentrated to approximately 2 mL. Upon cooling to −35 °C for 6 weeks, large red crystals of **2** were obtained. Yield: 0.061 g, 0.13 mmol, 73%. ^{1}H NMR (benzene-d_6): δ 6.89 (ov m, 3H, Ph), 5.19 (br, 2H, Ph), 1.98 (sp, 2H, CHMe$_2$, J_{HH} = 7.0 Hz), 1.68 (d, 2H, RuCH$_2$, $^3J_{HP}$ = 8.5 Hz), 1.41 (s, 15H, C$_5$Me$_5$), 1.24 (dd, 6H, CHMe_2, $^3J_{HP}$ = 14.5, J_{HH} = 7.0), 1.04 (dd, 6H, CHMe_2, $^3J_{HP}$ = 10.5, J_{HH} = 7.0), 0.25 (d, 3H, PMe, $^3J_{HP}$ = 5.0). ^{13}C{^{1}H} NMR (benzene-d_6): δ 146.2, 131.8, 118.9, 92.7 (aromatic C), 84.2 (C$_5$Me$_5$), 29.0 (d, CHMe$_2$, $^1J_{CP}$ = 18.8 Hz), 27.9 (RuCH$_2$), 20.6, 18.5 (CHMe_2), 10.2 (C$_5$Me$_5$), 3.9 (PMe). ^{31}P{^{1}H} NMR (benzene-d_6): δ 47.4. Anal. Calcd for C$_{24}$H$_{39}$PRu: C, 62.72; H, 8.55. Found: C, 62.46; H, 8.75.

Synthesis of Cp*(^{i}Pr$_2$MeP)(H)Ru=SiH(trip) (3). A 3 mL benzene solution of Cp*(^{i}Pr$_2$MeP)RuCl (1) (0.060 g, 0.15 mmol) was added dropwise to solid Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.026 g, 0.074 mmol). The reaction mixture immediately changed color from purple to orange-red, after which it was stirred for an additional 10 min and finally added dropwise to neat tripSiH$_3$ (0.035 g, 0.15 mmol). The reaction mixture was stirred for 20 min, during which time the solution gradually became deep red in color. The solvent was removed under vacuum to afford a thick red oil. The residue was extracted with pentane (3 × 2 mL) and the resultant solution was filtered. The solution was

concentrated to ca. 1 mL and then cooled to −35 °C. Large orange crystals of **3** were isolated after 2 days. Yield: 0.038 g, 0.063 mmol, 43%. ^{1}H NMR (benzene-d_6): δ 9.41 (br s, 1H, SiH), 7.16, (s, 2H, m-C$_6$H$_2$), 4.30−3.52 (br, 2H, o-CHMe$_2$), 2.88 (sp, 1H, p-CHMe$_2$, J_{HH} = 6.8 Hz), 1.88 (br, 2H, PCHMe$_2$), 1.85 (s, 15H, C$_5$Me$_5$), 1.60−1.32 (br ov m, 12H, o-CHMe_2), 1.29 (d, 6H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.27 (d, 3H, PMe, $^2J_{HP}$ = 9.1 Hz), 1.13 (dd, 6H, PCHMe_2, J_{HH} = 6.8 Hz, $^3J_{HP}$ = 15.1 Hz), 0.97 (br m, 6H, PCHMe_2), −13.5 (br, 1H, RuH). ^{13}C{^{1}H} NMR (benzene-d_6): δ 149.9, 128.3, 119.9 (aromatic C), 92.5 (C$_5$Me$_5$, $^2J_{C-P}$ = 1.7 Hz), 34.9 (o-CHMe$_2$), 34.1 (p-CHMe$_2$), 24.7 (d, PMe $^1J_{C-P}$ = 14 Hz), 24.4 (p-CHMe_2), 18.9, 18.8, 18.4, 18.2 (br, PCHMe_2), 12.3 (C$_5$Me$_5$), 11.2 (br, PMe) (o-CHMe$_2$, PCHMe$_2$ resonances not observed). ^{31}P{^{1}H} NMR (benzene-d_6): δ 55.5. Anal. Calcd for C$_{32}$H$_{57}$PRuSi: C, 63.85; H, 9.54. Found: C, 64.12; H, 9.89. Repeated attempts to obtain the ^{29}Si NMR signal for complex **3**, using direct detection and 2-D (HMBC) experiments (ambient and variable temperature), were unsuccessful.

