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Synthesis and Study of Ruthenium Silylene Complexes of the Type $[(\eta^5\text{-}C_5Me_5)(Me_3P)_2Ru{=}SiX_2]^+$ (X = Thiolate, Me, and Ph)

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Various ruthenium silyl complexes of the type $Cp^*(Me_3P)_2RuSiR_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$; $SiR_3 = SiCl_3$ (**1**), $Si(NMe_2)_3$ (**2**), $Si(SEt)_3$ (**3**), $Si(S\text{-}2\text{-}Naph)_3$ (**4**), $Si[S(CH_2)_3S]Ph$ (**5**), $Si(SCy)_2Cl$ (**6**), and $Si(SMes)_2Cl$ (**7**, Mes = 2,4,6-trimethylphenyl)) were prepared by the reaction of $Cp^*(Me_3P)_2RuCH_2SiMe_3$ with the appropriate silane $HSiR_3$. Compound **3** was converted to the triflate $Cp^*(Me_3P)_2RuSi(SEt)_2OTf$ (**8**) by the reaction of **3** with Me_3SiOTf. Similar reactions produced $Cp^*(Me_3P)_2RuSi(NMe_2)_2OTf$ (**13**), $Cp^*(Me_3P)_2RuSi(NMe_2)(OTf)_2$ (**14**), $Cp^*(Me_3P)_2RuSi(SMes)_2OTf$ (**18**), and $Cp^*(Me_3P)_2RuSi(SMes)(Cl)OTf$ (**19**). By NMR spectroscopy, compound **8** in dichloromethane solution appears to possess a labile triflate group. Reactions of the triflates **8** and $Cp^*(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)_2OTf$ (**10**) with $NaBPh_4$ provided the silylene complexes $[Cp^*(Me_3P)_2RuSi(SR)_2][BPh_4]$ (**20**, R = Et; **21**, R = *p*-Tol). Similarly, the reaction of **6** with $NaBPh_4$ gave $[Cp^*(Me_3P)_2RuSi(SCy)_2][BPh_4]$ (**22**), and the reaction of **4** with $B(C_6F_5)_3$ produced $[Cp^*(Me_3P)_2RuSi(S\text{-}2\text{-}Naph)_2][MeB(C_6F_5)_3]$ (**23**). Silylene complexes **20**−**23** display characteristic ^{29}Si NMR shifts in the region of δ 250−270. The non-heteroatom-stabilized silylene complexes $[Cp^*(Me_3P)_2RuSiR_2][B(C_6F_5)_4]$ (**24**, R = Me; **25**, R = Ph), obtained via reactions of $(Et_2O)LiB(C_6F_5)_4$ with $Cp^*(Me_3P)_2RuSiR_2OTf$ (**11**, R = Me; **12**, R = Ph) exhibit ^{29}Si NMR shifts around δ 300. The crystal structure of **24** revealed a Ru−Si distance of 2.238(2) Å, and the Cp*(centroid)−Ru−Si−Me dihedral angle is 34°. Compound **24** reacts quantitatively with 1 equiv of PMe_3 or PPh_3 in dichloromethane-d_2 to form the base-stabilized silylene complexes $[Cp^*(Me_3P)_2RuSiMe_2(PR_3)][B(C_6F_5)_4]$ (**28**, R = Me; **29**, R = Ph), identified by ^1H and ^{31}P NMR spectroscopy. These complexes are thermally labile and decompose with elimination of the dimethylsilylene fragment to give $[Cp^*(Me_3P)_2RuPR_3][B(C_6F_5)_4]$ (R = Me, Ph). The ylide CH_2PPh_3 reacts with **24** to form $[Cp^*(Me_3P)_2RuSiMe_2CH_2PPh_3][B(C_6F_5)_4]$ (**32a**), and the characterization of $[Cp^*(Me_3P)_2RuSiMe_2CH_2PPh_3][OTf]$ (**32b**) by X-ray crystallography suggests that the complex is best viewed as a ruthenium silyl derivative with the positive charge localized on the “ylide” phosphorus atom. Reactions of **20** and **24** with hydrogen proceed slowly and result in relatively complex product mixtures that contain various ruthenium hydride species. The reaction involving **20** also produced $HSi(SEt)_3$, perhaps via redistribution of initially formed $H_2Si(SEt)_2$. For the reaction of **24** with hydrogen, no H_2SiMe_2 was detected in the product mixture. The reaction of **20** with $H_3SiSiPh_3$ gave $[Cp^*(Me_3P)_2Ru(H)(SiH_2SiPh_3)][BPh_4]$ (**35**) and $HSi(SEt)_3$, and the corresponding reaction of H_3SiMes in dichloromethane gave $[Cp^*(Me_3P)_2RuHCl][BPh_4]$ (**34**), BPh_3, and $H_2SiMes(SEt)$, among other products. By NMR spectroscopy, the intermediate $[Cp^*(Me_3P)_2Ru(H)(SiH_2Mes)][BPh_4]$ (**36**) was observed for the latter process. Compound **36**, generated independently by reaction of $[Cp^*(Me_3P)_2Ru(NCMe)][BPh_4]$ with H_3SiMes, was shown to react with $HSi(SEt)_3$ to give $H_2SiMes(SEt)$.

Introduction

Transition metal−silylene complexes have been the focus of intense research interest in recent years.[1] This attention is largely derived from the possibility that metal−silicon double bonds might participate in a wide range of organosilicon transformations.[1−24] Several processes such as the dehydropolymerization of silanes,[1c,11] the transfer of silylenes to unsaturated compounds,[7b,c,8b,10,19] and the redistribution of substituents

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at silicon[1g,7a] have been proposed to involve silylene intermediates. Considerable effort has therefore been devoted to the verification of these proposals, and consequently dramatic advances in transition metal–silylene chemistry have been made in recent years. In 1987, the synthesis and characterization of donor-stabilized silylene complexes were reported,[5a,20a] and in 1990 base-free silylene complexes of the type $[Cp^*(Me_3P)_2Ru{=}Si(SR)_2]BPh_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$) were communicated.[22a] Since then, several more complexes with bonds between a transition metal and sp^2 silicon have been isolated,[22,23] and initial reactivity studies on such compounds have been carried out.[24]

In general, silylene complexes are much more difficult to prepare than the analogous carbene compounds, which are often obtained from unsaturated starting materials (e.g., CO or N_2CR_2) that do not have stable silicon analogues or by use of an electrophilic reagent to abstract a substituent (e.g., hydride, methoxide, or halide) from an alkyl complex.[25] Early attempts to apply the latter method to transition metal–silicon compounds were unsuccessful, because the extreme Lewis acidity of the resulting silylene ligand can give rise to secondary reactions (such as halide ion transfer) which form new bonds to silicon.[26] Nonetheless we have developed methods for the synthesis of cationic silylene complexes, based on abstraction of a group bound to silicon. This approach has focused on electron-rich metal fragments (e.g., $Cp^*(Me_3P)_2Ru$) expected to stabilize an electron-deficient silicon center. In addition, this method requires use of "noncoordinating" anions such as BPh_4^- and $B(C_6F_5)_4^-$, which exhibit low reactivities toward the resulting three-coordinate silicon centers. Here we report investigations into the synthesis, characterization, and reactivity of cationic ruthenium silylene complexes of the type $[Cp^*(Me_3P)_2Ru{=}SiX_2]^+$.

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(1) (a) Tilley, T. D. In *The Silicon-Heteroatom Bond;* Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10, pp 245 and 309. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (d) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271. (e) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95*, 1351. (f) Zybill, C. *Top. Curr. Chem.* **1991**, *160*, 1. (g) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

(2) (a) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (b) Pannell, K. H.; Rozell, J. M, Jr.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (c) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550. (d) Pannell, K. H.; Sharma, H. *Organometallics* **1991**, *10*, 954. (e) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (f) Hernandez, C.; Sharma, H. K.; Pannell, K. H. *J. Organomet. Chem.* **1993**, *462*, 259. (g) Pannell, K. H.; Brun, M.-C.; Sharma, H.; Jones, K.; Sharma, S. *Organometallics* **1994**, *13*, 1075. (h) Pannell, K. H.; Sharma, H. K.; Kapoor, R. N.; Cervantes Lee, F. *J. Am. Chem. Soc.* **1997**, *119*, 9315. (i) Zhang, Z. Y.; Sanchez, R.; Pannell, K. H. *Organometallics* **1995**, *14*, 2605.

(3) (a) Tobita, H.; Ueno, K.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2797. (b) Ueno, K.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1988**, *110*, 4092. (c) Ueno, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1990**, 369. (d) Ueno, K.; Kakano, K.; Ogino, H. *Chem. Lett.* **1996**, 459. (e) Okazaki, M.; Tobita, H.; Ogino, H. *J. Chem. Soc., Dalton Trans.* **1997**, 3531. (f) Tobita, H.; Ueno, K.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1990**, *112*, 3415. (g) Takeuchi, T.; Tobita, H.; Ogino, H. *Organometallics* **1991**, *10*, 835. (h) Koe, J.; Tobita, H.; Ogino, H. *Organometallics* **1992**, *11*, 2479. (i) Ueno, K.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *430*, 93. (j) Ueno, K.; Tobita, H.; Seki, S.; Ogino, H. *Chem. Lett.* **1993**, 1723. (k) Kobayashi, H.; Ueno, K.; Ogino, H. *Organometallics* **1995**, *14*, 5490. (l) Ueno, K.; Masuko, A.; Ogino, H. *Organometallics* **1997**, *16*, 5023.