Synthesis of Cp*(^{i}Pr$_2$MeP)(H)Ru=SiH(dmp) (4). A 4 mL toluene solution of Cp*(^{i}Pr$_2$MeP)RuCl (1) (0.10 g, 0.24 mmol) was added dropwise to solid Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.043 g, 0.12 mmol). The reaction mixture was stirred for 5 min and then added dropwise to solid dmpSiH$_3$ (0.085 g, 0.25 mmol). The reaction mixture was stirred for 15 min, during which time the solution gradually became deep red in color. The solvent was removed under vacuum to afford an oily red solid. The residue was extracted with pentane (3 × 5 mL), the resultant solution was filtered, and the solvent was removed *in vacuo* to give 0.139 g (0.19 mmol, 79%) of a fine orange powder. ^{1}H NMR (benzene-d_6): δ 8.00 (d, 1H, SiH, $^3J_{HP}$ = 11.9 Hz, $^1J_{HSi}$ = 151 Hz), 7.35 (t, 1H, p-C$_6$H$_3$, J_{HH} = 6.0 Hz), 7.00, (d, 2H, m-C$_6$H$_3$, J_{HH} = 6.0 Hz), 6.87 (s, 4H, C$_6$H$_2$), 2.45−2.14 (br ov m, 12H, o-C$_6$H$_2$Me$_3$), 2.21 (s, 6H, p-C$_6$H$_2$Me$_3$), 1.79 (ov s, 15H, C$_5$Me$_5$), 1.75 (ov sp, 1H, CHMe$_2$, J_{HH} = 6.8 Hz), 1.66 (sp, 1H, CHMe$_2$, J_{HH} = 6.8 Hz), 1.12 (d, 3H, PMe, $^2J_{HP}$ = 6.5 Hz), 0.88−0.68 (ov m, 12H, CHMe_2, J_{HH} = 8.0, 6.8 Hz), −14.4 (d, 1H, RuH, $^2J_{HP}$ = 27 Hz, $^2J_{HSi}$ = 8.6 Hz). ^{13}C{^{1}H} NMR (benzene-d_6): δ 148.0, 145.1, 139.7, 136.5 (aromatic C), 128.5 (m-C$_6$H$_2$), 128.4 (aromatic C), 128.1 (m-C$_6$H$_3$), 127.7 (p-C$_6$H$_3$), 90.2 (C$_5$Me$_5$), 29.2 (d, CHMe_2, $^1J_{CP}$ = 24.5 Hz), 28.3 (d, CHMe_2, $^1J_{CP}$ = 25.2 Hz), 21.7 (o-C$_6$H$_2$Me$_3$), 21.1 (p-C$_6$H$_2$Me$_3$), 19.0 (d, CHMe_2 $^2J_{CP}$ = 4.9 Hz), 18.5 (d, CHMe_2 $^2J_{CP}$ = 3.8 Hz), 17.7, 17.3 (CHMe_2), 12.7 (C$_5$Me$_5$), 10.0 (d, PMe $^2J_{CP}$ = 18.1 Hz). ^{29}Si NMR (benzene-d_6): δ 204. ^{31}P{^{1}H} NMR (benzene-d_6): δ 48.5. IR (Nujol, cm^{-1}): 2051 w (ν_{SiH}). Anal. Calcd for C$_{41}$H$_{59}$PRuSi: C, 69.16; H, 8.35. Found: C, 68.77; H, 7.98. Mp: 205−208 °C.