(4) Haynes, A.; George, M. W.; Haward, M. T.; Poliakoff, M.; Turner, J. J.; Boag, N. M.; Green, M. *J. Am. Chem. Soc.* **1991**, *113*, 2011.

(5) (a) Zybill, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 669. (b) Zybill, C.; Wilkinson, D. L.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 583. (c) Zybill, C.; Müller, G. *Organometallics* **1988**, *7*, 1368. (d) Zybill, C.; Wilkinson, D. L.; Leis, C.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 203. (e) Leis, C.; Zybill, C.; Lachmann, J.; Müller, G. *Polyhedron* **1991**, *10*, 1163. (f) Handwerker, H.; Paul, M.; Riede, J.; Zybill, C. *J. Organomet. Chem.* **1993**, *459*, 151. (g) Handwerker, H.; Paul, M.; Blumel, J.; Zybill, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1313. (h) Handwerker, H.; Leis, C.; Gamper, S.; Zybill, C. *Inorg. Chim. Acta* **1992**, *200*, 763.

(6) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173.

(7) (a) Kobayashi, T.; Hayahi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (b) Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227. (c) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1995**, *14*, 530. (d) Sakakura, T.; Kumberger, O.; Tan, R. P.; Arthur, M.-P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 193.

(8) (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1970**, *23*, C7. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263.

(9) Tamao, K.; Sun, G.-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043.

(10) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

(11) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

(12) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

(13) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 1369.

(14) (a) Corriu, R.; Lanneau, G. F.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *9*, 1130. (b) Corriu, R. J.; Lanneau, G. F.; Chauhan, P. S. *Organometallics* **1993**, *12*, 2001. (c) Corriu, R. J. P.; Chauhan, B. P. S.; Lanneau, G. F. *Organometallics* **1995**, *14*, 1646.

(15) Auner, N.; Wagner, C.; Herdtweck, E.; Heckel, M.; Hiller, W. *Bull. Soc. Chim. Fr.* **1995**, *132*, 599.

(16) (a) Braunstein, P.; Stern, C.; Strohmann, C.; Tong, N. *Chem. Commun.* **1996**, 2237. (b) Braunstein, P.; Huch, V.; Stern, C.; Veith, M. *Chem. Commun.* **1996**, 2041.

(17) Nlate, S.; Herdtweck, E.; Fischer, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1861.

(18) Clarke, M. P.; Davidson, I. M. T. *J. Organomet. Chem.* **1991**, *408*, 149.

(19) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824.

(20) (a) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872. (b) Straus, D.; 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. (c) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 127.

(21) (a) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917. (b) Mitchell, G. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5472. (c) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477. (d) Mitchell, G. P.; Tilley, T. D. *Organometallics* **1998**, *17*, 2912. (e) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635.

(22) (a) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801. (b) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358. (c) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L.; Arnold, F. P. *J. Am. Chem. Soc.* **1993**, *115*, 7884. (d) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495. (e) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524. (f) Feldman, J.; Mitchell, G. P.; Nolte, J.-P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184.

(23) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

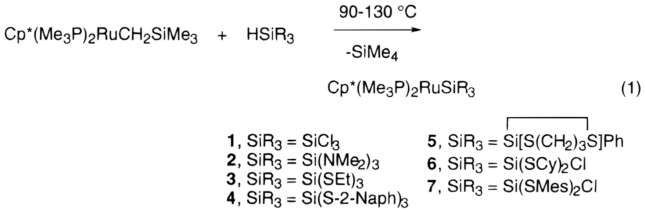
(24) (a) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 11236. (b) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

(25) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (c) Casey, C. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. II, p 135. (d) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (e) Tam., W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (f) Yu, Y. S.; Angelici, R. J. *Organometallics* **1983**, *2*, 1018. (g) Barefield, E. K.; McCarten, P.; Hillhouse, M. C. *Organometallics* **1985**, *4*, 1682. (h) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. (i) Hoskins, S. V.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1000. (j) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223.

(26) (a) Aylett, B. J. *J. Organomet. Chem. Lib.* **1980**, *9*, 327. (b) Marks, T. J.; Seyam, A. M. *Inorg. Chem.* **1974**, *13*, 1624. (c) Thum, G.; Malisch, W. *J. Organomet. Chem.* **1984**, *264*, C5. (d) Malisch, W. *Chem. Ber.* **1974**, *107*, 7, 3835. (e) Schmid, G.; Balk, H.-J. *J. Organomet. Chem.* **1974**, *80*, 257.

Results and Discussion

Synthesis of Precursor Ruthenium Silyl Complexes. We have previously described a general method for preparing ruthenium silyl complexes of the type $Cp^*(Me_3P)_2RuSiR_3$,[20b] which involves reaction of the ruthenium alkyl complex $Cp^*(Me_3P)_2RuCH_2SiMe_3$[27] with the appropriate silane in hot toluene. As shown in eq 1, this procedure was useful for the preparation of silyl complexes **1**−**7** (2-Naph = 2-naphthyl; Cy = cyclohexyl; Mes = mesityl). These light yellow silyl complexes are only somewhat air-sensitive, except for **2** and **5**, which decompose within 2 h when exposed to air. Attempts to form silyl complexes by reaction of $Cp^*(Me_3P)_2RuCH_2SiMe_3$ with the sterically demanding silanes $HSi(SMes)_3$, $HSi(SCy)_3$, $HSi[S(2,4,6\text{-}{}^iPr_3C_6H_2)]_3$, and $HSi(NPh_2)_2Cl$ in toluene were unsuccessful and instead gave the C−H activation products $Cp^*(Me_3P)_2Ru(m\text{-}Tol)$ and $Cp^*(Me_3P)_2Ru(p\text{-}Tol)$.[28]



$$Cp^*(Me_3P)_2RuCH_2SiMe_3 + HSiR_3 \xrightarrow[-SiMe_4]{90\text{-}130\ °C} Cp^*(Me_3P)_2RuSiR_3 \qquad (1)$$

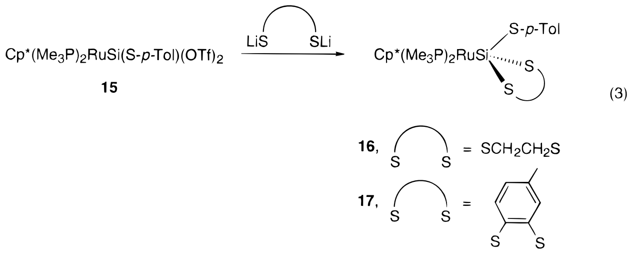
1, $SiR_3 = SiCl_3$
2, $SiR_3 = Si(NMe_2)_3$
3, $SiR_3 = Si(SEt)_3$
4, $SiR_3 = Si(S\text{-}2\text{-}Naph)_3$
5, $SiR_3 = Si[S(CH_2)_3S]Ph$
6, $SiR_3 = Si(SCy)_2Cl$
7, $SiR_3 = Si(SMes)_2Cl$

Our synthetic route to cationic silylene complexes employs labile triflato(silyl) derivatives of the type $Cp^*(Me_3P)_2RuSiR_2OTf$ ($OTf = OSO_2CF_3$), which are converted to the silylene complexes via exchange of triflate for a less-coordinating anion. These triflate derivatives are generally obtained by the abstraction of a group bound to silicon with trimethylsilyl triflate, as illustrated by the synthesis of **8** (eq 2). Complex **8** is similar to the previously reported ruthenium complexes $Cp^*(Me_3P)_2RuSiR_2OTf$ (**9**, R = Cl; **10**, R = S-*p*-Tol; **11**, R = Me; **12**, R = Ph),[20b,c] which possess covalently bound triflate groups as determined by X-ray crystallography and infrared spectroscopy[29] ($\nu(SO_3)$ vibrational modes corresponding to covalently bound triflates were observed at ca. 1360 cm^{-1}). These triflates are chemically labile and can be displaced by a donor such as acetonitrile to give base-stabilized silylene complexes of the type $[Cp^*(Me_3P)_2RuSiR_2(NCMe)][OTf]$.[20b,c] In acetonitrile, triflate is displaced from **8** to produce $[Cp^*(Me_3P)_2RuSi(SEt)_2(NCMe)][OTf]$, as indicated by an $\nu(SO_3)$ infrared band for ionic triflate (1268 cm^{-1}).[29]

$$\underset{\mathbf{3}}{Cp^*(Me_3P)_2RuSi(SEt)_3} \xrightarrow[-Me_3SiSEt]{Me_3SiOTf} \underset{\mathbf{8}}{Cp^*(Me_3P)_2RuSi(SEt)_2OTf} \rightleftarrows [Cp^*(Me_3P)_2RuSi(SEt)_2][OTf] \qquad (2)$$

The triflate complex **8** appears to be in equilibrium with the cationic silylene complex $[Cp^*(Me_3P)_2Ru{=}Si(SEt)_2][OTf]$, as evidenced by NMR spectroscopy. In dichloromethane-d_2 the inequivalent methylene protons of the SEt groups exchange rapidly, appearing as a single ^1H NMR resonance (q, δ 2.88) down to −70 °C. However in the less polar solvent toluene-d_8, the process that exchanges these protons is slowed considerably, resulting in an observed coalescence temperature of 21 °C ($\Delta G^\ddagger = 14.9 \pm 0.3$ kcal mol^{-1}). These results are most consistent with an exchange mechanism involving dissociation of triflate anion to form the silylene complex, followed by return of the triflate anion to the opposite face of the silylene ligand (possibly assisted by rapid rotation about the Ru−Si bond). A similar exchange process has been observed for $Cp(NO)(Ph_3P)ReGePh_2OTf$.[30]

Attempts to convert the tri(amino)silyl complex **2** to the triflate $Cp^*(Me_3P)_2RuSi(NMe_2)_2OTf$ (**13**) were complicated by the competing reaction of **13** with Me_3SiOTf to produce $Cp^*(Me_3P)_2RuSi(NMe_2)(OTf)_2$ (**14**). A sample of pure **13** was obtained in 17% yield from the 1:1 reaction of **2** with Me_3SiOTf, and **14** was isolated with use of excess Me_3SiOTf reagent. For comparison, the triflate $Cp^*(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)_2OTf$ (**10**), which may be isolated cleanly from the reaction of $Cp^*(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)_3$ with Me_3SiOTf, is also readily converted to the bis(triflate) $Cp^*(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)(OTf)_2$ (**15**).[20c] The latter complex has proven to be a valuable precursor to complexes possessing the Si(S-*p*-Tol) "silylyne" fragment[22b,31] and may also be used to prepare silyl complexes with chelating dithiolate groups, as shown in eq 3. Unfortunately, attempts to convert complexes **16** and **17** to triflato(silyl) complexes via reactions with trimethylsilyl triflate or triflic acid met with limited success. Although the expected triflates were obtained, they were contaminated by 10−20% of decomposition products, and attempts at further purification resulted in the accumulation of more impurities (presumably decomposition products).



(3)

Reaction of Me_3SiOTf with **7** produced two different complexes resulting from competitive abstraction of both chloride and thiolate (eq 4). In dichloromethane-d_2, **18** and **19** were observed to form in a 2:1 ratio (by ^1H and ^{31}P NMR spectroscopy). When carried out on a pre-

$$\underset{\mathbf{7}}{Cp^*(Me_3P)_2RuSi(SMes)_2Cl} \xrightarrow[-Me_3SiCl,\ -Me_3SiSMes]{+Me_3SiOTf} \underset{\mathbf{18}}{2/3\ Cp^*(Me_3P)_2RuSi(SMes)_2OTf} + \underset{\mathbf{19}}{1/3\ Cp^*(Me_3P)_2RuSi(SMes)(Cl)OTf} \qquad (4)$$

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[27] Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.

[28] (a) Tilley, T. D.; Togni, A.; Paciello, R. A.; Bercaw, J. E.; Grubbs, R. H. Unpublished results. (b) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379. (c) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J.; Mauermann; H.; Krüger, C. *Chem. Ber.* **1988**, *121*, 1719.

[29] Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

[30] Lee, K. E.; Gladysz, J. A. *Polyhedron* **1988**, *7*, 2209.

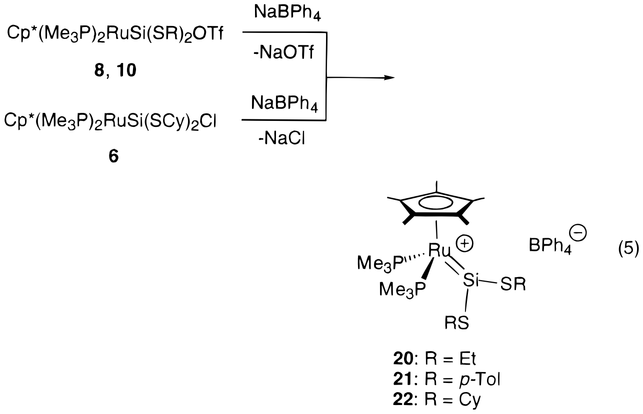
[31] Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518.

Table 1. ^{29}Si NMR Shift Data for Silylene Complexes

complex	^{29}Si NMR shift (ppm)
$[Cp^*(Me_3P)_2RuSi(SEt)_2][BPh_4]$ (**20**)	264.4 br
$[Cp^*(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)_2][BPh_4]$ (**21**)	259.4 (t, $^2J_{SiP} = 34$ Hz)
$[Cp^*(Me_3P)_2RuSi(SCy)_2][BPh_4]$ (**22**)	268.67 (t, $^2J_{SiP} = 35$ Hz)
$[Cp^*(Me_3P)_2RuSi(S\text{-}2\text{-}Naph)_2][B(C_6F_6)_3(S\text{-}2\text{-}Naph)]$ (**23**)	260.51 (t, $^2J_{SiP} = 33$ Hz)
$[Cp^*(Me_3P)_2RuSiMe_2][B(C_6F_5)_4]$ (**24**)	311.41 br
$[Cp^*(Me_3P)_2RuSiPh_2][B(C_6F_5)_4]$ (**25**)	299 (t, $^2J_{SiP} = 32$ Hz)

parative scale, only **19** was isolated, in 49% yield. The inequivalent phosphorus atoms in **19** are observed in benzene-d_6 as doublets in the ^{31}P NMR spectrum, at 0.52 and 2.06 ppm ($J_{PP} = 39$ Hz); however when the same spectrum was taken in dichloromethane-d_2, one broad peak was observed at 2.03 ppm. This phosphorus-exchange process is probably due to the rapid and reversible dissociation of triflate in dichloromethane-d_2, as observed for $Cp^*(Me_3P)_2RuSi(SEt)_2OTf$ (**8**).

Synthesis and Characterization of Thiolate-Substituted Silylene Complexes. The ruthenium silyls described in the previous section were examined as precursors to cationic silylene complexes. The synthetic strategy involved anion exchange, with introduction of a less-coordinating anion. As shown in eq 5, the triflate derivatives **8** and **10** react with $NaBPh_4$ in dichloromethane to produce the heteroatom-stabilized silylene complexes $[Cp^*(Me_3P)_2RuSi(SR)_2][BPh_4]$ (**20**, R = SEt; **21**, R = S-*p*-Tol), which were isolated as yellow, crystalline solids. Somewhat surprisingly, the chloride group of **6** also participates in a salt-elimination reaction with $NaBPh_4$, to give **22**.

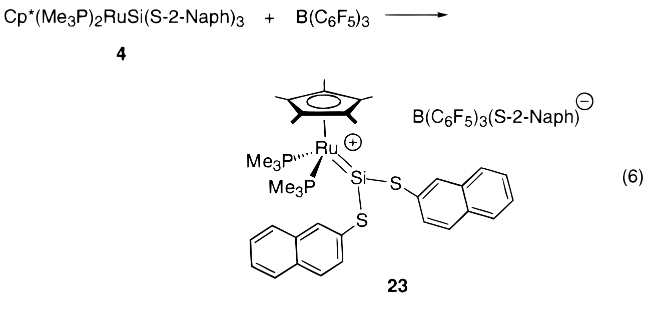


Elemental analyses showed that these materials do not contain solvent which could be coordinated to the silylene silicon atom. Compounds **20**−**22** exhibit ^{29}Si NMR resonances characteristic of silylene complexes, falling in the 250−270 ppm range (Table 1), significantly downfield of the resonances for ruthenium silyl complexes (−1 to 112 ppm).[1a,b,20b] This is to be expected on the basis of ^{29}Si correlations to ^{13}C NMR spectroscopy[32] since the ^{13}C shifts in terminal carbene complexes are generally in the range 240−370 ppm. For example, the ^{13}C NMR shift for the carbene carbon in $[Cp(CO)_2Ru{=}C(SMe)_2][PF_6]$ is 285.3 ppm.[33] At 23 °C, compound **21** exhibits a broad ^{29}Si NMR resonance at 250.6 ppm, which sharpens to a well-defined triplet at −80 °C (δ 259.4, $J_{SiP} = 34$ Hz). For **22**, a broad peak at δ 264.4 was observed at −60 °C. The J_{SiP} coupling constants for these silylene complexes are similar to those observed for the precursor silyl complexes, but this is perhaps not surprising given the insensitivity of J_{CP} coupling constants for related alkyl and cationic carbene complexes to changes in hybridization at carbon.[34]

Since bridging silylene complexes are also known to exhibit downfield ^{29}Si NMR shifts,[1a,b] it was important to establish the degrees of association for **20** and **21**. The fact that the silicon atoms in these complexes are coupled to only two phosphorus nuclei rules out alternative structures with bridging silylene ligands. In addition, a molecular weight determination for **21** (isopiestic method, dichloromethane) gave a value of 990 g mol^{-1}, which is consistent with a tight ion pair in solution (calcd: 982). The ionic nature of **20** and **21** is also supported by solution conductivity measurements (see Experimental Section).

Numerous attempts to grow X-ray quality crystals of **20**−**22** were unsuccessful. We therefore examined use of anions other than BPh_4^- as counteranions for the cationic silylene complexes. A suitable anion must be noncoordinating and inert toward the reactive, electrophilic silylene center.[35] Some of the salts that produced reasonably stable silylene complexes (from **10**, as determined by ^{1}H and ^{31}P NMR spectra) were $NaB(p\text{-}Tol)_4$, $NaB(3,5\text{-}Me_2C_6H_3)_4$, $LiB(C_6F_5)_4$, $NaC_2B_9H_{12}$, and $NaCo(C_2B_9H_{12})_2$. Unfortunately, these variations of the anion did not produce X-ray quality crystals. Anions that produced mainly decomposition products included PF_6^-, ClO_4^-, $Ph_3BNCBPh_3^-$, and $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$.

A related synthetic approach involves use of a strong Lewis acid to abstract a group bound to silicon in a metal silyl complex. The feasibility of this method was demonstrated by the reaction in eq 6, which gives the new silylene complex **23**. The ^{29}Si NMR chemical shift for **23** (260.5 ppm, t, $J_{SiP} = 33$ Hz; dichloromethane-d_2 solution) is characteristic for a silylene complex. This



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(32) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(33) Matachek, J. R.; Angelici, R. J. *Inorg. Chem.* **1986**, *25*, 2877.