Synthesis of Cp*(^{i}Pr$_2$MeP)(H)Ru=SiH(Mes^F) (5). A 3 mL benzene solution of Cp*(^{i}Pr$_2$MeP)RuCl (1) (0.050 g, 0.12 mmol) was added dropwise to solid Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.022 g, 0.0062 mmol). The reaction mixture immediately changed color from purple to orange-red, after which it was stirred for an additional 10 min and then added dropwise to neat H$_3$SiMes^F (0.035 g, 0.12 mmol). After an additional 10 min the solvent was removed *in vacuo* to afford a waxy orange solid. The residue was extracted with hexanes (3 × 2 mL) and the solution was filtered to give a deep red solution. The solvent was then removed to yield 66 mg (0.097 mmol, 81%) of **5** as an analytically pure ruby red powder. ^{1}H NMR (benzene-d_6): δ 7.83 (s, 2H, m-C$_6$H$_2$), 1.81 (sp, 2H, CHMe$_2$, J_{HH} = 7.2 Hz), 1.68 (s, 15H, C$_5$Me$_5$), 1.13 (dd, 6H, CHMe_2, J_{HH} = 7.2 Hz, $^3J_{HP}$ = 6.8 Hz), 1.08 (d, 3H, PMe, $^2J_{HP}$ = 6.9 Hz) 0.92 (dd, 6H, CHMe_2, J_{HH} = 7.2 Hz, $^3J_{HP}$ = 6.8 Hz), −13.4 (br, 1H, RuH) (SiH not observed). ^{19}F{^{1}H} NMR (benzene-d_6): δ −56.7 (br s, 6F, o-CF$_3$), −62.0 (s, 3F, p-CF$_3$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 53.6. Anal. Calcd for C$_{26}$H$_{34}$F$_9$PRuSi: C, 46.08; H, 5.06. Found: C, 45.73; H, 5.41. Repeated attempts to obtain the ^{29}Si NMR signal for complex **5**, using direct detection and 2-D (HMBC) experiments (ambient and variable temperature), were unsuccessful. This is likely due to significant broadening of the signal caused by coupling to nine ^{19}F nuclei in the aryl substituent.[16]

(23) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
(24) Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2000**, *609*, 161–168.

Table 1. Crystal Data and Structure Refinement Parameters for Complexes 2, 3, 5, and 9

	2	3	5	9
empirical formula	$C_{24}H_{39}PRu$	$C_{32}H_{57}PRuSi$	$C_{26}H_{36}F_9PRuSi$	$C_{32}H_{57}GePRu$
fw	459.59	601.91	679.68	646.41
cryst color, habit	red block	orange block	orange block	orange block
cryst size/mm	$0.20 \times 0.19 \times 0.17$	$0.15 \times 0.10 \times 0.08$	$0.11 \times 0.10 \times 0.08$	$0.16 \times 0.14 \times 0.11$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$C2/c$	$P2_1/c$
T/K	152(2)	168(2)	152(2)	145(2)
a/Å	8.929(1)	18.746(5)	19.556(2)	18.806(3)
b/Å	12.617(2)	9.242(2)	8.7330(7)	9.128(2)
c/Å	10.890(1)	19.371(5)	34.735(3)	19.516(3)
α/deg	90	90	90	90
β/deg	112.285(2)	98.959(2)	100.308(2)	98.258(2)
γ/deg	90	90	90	90
unit cell vol/Å^3	1135.3(2)	3313.1(15)	5836.3(8)	3315.5(9)
Z	2	4	8	4
μ/mm^{-1}	0.766	0.575	0.705	
D_{calc} (mg/mm^3)	1.344	1.206	1.547	1.295
F_{000}	484	1288	2768	1360
θ range/deg	2.02−26.37	3.06−24.80	1.19−26.38	3.16−24.73
N	6603	14 704	16 592	14 541
N_{ind}	4210	5651	5951	5635
T_{min}; T_{max}	0.8618; 0.8808	0.9555; 0.9187	0.9265; 0.9457	0.8038; 0.8588
params	235	324	351	324
data; param	17.91	17.44	16.95	17.39
GoF on R_1	0.996	0.890	1.033	0.801
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0246	0.0409	0.0406	0.0325
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.0593	0.0851	0.1011	0.0601
$\Delta\rho_{max}$ and $\Delta\rho_{min}$/e Å^3	0.500, −0.278	0.502, −0.595	0.646, −0.658	0.527, −0.507

$^a R_1 = \sum ||F_o| - |F_c||/\sum|F_o|.$ $^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}.$

Synthesis of Cp*(ᶦPr₂MeP)(H)Ru=SiPh(trip) (6). A 25 mL flask equipped with a magnetic stir bar was charged with Cp*-(ᶦPr₂MeP)RuCl (**1**) (0.050 g, 0.12 mmol) and benzene (5 mL). The resultant solution was cannula transferred onto solid Mg-(CH₂Ph)₂(THF)₂ (0.022 g, 0.063 mmol). The reaction mixture was stirred for an additional 10 min and then added dropwise to neat Ph(trip)SiH₂ (0.039 g, 0.13 mmol). The red solution was stirred for 5 min and the solvent was removed under reduced pressure. The residue was extracted with pentane (2 × 3 mL), and the resultant solution was filtered. Removal of the solvent *in vacuo* afforded **6** as a pale red-pink solid. Yield: 0.044 g, 0.065 mmol, 54%. ¹H NMR (benzene-d_6): δ 7.85 (br, 2H, Ph), 7.28 (s, 1H, m-C₆H₂), 7.15 (br, 1H, Ph), 7.07 (s, 2H, Ph), 7.00 (s, 1H, m-C₆H₂), 4.79 (sp, 1H, CHMe₂, J_{HH} = 7.0 Hz), 2.94 (sp, 1H, CHMe₂, J_{HH} = 7.0 Hz), 2.83 (sp, 1H, CHMe₂, J_{HH} = 7.0 Hz), 1.91 (s, 15H, C₅Me₅), 1.62 (d, 3H, o-CHMe_2, J_{HH} = 7.0 Hz), 1.61 (m, 1H, PCHMe₂), 1.52 (m, 1H, PCHMe₂), 1.49 (d, 3H, o-CHMe_2, J_{HH} = 7.0 Hz), 1.38 (d, 3H, o-CHMe_2, J_{HH} = 7.0 Hz), 1.26 (ov d, 6H, p-CHMe_2, J_{HH} = 7.0 Hz), 1.08−1.00 (ov m, 9H, PCHMe_2, PMe), 0.84−0.80 (ov m, 6H, PCHMe_2), 0.50 (d, 3H, o-CHMe_2, J_{HH} = 7.0 Hz), −12.5 (d, 1H, RuH, $^2J_{HP}$ = 30 Hz). ¹³C{¹H} NMR (benzene-d_6): δ 154.1, 151.2, 150.1, 134.6, 129.2, 128.7, 127.3, 127.1, 121.2, 121.1 (aromatic C), 93.5 (C₅Me₅), 35.8 (CHMe₂), 34.8 (CHMe₂), 33.6 (CHMe₂), 29.9 (PCHMe₂), 29.6 (PCHMe₂), 26.7 (CHMe_2), 24.8 (CHMe_2), 24.6 (CHMe_2), 24.5 (CHMe_2), 24.3 (CHMe_2), 24.2 (CHMe_2), 18.8 (PCHMe_2), 18.3 (PCHMe_2), 16.6 (PCHMe_2), 13.7 (PCHMe_2), 12.7 (C₅Me_5), 11.6 (PMe). ²⁹Si NMR (benzene-d_6): δ 229. ³¹P{¹H} NMR (benzene-d_6): δ 55.7 (br) IR (Nujol, cm^{-1}): 2018 s (ν_{RuH}). Anal. Calcd for C₃₈H₆₁PRuSi: C, 67.32; H, 9.07. Found: C, 67.32; H, 8.80. Mp: 129−133 °C.