(34) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (c) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (d) Kiel, W. A.; Buhro, W. E.; Gladysz, J. A. *Organometallics* **1984**, *3*, 879. (e) Bly, R. S.; Wu, R.; Bly, R. K. *Organometallics* **1990**, *9*, 936.

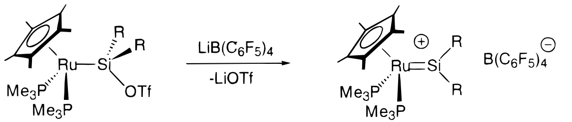
(35) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

reaction seems to be reversible, since only the starting silyl complex **4** was isolated upon attempted crystallization of **23** from dichloromethane/di(*n*-butyl) ether. In a similar manner, Ph_3CBPh_4[36] reacts with Cp*$(Me_3P)_2RuSi(S\text{-}p\text{-}Tol)_3$ in dichloromethane-d_2 to give the silylene complex **21** and $Ph_3C(S\text{-}p\text{-}Tol)$ (by ^1H, ^{31}P, and ^{29}Si NMR spectroscopy). Attempts to form silylene complexes via abstraction of chloride from Cp*$(Me_3P)_2$-$RuSi(SCy)_2Cl$ (**6**) with the Lewis acids YCp_3, $AlCl_3$, and $ZnCl_2$ were not successful. In addition, the reaction of **6** with $SbCl_5$ in dichloromethane-d_2 slowly produced **1** through a series of chlorination reactions.

Attempts were made to prepare silylene complexes via reactions of $NaBPh_4$ with the triflate complexes **9**, **11**, **12**, **13**, **15**, and **19**. These reactions did not produce isolable silylene complexes and typically resulted in production of multiple products (by ^1H and ^{31}P NMR spectroscopy; dichloromethane-d_2) over an 8−30 h period.

Synthesis and Characterization of Non-Heteroatom-Stabilized Silylene Complexes. The base-free silylene complexes described above feature π-donation from sulfur, which is expected to significantly stabilize the electron-deficient silicon center.[22c] Initial attempts to obtain silylene complexes without heteroatom substituents involved reactions of Cp*$(Me_3P)_2RuSiR_2OTf$ (**11**, R = Me; **12**, R = Ph) with $NaBPh_4$ in dichloromethane. These reactions produced complex mixtures, presumably resulting from decompositions of the initially generated silylene complexes. Reasoning that these decompositions might result from reactions between the silylene silicon center and the BPh_4^- anion, we employed the more chemically inert anion $B(C_6F_5)_4^-$, which is available as a dichloromethane-soluble lithium salt.

The reagent $LiB(C_6F_5)_4{\cdot}OEt_2$[37] reacts rapidly with **11** and **12** in dichloromethane-d_2 at −30 °C to quantitatively form the silylene complexes [Cp*$(Me_3P)_2$-$Ru{=}SiMe_2$][$B(C_6F_5)_4$] (**24**) and [Cp*$(Me_3P)_2Ru{=}SiPh_2$]-[$B(C_6F_5)_4$] (**25**), respectively (eq 7; by NMR spectroscopy).



(7)

24, R = Me
25, R = Ph

The formations of **24** and **25** are signaled by characteristic downfield ^{29}Si NMR shifts, at δ 299 (t, J_{SiP} = 32 Hz) and 311 (br), respectively. These silylene complexes are unstable at room temperature in dichloromethane and decompose with half-lives of 7 and 3 h, respectively. Upon cooling a concentrated dichloromethane solution of **25** to −78 °C, orange-red crystals formed which desolvated upon isolation to the formula [Cp*$(Me_3P)_2$-$Ru{=}SiPh_2$][$B(C_6F_5)_4$]$\cdot 0.1CH_2Cl_2$ (by combustion analysis). As expected, both **24** and **25** react with acetonitrile to give the previously characterized adducts [Cp*-$(Me_3P)_2RuSiR_2(NCMe)]^+$ (R = Me,[20c] Ph[20a,b]) (which display ^{29}Si NMR shifts of δ 110 and 96, respectively).

X-ray quality crystals of **24** were eventually obtained by addition of a $^nBu_2O$ solution of $LiB(C_6F_5)_4{\cdot}OEt_2$ to a 1,2-dichlorobenzene solution of **11** at 23 °C, followed by slow addition of $^nBu_2O$ (over ca. 5 min) until crystals began to form. Further crystallization at room temperature occurred over ca. 0.5 h to afford **24** in 38% yield. The molecular structure of the cation in **24** (Figure 1) consists of a dimethylsilylene ligand that is planar at silicon (summation of bond angles = 359(1)°) and coordinated to a Cp*$(Me_3P)_2Ru^+$ fragment. The Ru−Si distance of 2.238(2) Å is the shortest yet reported and slightly shorter than the Ru−Si bond lengths in Cp*-$(Me_3P)_2RuSi[S(p\text{-}Tol)]Os(CO)_4$, 2.286(2) Å,[22b] and Cp*-$(Me_3P)_2RuSi[S(p\text{-}Tol)](phen)^{2+}$, 2.269(5) Å.[31] The Cp*-(centroid)−Ru−Si−Me dihedral angle is 34°. This angle deviates from what might be expected on the basis of efficient π-overlap involving the frontier orbitals of a CpL_2M^+ fragment,[22d,38] which is expected to result in a dihedral angle of 0°.[39]

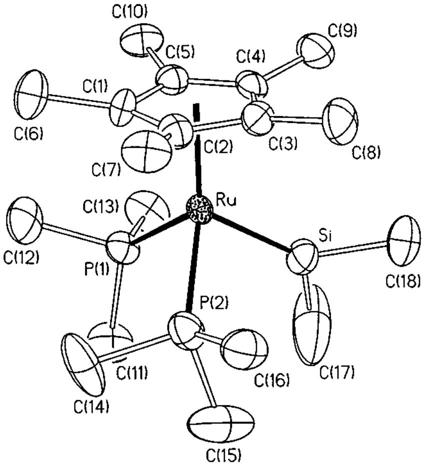


Figure 1. ORTEP view of the cation in [Cp*$(Me_3P)_2Ru{=}SiMe_2$][$B(C_6F_5)_4$] (**24**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 24

(a) Bond Distances			
Ru−P(1)	2.290(3)	Ru−C(1)	2.277(10)
Ru−P(2)	2.293(3)	Ru−C(2)	2.288(10)
Ru−Si	2.238(3)	Ru−C(3)	2.263(10)
Si−C(17)	1.721(16)	Ru−C(4)	2.271(10)
Si−C(18)	1.826(12)	Ru−C(5)	2.275(10)
(b) Bond Angles			
P(1)−Ru−P(2)	93.0(1)	C(17)−Si−C(18)	99.7(8)
P(1)−Ru−Si	92.8(1)	Ru−Si−C(17)	133.5(7)
P(2)−Ru−Si	89.1(1)	Ru−Si−C(18)	125.5(5)
Si−Ru−C(1)	154.3(3)	Si−Ru−C(2)	135.5(3)
Si−Ru−C(3)	101.3(3)	Si−Ru−C(4)	93.6(3)
Si−Ru−C(5)	119.4(3)	P(1)−Ru−C(1)	98.9(2)

Thermal Decompositions of Silylene Complexes. Thiolate-substituted silylene complexes of the type [Cp*-$(Me_3P)_2Ru{=}Si(SR)_2$][BPh_4] thermally decompose via phenyl transfer from the BPh_4 anion. For example, when [Cp*$(Me_3P)_2Ru{=}Si[S(p\text{-}Tol)]_2$][$BPh_4$] (**21**) is heated to 120 °C in a *o*-dichlorobenzene solution, complete conversion to Cp*$(Me_3P)_2RuSi[S(p\text{-}Tol)]_2Ph$ (**26**) within 10 min is observed (by ^{31}P NMR spectroscopy). Compound **26** was identified by comparison of ^1H and ^{31}P NMR spectra with those for an authentic sample.

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[36] Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13.

[37] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

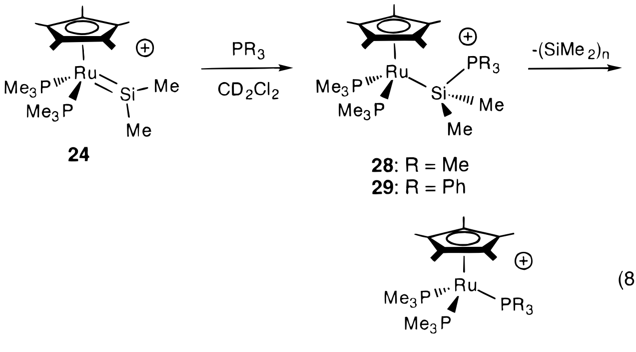
[38] Albright, T. A.; Burdett, J. K.; Whangbo, M.-W. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York: 1985.

[39] Recent calculations at the RHF level of theory indicate that this twist of 34° is electronically preferred: Arnold, F. P. Unpublished results.

Similarly, attempts to generate $[Cp^*(Me_3P)_2Ru{=}SiMe_2][BPh_4]$ are complicated by the low solubility for the $NaBPh_4$ reagent, which results in a slow reaction with $Cp^*(Me_3P)_2RuSiMe_2OTf$ in dichloromethane-d_2 to produce thermally unstable $[Cp^*(Me_3P)_2Ru{=}SiMe_2][BPh_4]$ (over 3 days, as monitored by ^{31}P NMR spectroscopy). The latter silylene complex decomposes to $Cp^*(Me_3P)_2RuSiMe_2Ph$ (**27**) (75−95%) as it is produced.