Synthesis of Cp*(ᶦPr₂MeP)(H)Ru=SiCl(trip) (7). To a 5 mL benzene solution of Mg(CH₂Ph)₂(THF)₂ (0.043 g, 0.12 mmol) was added dropwise a 4 mL benzene solution of Cp*-(ᶦPr₂MeP)RuCl (**1**) (0.10 g, 0.24 mmol). After stirring for 10 min the reaction mixture was added to solid tripSiH₂Cl (0.077 g, 0.29 mmol), resulting in a rapid color change from orange to red-pink. The reaction mixture was stirred for 5 min, whereupon the solvent was removed under reduced pressure.

The resultant solid was extracted with hexanes (4 × 2 mL) and the solution was filtered. The solution was then concentrated to ca. 1 mL and cooled to −35 °C for 24 h. Complex **7** was isolated as a microcrystalline red-pink solid in 62% yield (0.095 g, 0.15 mmol). ¹H NMR (benzene-d_6): δ 7.11, (s, 1H, m-C₆H₂), 7.05 (s, 1H, m-C₆H₂), 4.55 (sp, 1H, o-CHMe₂, J_{HH} = 6.8 Hz), 3.65 (br m, 1H, o-CHMe₂), 2.80 (sp, 1H, p-CHMe₂, J_{HH} = 6.8 Hz), 1.91 (ov m, 1H, PCHMe₂), 1.87 (s, 15H, C₅Me₅), 1.84 (ov m, 1H, PCHMe₂), 1.52 (d, 3H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.46 (d, 3H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.44 (d, 3H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.42 (d, 3H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.23 (d, 6H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.15 (dd, 3H, PCHMe_2, J_{HH} = 6.8 Hz, $^3J_{HP}$ = 2.8 Hz), 1.08 (d, 3H, PMe, $^2J_{HP}$ = 7.3 Hz), 1.04 (ov m, 3H, PCHMe_2), 1.02 (dd, 3H, PCHMe_2, J_{HH} = 6.8 Hz, $^3J_{HP}$ = 2.8 Hz), 0.89, (dd, 3H, PCHMe_2, J_{HH} = 6.8 Hz, $^3J_{HP}$ = 2.8 Hz), −12.68 (d, 1H, RuH, $^2J_{HP}$ = 30 Hz). ¹³C{¹H} NMR (benzene-d_6): δ 151.0, 150.6, 150.4, 120.7 (aromatic C), 93.8 (C₅Me₅), 35.4 (o-CHMe₂), 34.8 (p-CHMe₂), 34.3 (o-CHMe₂), 28.6 (ov d, PCHMe₂, $^1J_{C-P}$ = 29 Hz), 26.7, 26.6 (o-CHMe₂), 24.2 (p-CHMe₂), 23.5, 23.2 (o-CHMe_2), 19.1 (PCHMe_2), 18.2 (br, PCHMe_2), 17.8, 17.0 (PCHMe_2), 12.2 (C₅Me_5), 9.9 (d, PMe $^1J_{C-P}$ = 22 Hz). ²⁹Si NMR (benzene-d_6): δ 221.7. ³¹P{¹H} NMR (benzene-d_6): δ 56.9. IR (Nujol, cm^{-1}): 1920 s (ν_{RuH}). Anal. Calcd for C₃₂H₅₆ClPRuSi: C, 60.40; H, 8.87. Found: C, 60.63; H, 9.04. Mp: 124−126 °C.