Reactions of Silylene Complexes with Lewis Bases. We have previously reported the interactions of silylene complexes with nitrogen-based donors such as acetonitrile and 4-(dimethylamino)pyridine (DMAP).[20] Generally, it is found that adducts of the type $[Cp^*(Me_3P)_2RuSiX_2(base)]^+$ form readily, and the stability of these adducts appears to correlate with the strength of the donor−acceptor interaction.[20c] Thus, the DMAP adduct $[Cp^*(Me_3P)_2RuSiMe_2(DMAP)][BPh_4]$ is exceptionally stable.[20c] Such adducts tend to thermally decompose via elimination of the silylene group, with formation of a $[Cp^*(Me_3P)_2Ru(base)]^+$ cation. It remains unclear whether these decompositions proceed via dissociation of silylene from the base-free complex (which is in equilibrium with the adduct) or via dissociation of the silylene adduct $:SiX_2(base)$.[20c]

Compound **24** reacts quantitatively with 1 equiv of PMe_3 or PPh_3 in dichloromethane-d_2 to form the base-stabilized silylene complexes $[Cp^*(Me_3P)_2RuSiMe_2(PR_3)][B(C_6F_5)_4]$ (**28**, R = Me; **29**, R = Ph), identified by ^1H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of both complexes contain two inequivalent phosphorus resonances in a 2:1 ratio, and the SiMe resonance for each is split into a doublet with $^3J_{PH} = 4.5$ Hz. Unfortunately, the thermal instability of **28** and **29** prevented their isolation and full characterization. In dichloromethane solution, **28** decomposes ($t_{1/2} \approx 5$ h at 0 °C) to $[Cp^*(Me_3P)_3Ru][B(C_6F_5)_4]$ (**30**, confirmed by independent synthesis of $[Cp^*(Me_3P)_3Ru][OTf]$) as the only phosphorus-containing product. In addition, **29** cleanly decomposes ($t_{1/2} \approx 5$ h at 0 °C) to $[Cp^*(Me_3P)_2RuPPh_3][B(C_6F_5)_4]$ (**31**, by ^1H and ^{31}P NMR spectroscopy). Presumably, both **28** and **29** decompose via extrusion and rapid oligomerization of the silylene fragment (eq 8). Consistent with this is the appearance in the ^1H NMR spectra of several resonances in the region of δ 0.0−0.2. However, when **28** decomposed in the presence of the known silylene trapping agents $HSiEt_3$ and $HSi(SiMe_3)_3$,[2e] the respective insertion products $HSiMe_2SiEt_3$ and $HSiMe_2Si(SiMe_3)_3$ were not observed by ^1H NMR spectroscopy nor GC/MS.



24

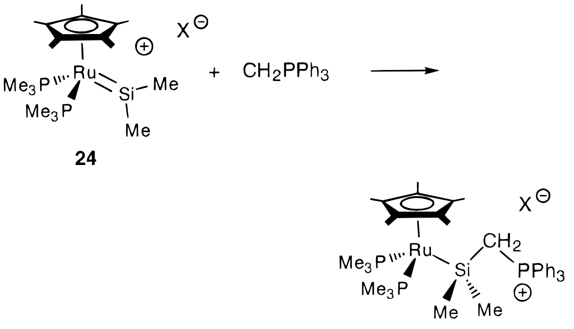
28: R = Me
29: R = Ph

(8)

30: R = Me
31: R = Ph

There is a marked difference in stability between the nitrogen-donor-stabilized compounds reported previously and the phosphine adducts described here. For example, the stabilized silylene complex $[Cp^*(Me_3P)_2RuSiMe_2(NCMe)][BPh_4]$ has a half-life of about 17 days in dichloromethane, and $[Cp^*(Me_3P)_2RuSiMe_2(DMAP)][BPh_4]$ is similarly stable (3% decomposition after 1 day in dichloromethane-d_2).[20c] Although the reasons for this difference in stability are not yet fully understood, it appears that the strength of the donor−acceptor interaction plays an important role.

The ylide CH_2PPh_3 reacts rapidly with **24** to form a single product (**32a**), isolated as yellow crystals in 80% yield (eq 9). Likewise, the complex $Cp^*(Me_3P)_2RuSiMe_2OTf$ reacts with CH_2PPh_3 to form the analogous triflate salt **32b**. Compounds **32a** and **32b** display remarkable stabilities, exhibiting no decomposition after 1 week in dichloromethane-d_2 at room temperature (by ^1H and ^{31}P NMR spectroscopy). Heating a toluene solution of **32a** for 1 day at 100 °C, however, resulted in decomposition to many products. The ^1H NMR spectra reveal equivalent SiMe groups, and the ^{31}P NMR spectra display a single resonance for the PMe_3 ligands, indicating the presence of a molecular plane of symmetry. The connectivity depicted in eq 9 was confirmed by a single-crystal X-ray diffraction study of **32b** (vide infra). The ^{29}Si spectrum contains a triplet of doublets ($^2J_{SiP} = 32$ and 15 Hz for the triplet and doublet, respectively) centered at 35.24 ppm, a shift of 276.17 ppm upfield from the resonance of **24**. Such an upfield chemical shift indicates little, if any, silylene character in the bonding of **32b** and is more characteristic for a saturated Ru(II) silyl complex.



24

(9)

32a: $X^- = B(C_6F_5)_4^-$
32b: $X^- = OTf^-$

The molecular structure of the cation in **32b** is shown in Figure 2. Ruthenium adopts a three-legged piano stool geometry, with the phosphine and silyl groups approximately evenly distributed about the metal. The Ru−Si bond length of 2.381(2) Å is slightly longer than the analogous separation in the base-stabilized silylene complex $[Cp^*(Me_3P)_2RuSiPh_2(NCMe)][BPh_4]$ (2.328(2) Å)[20a,b] and is comparable to the corresponding distance in $Cp^*(Me_3P)_2RuSiPh_2H$ (2.387(5) Å).[20b] The silicon atom is in a pseudo-tetrahedral environment, with distances of 1.920(9) and 1.899(9) Å to the two methyl carbon atoms and a somewhat longer distance of 1.976(7) Å to the ylide carbon atom. The C(19)−P(3) distance of 1.779(6) Å is considerably longer than the 1.692(3) Å C=P distance in free CH_2PPh_3,[40] indicating significant loss of double-bond character in the ylide upon coordi-

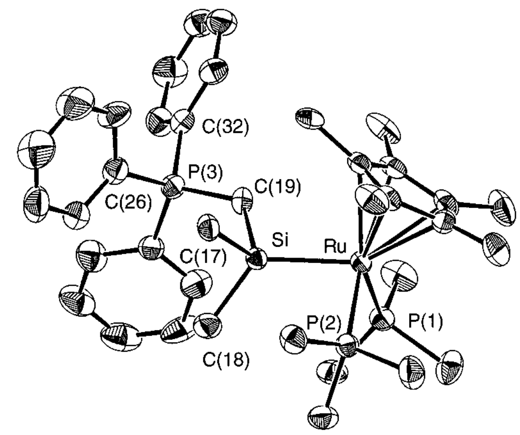


Figure 2. ORTEP view of the cation in [Cp*(Me$_3$P)$_2$RuSiMe$_2$(CH$_2$PPh$_3$)]OTf (**32b**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for 32b·CH$_2$Cl$_2$

(a) Bond Distances			
Ru−P(1)	2.261(2)	Si−C(19)	1.976(7)
Ru−P(2)	2.273(2)	P(3)−C(19)	1.779(6)
Ru−Si	2.381(2)	P(3)−C(20)	1.796(8)
Si−C(17)	1.920(9)	P(3)−C(26)	1.805(8)
Si−C(18)	1.899(9)	P(3)−C(32)	1.811(7)
(b) Bond Angles			
P(1)−Ru−P(2)	92.71(8)	C(18)−Si−C(19)	103.4(4)
P(1)−Ru−Si	94.83(8)	C(19)−P(3)−C(20)	111.9(4)
P(2)−Ru−Si	89.51(6)	C(19)−P(3)−C(26)	110.0(4)
Ru−Si−C(17)	116.1(3)	C(19)−P(3)−C(32)	108.4(3)
Ru−Si−C(18)	125.7(3)	C(20)−P(3)−C(26)	110.9(4)
Ru−Si−C(19)	108.1(2)	C(20)−P(3)−C(32)	106.1(4)
C(17)−Si−C(18)	97.7(4)	C(26)−P(3)−C(32)	109.4(4)
C(17)−Si−C(19)	103.3(4)	P(3)−C(19)−Si	126.8(3)

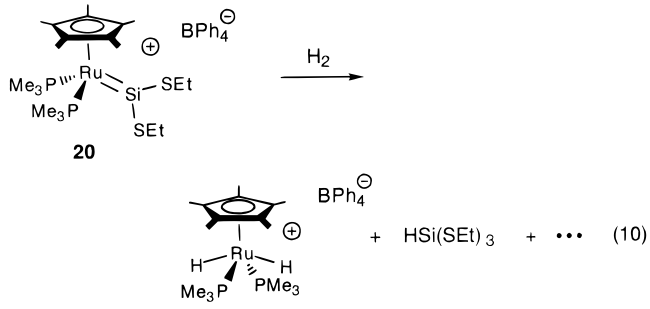
nation to silicon. The adducts **32a** and **32b** are therefore best viewed as ruthenium silyl complexes of the type Cp*(Me$_3$P)$_2$RuSiR$_2$R′, with the positive charge localized on the phosphonium phosphorus atom.