Synthesis of Cp*(ᶦPr₂MeP)(H)Ru=SiCl(dmp) (8). To a 1 mL benzene solution of Mg(CH₂Ph)₂(THF)₂ (0.043 g, 0.12 mmol) was added dropwise a 4 mL benzene solution of Cp*-(ᶦPr₂MeP)RuCl (**1**) (0.10 g, 0.24 mmol). After stirring for 10 min the reaction mixture was added to solid dmpSiH₂Cl (0.094 g, 0.25 mmol). The reaction mixture was stirred for an additional 18 h, whereupon the solvent was removed under reduced pressure to afford a red-brown foam, which was recrystallized from hexanes (1 mL) at −35 °C. Yield: 0.108 g, 0.063 mmol, 59%. ¹H NMR (benzene-d_6): δ 7.11 (t, 1H, p-C₆H₃, J_{HH} = 7.8 Hz), 6.84 (s, 4H, C₆H₃), 6.80, (d, 2H, m-C₆H₃, J_{HH} = 7.8 Hz), 2.50 (s, 6H, p-C₆H₂Me_3), 2.22 (ov m, 14H, PCHMe_2, o-C₆H₂Me_3), 1.75 (ov sp, 2H, CHMe₂, J_{HH} = 6.8 Hz), 1.72 (ov s, 15H, C₅Me₅), 0.93−0.85 (ov m, 15H, PMe, PCHMe_2),

-13.0 (d, 1H, RuH, $^2J_{HP}$ = 28 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 152.2, 139.8, 137.8, 136.7 (aromatic C), 129.9 (p-C_6H_3), 129.0 (m-C_6H_3), 128.6 (m-C_6H_2), 128.3, (aromatic C), 94.1 (C_5Me_5, $^2J_{CP}$ = 1.7 Hz), 23.0 (p-$C_6H_2Me_3$), 22.5, 21.8 (br, CHMe_2), 21.1 (o-$C_6H_2Me_3$), 20.2, 18.9, 18.3, 18.2 (CHMe_2), 11.8 (C_5Me_5), 11.2 (br, PMe). ^{29}Si NMR (benzene-d_6): δ 205. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 57.9. Anal. Calcd for $C_{41}H_{58}ClPRuSi$: C, 65.97; H, 7.83. Found: C, 65.32; H, 7.56.

Synthesis of Cp*($^iPr_2MeP$)(H)Ru=GeH(trip) (9). A 4 mL benzene solution of Cp*($^iPr_2MeP$)RuCl (1) (0.10 g, 0.24 mmol) was added dropwise to solid Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.043 g, 0.12 mmol). The reaction mixture immediately changed in color from purple to orange-red, after which it was stirred for an additional 10 min and then added dropwise to neat tripGeH$_3$ (0.14 g, 0.36 mmol). The reaction mixture was stirred for 10 min, during which time the solution gradually became deep orange in color. The solvent was removed under vacuum to afford an orange solid, which was extracted with hexanes (5 × 2 mL) and filtered. The resultant solution was reduced to 1 mL and cooled to -35 °C for 24 h. Yield: 0.10 g, 0.16 mmol, 67%. ^1H NMR (benzene-d_6): δ 12.39 (s, 1H, GeH), 7.14 (s, 2H, m-C_6H_2), 3.56 (br m, 2H, o-CHMe_2), 2.87 (sp, 1H, p-CHMe_2, J_{HH} = 6.9 Hz), 1.85, 1.83 (ov m, 2H, PCHMe_2, J_{HH} = 6.9 Hz), 1.84 (s, 15H, C_5Me_5), 1.40, 1.34 (br ov m, 12H, o-CHMe_2), 1.29 (d, 6H, p-CHMe_2, J_{HH} = 6.9 Hz), 1.23 (d, 3H, PMe, $^2J_{HP}$ = 7.3 Hz), 1.09 (dd, 6H, PCHMe_2, J_{HH} = 6.9 Hz, $^3J_{HP}$ = 2.8 Hz), 1.09 (ov m, 6H, PCHMe_2, J_{HH} = 6.9 Hz), -12.81 (d, 1H, RuH, $^2J_{HP}$ = 31 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 151.6, 150.7, 149.3, 120.3 (aromatic C), 92.6 (d, C_5Me_5, $^2J_{HP}$ = 1.9 Hz), 34.9 (p-CHMe_2), 33.9 (o-CHMe_2), 32.1 (br, o-CHMe_2), 29.6 (d, PCHMe_2, $^2J_{C-P}$ = 23 Hz), 27.4 (d, PCHMe_2, $^1J_{C-P}$ = 27 Hz), 24.5 (ov m, p-CHMe_2, o-CHMe_2), 18.7, 17.9, 17.1 (PCHMe_2), 12.4 (C_5Me_5), 10.6 (d, PMe $^1J_{C-P}$ = 22 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 57.6. IR (Nujol, cm^{-1}): 1969 s (ν_{RuH}). Anal. Calcd for $C_{32}H_{57}GePRu$: C, 59.45; H, 8.89. Found: C, 59.53; H, 8.67. Mp: 135−137 °C.