Reactions of Silylene Complexes with Hydrogen and Hydrosilanes. Many of the hypothetical catalytic cycles that have been proposed in the context of intermediate silylene complexes involve hydrogen and/or hydrosilanes as reagents or products.[1] It is therefore of interest to characterize the reactivity of isolated silylene complexes toward these small molecules. Note that we have previously shown that silylene complexes of the type [Cp*(Me$_3$P)$_2$Ru=SiX$_2$]$^+$ exhibit low reactivities toward nonpolar unsaturated substrates, probably due to the coordinatively saturated nature of the ruthenium center.[24a]

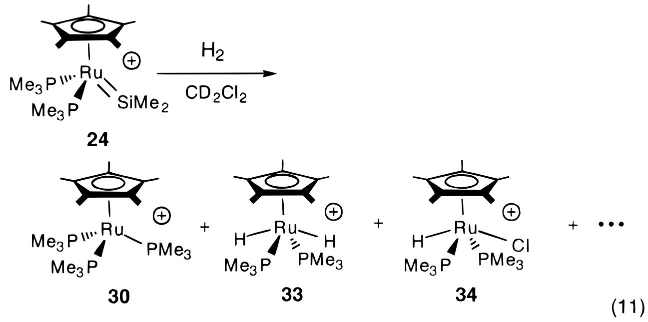
The reaction of [Cp*(Me$_3$P)$_2$RuSi(SEt)$_2$]BPh$_4$ (**20**) with H$_2$ (1 atm) in dichloromethane-d_2 resulted in slow conversion to a ruthenium hydride complex **33** (δ_{RuH} = −10.04; 35% conversion after 9 h) and the silane HSi(SEt)$_3$ (by NMR spectroscopy and GC/MS). A preparative scale reaction (50 psi H$_2$) generated isolable quantities of **33**, which was characterized as the hydride complex shown in eq 10. The latter compound exhibits a triplet in the ^{31}P NMR spectrum ($^2J_{PH}$ = 33 Hz) due to coupling to equivalent hydride ligands, after selective decoupling of the methyl protons. The HSi(SEt)$_3$ may result from redistribution of the kinetic product H$_2$Si(SEt)$_2$, as was observed in attempts to prepare this silane independently from H$_2$SiCl$_2$, HSEt and NEt$_3$, which resulted in the isolation of HSi(SEt)$_3$.[41] This type of redistribution reaction of thiosilanes has also been observed for the silane Cl$_2$Si(SMes)$_2$.[5e]

Table 4. Summary of Crystallographic Data for 24 and 32b·CH$_2$Cl$_2$

	24	**32b**·CH$_2$Cl$_2$
formula	C$_{42}$H$_{39}$BF$_{20}$P$_2$RuSi	C$_{39}$H$_{58}$Cl$_2$F$_3$P$_3$RuSSi
fw	1125.6	956.93
cryst color, habit	yellow block	yellow trapezoidal
cryst size, mm	0.30 × 0.34 × 0.34	0.15 × 0.20 × 0.30
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
a, Å	13.577(2)	10.1344(3)
b, Å	22.314(4)	14.7333(4)
c, Å	15.423(3)	15.1684(5)
β, deg	94.44(2)	95.183(1)
V, Å^3	4658.4(15)	2255.6(1)
Z	4	2
D(calc), g cm^{-3}	1.605	1.409
μ (Mo Kα), cm^{-1}	5.42	8.06
F(000)	2256	908.00
temp, K	240	157
2θ_{max}, deg	50.0	46.5
total no. of data	8444	9339
no. of unique obsd data	4112	3557
no. of variables	604	477
R(int)	0.0265	0.032
goodness of fit indicator	1.31	2.75
$R(F)$, %	5.78	4.1
$R(wF)$, %	7.46	5.0
max./min. residual density, e Å^{-3}	0.80/−0.52	0.93/−1.01



Reaction of **24** with H$_2$ (1 atm) at −78 °C in dichloromethane-d_2 led to a mixture of products that included **30**, **33**, and **34** (eq 11).[24a] The ^{1}H NMR spectra of the reaction mixture showed that the SiMe resonances for **24** diminished over the course of 4 days and were replaced by various peaks in the δ 0.0−0.2 region, presumably representing species derived from the displaced silylene fragment. Although the hydride ligands



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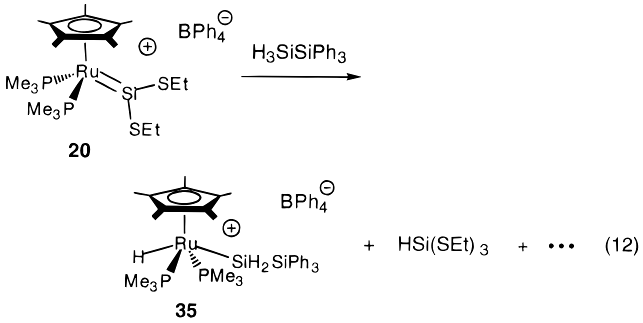
(40) Schmidbaur, H.; Jeong, J.; Schier, A.; Graf, W.; Wilkinson, D. L.; Müller, G.; Krüger, C. *New J. Chem.* **1989**, *13*, 341.

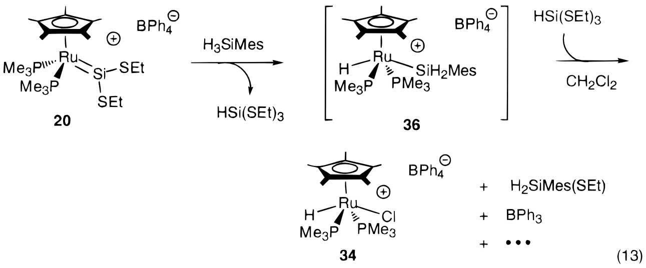
(41) Grumbine, S. K., Ph.D. Thesis, UC San Diego, 1993.

of **33** and **34** are most likely derived from H_2, no formation of H_2SiMe_2 was detected (by ^1H NMR spectroscopy and GC/MS).

The reaction of **20** with $H_3SiSiPh_3$ in dichloromethane-d_2 proceeded slowly (75% conversion after 3 days) to one ruthenium product and two main Si−H products, one of which is $HSi(SEt)_3$. In a scaled-up version of this reaction, the new product [Cp*(Me$_3$P)$_2$Ru(H)(SiH$_2$SiPh$_3$)][BPh$_4$] (**35**) was crystallized from the reaction mixture in 24% yield (eq 12). The Si−H ^1H NMR resonance for this compound appeared as a virtual triplet at δ 3.81, and the hydride ligand appeared as a triplet at δ −10.10 (J_{PH} = 9 Hz). The volatile products from the reaction mixture were found to contain mainly $HSi(SEt)_3$ (by ^1H NMR and mass spectrometry). Thus, it appears that this reaction is also complicated by a redistribution at silicon.



The reaction of **20** with H_3SiMes proceeds very slowly (70% conversion after 7 h in dichloromethane-d_2) to a mixture of products (eq 13). The hydride **34** and BPh_3 were isolated from the reaction mixture in 34% and 24% yields, respectively. In addition, the major silane product was identified as $H_2SiMes(SEt)$, by comparison of its ^1H, ^{13}C, ^{29}Si NMR and mass spectra to those for an independently prepared sample. Monitoring the reaction by ^1H NMR spectroscopy provided evidence for an intermediate in this transformation, characterized by triplet resonances assigned to RuSiH (δ 4.69, $^3J_{PH}$ = 8 Hz) and RuH (δ −11.23, $^2J_{PH}$ = 9 Hz) groups. After speculating that this intermediate might be analogous to **35**, we generated [Cp*(Me$_3$P)$_2$Ru(H)(SiH$_2$Mes)][BPh$_4$] (**36**) independently via reaction of [Cp*(Me$_3$P)$_2$Ru(NCMe)][BPh$_4$] with 1 equiv of H_3SiMes in dichloromethane-d_2. Compound **36**, which exists in a 1:12 equilibrium with [Cp*(Me$_3$P)$_2$Ru(NCMe)][BPh$_4$], was identified as the intermediate indicated in eq 13. To the solution containing **36** was added $HSi(SEt)_3$, and after 6 days the main SiH-containing product was $H_2SiMes(SEt)$ (90% by ^1H and ^{29}Si NMR spectroscopy). It therefore seems that reactions of **20** with $H_3SiSiPh_3$ and H_3SiMes proceed via similar pathways that initially produce $HSi(SEt)_3$ and a silyl hydride complex of the type [Cp*(Me$_3$P)$_2$Ru(H)(SiH$_2$R)]$^+$. When R = Mes, these products react further to produce $H_2SiMes(SEt)$, by an unknown mechanism.



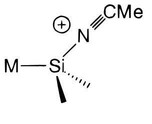
As with the reaction of **24** with H_2, reactions of **24** with H_2SiPh_2, $HSiEt_3$, and $HSi(SiMe)_3$ in dichloromethane-d_2 at 0 °C gave a complex mixture of products consisting primarily of **30**, **33**, and **34** (by ^1H and ^{31}P NMR spectroscopy). The chloride ligand of **34** is presumed to originate from the solvent, and no redistribution or Si−Si bond formation was observed.

Concluding Remarks

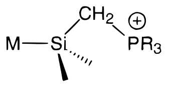
In this paper we have described a synthetic route to ruthenium silylene complexes of the type [Cp*(Me$_3$P)$_2$Ru=SiX$_2$]$^+$. This method works well in selected cases, where X = thiolate, Me, or Ph, but so far has not proven successful with a number of other substituents at silicon. The key precursor compounds in this approach are triflato(silyl) derivatives of the type Cp*(Me$_3$P)$_2$RuSiX$_2$OTf, which possess labile triflate groups. In solution, the triflate may be exchanged for less coordinating anions that result in stabilization of the three-coordinate silicon compounds. In one case, this exchange was successful with use of a starting silyl chloride derivative (**6**), presumably because a relatively stable silylene complex, [Cp*(Me$_3$P)$_2$RuSi(SCy)$_2$][BPh$_4$] (**22**), is formed. Note that the BPh_4^- anion is compatible with thiolate-substituted silylene complexes, but isolation of the less stable dimethyl- and diphenylsilylene complexes (**24** and **25**) requires use of the more inert anion $B(C_6F_5)_4^-$. The silylene complexes reported here are characterized by highly downfield-shifted ^{29}Si NMR resonances in the region δ 250−310. These shift values are consistent with others that have been characterized for silylene complexes, including [*trans*-(Cy$_3$P)$_2$(H)PtSi(SEt)$_2$][BPh$_4$] (δ 308.65),[22c] [(^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$)(H)Pt=SiMes$_2$][BMe(C$_6$F$_5$)$_3$] (δ 338.5),[22e] (Cy$_3$P)$_2$Pt=SiMes$_2$ (δ 358),[22f] and (^{i}Pr$_3$P)$_2$Pt=SiMes$_2$ (δ 367).[22f] The complete characterization of **20**−**25** represents a significant advance in the development of transition metal−silylene chemistry. Now that stable examples with a number of substitution patterns are known, it is clear that such species are viable synthetic targets and reasonable chemical intermediates.

Many of the reactions observed for silylene complexes reflect the presence of a highly electrophilic silicon center. Thus, the silylene complexes reported here readily form adducts with a number of Lewis bases. It is interesting to compare the structural and spectroscopic properties for adducts of these types, which have often been described as having considerable silylene character, with authentic silylene complexes possessing sp^2 silicon. This comparison shows that the “donor-stabilized” silylene complexes possess structural and spectroscopic properties that are much more similar to metal silyl complexes and reflect the presence of sp^3 silicon. This is perhaps dramatically illustrated by formation of the ylide “adduct” **32**, which exhibits structural parameters and an ^{29}Si NMR shift that are highly consistent with a simple ruthenium silyl complex. Similar observations for other donor-stabilized silylene complexes[3,5,14−17,20] suggest that these compounds are also best represented by resonance structures reflecting tetrahedral silicon centers with four covalent bonds (e.g., structures **A**−**E**).

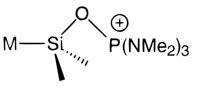
Finally, initial reactivity studies with the ruthenium silylene complexes reported here demonstrate that they are relatively unreactive toward nonpolar substrates such as hydrosilanes and hydrogen. This appears to reflect the coordinative saturation of the metal center, and in fact in other studies we have observed that the 16-electron silylene complex $(Cy_3P)_2Pt{=}SiMes_2$ reacts more readily with hydrogen.[22f]



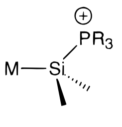
A



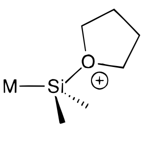
B



C



D



E

Experimental Section

General Procedures. Manipulations were performed under an inert atmosphere of nitrogen or argon. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Pascher Analytical Laboratories, Desert Analytics, and the UC Berkeley College of Chemistry Microanalytical Facility. All NMR spectra were recorded at room temperature unless otherwise indicated. ^{29}Si NMR spectra were obtained on a GE QE-300 or a Bruker AM 300 instrument at 59.6 MHz, using single-pulse techniques (typically with a 2−4 s delay time and ca. 10 000 transients) or DEPT. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained at 300, 75.5, and 121.5 MHz, respectively, unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer as Nujol mulls on CsI plates, unless otherwise indicated, and all absorptions are reported in cm^{-1}. Conductivity measurements were acquired with a YSI model 3S conductance meter. The compounds HSMes,[42] $LiB(C_6F_5)_4{\cdot}Et_2O$,[37] $B(C_6F_5)_3$,[43] $NaC_2B_9H_{12}$,[44] Ph_3CBPh_4,[36] $NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$,[45] $NaPh_3BNCBPh_3$,[46] and $NaCo(C_2B_9H_{12})_2$[47] were prepared by literature methods. The complex $[Cp^*(Me_3P)_2Ru(NCMe)][BPh_4]$ was prepared by the reaction of $Cp^*(Me_3P)_2RuCl$[27] with $AgBPh_4$ in acetonitrile.

$HSi(SEt)_3$. NEt_3 (32 mL, 240 mmol) was added to a 1 L flask containing diethyl ether (800 mL), $HSiCl_3$ (8.0 mL, 80 mmol), and HSEt (18 mL, 240 mmol). A large volume of white precipitate ($HNEt_3Cl$) formed, creating a viscous solution that was stirred for 10 h. The reaction was then filtered, and the solid was extracted with 200 mL of diethyl ether. The combined diethyl ether solutions were concentrated to an oil, and vacuum distillation (bp 110−113 °C/0.01 Torr) gave 10 g of the product (59%). GC/MS (EI) parent ion: calcd *m*/*e* 212; found *m*/*e* 212. ^{1}H NMR (benzene-d_6): δ 1.13 (t, $J = 8$ Hz, 9 H, SCH_2CH_3), 2.55 (q, $J = 8$ Hz, 6 H, SCH_2CH_3), 5.89 (s, 1 H, SiH). $^{13}C\{^{1}H\}$ NMR (benzene-d_6): δ 17.16 (SCH_2CH_3), 22.42 (SCH_2CH_3). $^{29}Si\{^{1}H\}$ NMR (benzene-d_6): δ 12.12 (s).

$HSi(S\text{-}2\text{-}Naph)_3$. The procedure for $HSi(SEt)_3$ was followed, using NEt_3 (12 mL, 90 mmol), diethyl ether (300 mL), $HSiCl_3$ (2.1 mL, 21 mmol), and HS(2-Naph) (10 g, 62 mmol). The silane was crystallized from diethyl ether at −35 °C. Yield: 0.92 g/9% (not optimized). MS (EI) parent ion: calcd *m*/*e* 506; found *m*/*e* 506. ^{1}H NMR (benzene-d_6): δ 6.20 (s, 1 H, SiH), 7.15 (m, 2 H, Naph), 7.29 (m, 2 H, Naph), 7.45 (m, 2 H, Naph), 7.85 (s, 1 H, Naph).

$HSi(SCy)_3/HSi(SCy)_2Cl$ Mixture (4:1). The procedure for $HSi(SEt)_3$ was followed, using NEt_3 (8.1 mL, 60 mmol), diethyl ether (800 mL), $HSiCl_3$ (2.3 mL, 23 mmol), and HSCy (5.4 mL, 44 mmol). The silane was isolated by filtration (from $HNEt_3Cl$) followed by vacuum distillation (bp 145−180 °C/0.1 Torr). Yield: 2.5 g. ^{1}H NMR (benzene-d_6): δ 0.9−1.3 (m, SCy, di and tri), 1.78 (m, SCy, di), 1.95 (m, SCy, tri), 2.98 (m, SCy, di), 3.16 (m, SCy, tri), 5.87 (s, SiH, di), 6.14 (s, SiH, tri).

$HSi(SMes)_3/HSi(SMes)_2Cl$ Mixture (4:1). The above procedure was employed, starting with 3.0 equiv of HSMes. The product mixture crystallized from diethyl ether as a mixture of $HSi(SMes)_3$ and $HSi(SMes)_2Cl$ (4:1 ratio). ^{1}H NMR (benzene-d_6) $HSi(SMes)_2Cl$: δ 1.98 (s, 6 H, $C_6Me_2H_2Me$), 2.36 (s, 12 H, $C_6Me_2H_2Me$), 5.73 (s, 1 H, SiH), 6.68 (s, 4 H, $C_6Me_2H_2Me$). $HSi(SMes)_3$: δ 2.00 (s, 9 H, $C_6Me_2H_2Me$), 2.32 (s, 18 H, $C_6Me_2H_2Me$), 5.27 (s, 1 H, SiH), 6.69 (s, 6 H, $C_6Me_2H_2Me$).

$H\overline{Si(SCH_2CH_2CH_2S})Ph$. The procedure for $HSi(SEt)_3$ was followed, using NEt_3 (7.3 mL, 55 mmol), diethyl ether (600 mL), $HSiCl_2Ph$ (4.0 mL, 14 mmol), and $HS(CH_2)_3SH$ (1.4 mL, 14 mmol). Evaporation of the diethyl ether solvent produced the product as a reasonably pure, viscous liquid. Yield: 55%. MS (EI) parent ion: calcd *m*/*e* 211; found *m*/*e* 211.

$Cp^*(Me_3P)_2RuSiCl_3$ (1). $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (1.5 g, 3.2 mmol), $HSiCl_3$ (0.33 mL, 3.4 mmol), PMe_3 (0.054 mL, 0.7 mmol), and toluene (40 mL) were added to a flask equipped with a Teflon valve. The flask was closed and heated to 130 °C for 12 h, which resulted in precipitation of the product. After removing the volatile materials in vacuo, the precipitate was washed with pentane (10 mL) and extracted with benzene (3 × 40 mL). After removing the benzene from the combined extracts, the remaining solid was extracted again with 3 × 15 mL of benzene. The combined extracts were evaporated to dryness to give a slightly yellow precipitate. Yield: 0.36 g, 22%. Anal. Calcd for $C_{16}H_{33}Cl_3P_2RuSi$: C, 36.8; H, 6.36. Found: C, 37.1; H, 6.38. ^{1}H NMR (benzene-d_6): δ 1.18 (vir t, 18 H, PMe_3), 1.58 (t, $J_{HP} = 1$ Hz, 15 H, C_5Me_5). $^{13}C\{^{1}H\}$ NMR (benzene-d_6): δ 11.44 (C_5Me_5), 22.90 (vir t, PMe_3), 95.25 (C_5Me_5). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): δ 3.33. $^{29}Si\{^{1}H\}$ NMR (benzene-d_6): δ 42.69 (t, $^{2}J_{SiP} = 38$ Hz). IR: 1300 w, 1271 m, 1065 w, 1023 m, 956 s, 939 s, 855 m, 715 s, 619 m, 486 vs, 433 vs.