***In Situ* Generation of Cp*($^iPr_2MeP$)(H)$_2$Ru−GeH(OH)(trip) (10).** A 10 μL syringe was utilized to add thoroughly deoxygenated water (0.43 μL, 0.024 mmol) dropwise to a 0.5 mL benzene-d_6 solution of Cp*($^iPr_2MeP$)(H)Ru=GeH(trip) (9) (0.010 g, 0.024 mmol). The reaction mixture immediately changed from orange-red to colorless. ^1H NMR (benzene-d_6): δ 7.14 (s, 2H, m-C_6H_2), 6.97 (s, 1H, GeH), 3.98 (sp, 2H, o-CHMe_2, J_{HH} = 6.8 Hz), 2.85 (sp, 1H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.82−1.72 (ov m, 17H, PCHMe_2, C_5Me_5), 1.52 (d, 12H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.30 (d, 6H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.20 (d, 3H, PMe, $^2J_{HP}$ = 7.3 Hz), 0.99−0.81 (ov m, 12H, PCHMe_2), 0.55 (s, 1H, OH), -11.1 (d, 1H, RuH, $^2J_{HP}$ = 28 Hz), -11.6 (d, 1H, RuH, $^2J_{HP}$ = 28 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 63.9.

***In Situ* Generation of Cp*($^iPr_2MeP$)(H)(D)Ru−GeH(OD)-(trip) (10-d_2).** A 10 μL syringe was utilized to add thoroughly deoxygenated D$_2$O (0.43 μL, 0.024 mmol) dropwise to a 0.5 mL benzene-d_6 solution of Cp*($^iPr_2MeP$)(H)Ru=GeH(trip) (9) (0.010 g, 0.024 mmol). The reaction mixture immediately changed from orange-red to colorless. ^1H NMR (benzene-d_6): δ 7.14 (s, 2H, m-C_6H_2), 6.97 (s, 1H, GeH), 3.98 (sp, 2H, o-CHMe_2, J_{HH} = 6.8 Hz), 2.85 (sp, 1H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.82−1.72 (ov m, 17H, PCHMe_2, C_5Me_5), 1.52 (d, 12H, o-CHMe_2, J_{HH} = 6.8 Hz), 1.30 (d, 6H, p-CHMe_2, J_{HH} = 6.8 Hz), 1.20 (d, 3H, PMe, $^2J_{HP}$ = 7.3 Hz), 0.99−0.81 (ov m, 12H, PCHMe_2), -11.1 (d, 1H, RuH, $^2J_{HP}$ = 28 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 63.9.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker APEX CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)). Suitable crystals of the complexes were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using a Patterson search for heavy elements and standard difference map techniques. Refinement was done by full-matrix least-squares procedures on F^2 with SHELXTL.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. Hydrogen atoms on ruthenium (H(1) for **3** and **9**) and silicon or germanium (H(2) for **3**, **5**, and **9**) were located in the Fourier difference map and freely refined. Crystal data and refinement details are presented in Table 1. Complexes **3**, **5**, and **9** displayed minor disorder of the methyl substituents that had no serious effect on the solution of the structures. Nonmodeled solutions are presented for simplicity given limited improvement in quality of refinement that modeling provided.

Supporting Information Available: Experimental details and crystallographic data (CIF) for **2**, **3**, **5**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.