$Cp^*(Me_3P)_2RuSi(NMe_2)_3$ (2). $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (0.28 g, 0.59 mmol) and $HSi(NMe_2)_3$ (0.29 mL, 1.5 mmol) were heated (90 °C) in a closed flask for 12 h with stirring. The resulting solid was exposed to vacuum to remove the volatile materials and then extracted into pentane (20 mL). After concentrating to 1 mL and cooling to −35 °C, light yellow crystals formed (0.21 g; 64%). When the reaction was carried out in toluene, the only product isolated was $Cp^*(Me_3P)_2Ru(m/p\text{-}Tol)$. Anal. Calcd for $C_{22}H_{51}P_2RuN_3Si$: C, 48.2; H, 9.37; N, 7.65. Found: C, 48.2; H, 9.29; N, 7.64. ^{1}H NMR (benzene-d_6): δ 1.22 (vir t, 18 H, PMe_3), 1.66 (t, $J_{HP} = 1$ Hz, 15 H, C_5Me_5), 2.74 (br s, 18 H, NMe_2). $^{13}C\{^{1}H\}$ NMR (benzene-d_6): δ 11.93 (C_5Me_5), 24.61 (vir t, PMe_3), 42.45 (NMe_2), 93.88 (C_5Me_5). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): δ 5.40. IR: 1292 m, 1224 s, 1210 s, 1180 s, 1135 w, 1060 m, 985 s, 964 s, 938 s, 847 m, 700 m, 667 m, 642 m, 620 m, 600 s, 584 s, 462 m.

$Cp^*(Me_3P)_2RuSi(SEt)_3$ (3). This compound was prepared by the procedure reported for $Cp^*(PMe_3)_2RuSi[S(p\text{-}Tol)]_3$.[20c] Yield: 74% of yellow crystals, mp 190−195 °C. Anal. Calcd for $C_{22}H_{48}P_2RuS_3Si$: C, 44.1; H, 8.00. Found: C, 44.1; H, 8.20. ^{1}H NMR (benzene-d_6): δ 1.37 (virtual t, 18 H, PMe_3), 1.41 (t, $J = 7$ Hz, 9 H, SCH_2CH_3), 1.80 (s, 15 H, C_5Me_5), 2.99 (q, $J = 7$ Hz, 6 H, SCH_2CH_3). ^{13}C NMR (dichloromethane-d_2): δ 12.23 (q, $J_{CH} = 127$ Hz, C_5Me_5), 18.28 (q, $J = 127$ Hz, SCH_2CH_3),

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(42) Szmuszkovicz, J. *Org. Prep. Proced.* **1969**, *1*, 43.

(43) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218.

(44) Plesek, J.; Hermanek, S.; Stibr, B. *Inorg. Synth.* **1983**, *22*, 231.

(45) Nishida, H.; Takada, N.; Yoshimur, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.

(46) Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *99*, 1406.

(47) Hawthorne, M. F.; Andrews, T. D.; Garrett, P. M.; Olsen, F. P.; Reintjes, M.; Tebbe, R. N.; Warren, L. F.; Wegner, P. A.; Young, D. C. *Inorg. Synth.* **1967**, *10*, 91.

23.81 (br q, $J = 127$ Hz, PMe_3), 26.21 (t, $J_{CH} = 135$ Hz, $S\mathit{C}H_2CH_3$), 94.74 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 3.04. ^{29}Si NMR (dichloromethane-d_2): δ 60.34 (t, $J_{SiP} = 34$ Hz). IR: 1292 m, 1276 m, 1250 m, 1063 w, 1022 w, 953 s, 938 s, 852 w, 708 m, 663 m.

$Cp^*(Me_3P)_2RuSi(S\text{-}2\text{-}Naph)_3$ (4). Toluene (20 mL) was added to $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (1.36 g, 2.86 mmol) and $HSi(S\text{-}2\text{-}Naph)_3$ (1.39 g, 2.86 mmol), and the resulting solution was stirred and heated (100 °C) in a closed flask for 5 h. After removing the volatile materials in vacuo, the solid was washed with diethyl ether (3 × 15 mL) and was then extracted into dichloromethane (3 × 30 mL). The combined extracts were reduced in volume and cooled to −35 °C to afford yellow crystals. A second crop was obtained by reducing the volume further and cooling to −35 °C. Total yield = 1.45 g, 57%. Anal. Calcd for $C_{46}H_{54}P_2RuS_3Si$: C, 61.8; H, 6.09. Found: C, 61.0; H, 5.95. Mp: 198−205 °C (dec). ^1H NMR (dichloromethane-d_2): δ 1.57 (vir t, 18 H, $P\mathit{Me}_3$), 1.97 (t, $J_{HP} = 1$ Hz, 15 H, $C_5\mathit{Me}_5$), 6.85 (d, $J = 8$ Hz, 3 H, Naph), 7.14−7.41 (m, 15 H, Naph), 7.56 (d, $J = 8$ Hz, 3 H, Naph). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 12.37 ($C_5\mathit{Me}_5$), 24.33 (vir t, $P\mathit{Me}_3$), 95.62 (C_5Me_5), 125.24, 125.71, 126.93, 127.49, 127.85, 128.17, 131.87, 132.89, 133.06, 135.45 (aryl carbons). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ 2.32. IR: 1300 m, 1228 m, 1218 m, 1128 m, 1067 m, 1067 w, 1019 w, 952 br s, 936 br s, 897 m, 859 m, 845 m, 812 s, 741 s, 720 m, 471 w, 430 br s.

$Cp^*(Me_3P)_2RuSi(SCH_2CH_2CH_2S)Ph$ (5). Toluene (15 mL) was added to $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (1.8 g, 2.1 mmol) and $HSi(SCH_2CH_2CH_2S)Ph$ (1.3 g, 2.1 mmol), and the resulting solution was heated (120 °C) in a closed flask for 12 h. After removing the volatile materials by vacuum transfer, the resulting solid was extracted into diethyl ether, and then pentane was added until the solution became cloudy. Two types of crystals formed upon cooling to −35 °C, which were separated by hand and determined (by ^1H and ^{31}P NMR spectroscopy) to be the starting material, $Cp^*(Me_3P)_2RuCH_2SiMe_3$, and the new product **5**. Yield: 0.42 g, 34%. Anal. Calcd for $C_{25}H_{44}P_2RuS_2Si$: C, 50.1; H, 7.40. Found: C, 49.8; H, 7.49. ^1H NMR (benzene-d_6): δ 1.43 (vir t, 18 H, $P\mathit{Me}_3$), 1.52 (s, 15 H, $C_5\mathit{Me}_5$), 2.00 (m, 2 H, $CH_2\mathit{CH}_2CH_2$), 2.69 (m, 4 H, $\mathit{CH}_2CH_2\mathit{CH}_2$), 7.72 (t, $J = 7$ Hz, 2 H, Ph), 7.39 (t, $J = 7$ Hz, 2 H, Ph), 8.35 (d, $J = 7$ Hz, 1 H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 11.70 ($C_5\mathit{Me}_5$), 24.76 (vir t, $P\mathit{Me}_3$), 28.72 ($CH_2\mathit{CH}_2CH_2$), 31.80 ($\mathit{CH}_2CH_2\mathit{CH}_2$), 93.83 ($\mathit{C}_5Me_5$), 126.69, 127.34, 136.81, 147.16 (phenyl). $^{31}P\{^1H\}$ NMR (23 °C, benzene-d_6): δ 5.87. $^{29}Si\{^1H\}$ NMR (benzene-d_6): δ 48.23 (t, $^2J_{SiP} = 29$ Hz).

$Cp^*(Me_3P)_2RuSi(SCy)_2Cl$ (6). Toluene (15 mL) was added to $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (0.80 g, 1.7 mmol) and the $HSi(SCy)_3/HSi(SCy)_2Cl$ (4:1) mixture (2.2 g, 1.4 mmol of $HSi(SCy)_2Cl$), and the resulting mixture was stirred with heating (120 °C) in a closed flask for 5 h, resulting in some precipitation. After removing the volatile material in vacuo, the precipitate was washed with pentane (2 × 10 mL). The remaining yellow powder was extracted into diethyl ether (15 mL), and the resulting solution was cooled to −78 °C, resulting in 0.50 g of light yellow crystals. Yield: 52% (based on $HSi(SCy)_2Cl$). Anal. Calcd for $C_{28}H_{55}ClP_2RuS_2Si$: C, 49.3; H, 8.12. Found: C, 48.8; H, 8.07. Mp: 215−218 °C, dec. ^1H NMR (dichloromethane-d_2): δ 1.1−1.9 (m, 16 H, Cy), 1.46 (vir t, 18 H, $P\mathit{Me}_3$), 1.80 (s, 15 H, $C_5\mathit{Me}_5$), 2.07 (br m, 4 H, Cy), 3.15 (br m, 2 H, Cy). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 12.21 ($C_5\mathit{Me}_5$), 23.55 (vir t, $P\mathit{Me}_3$), 26.34, 27.24, 27.43, 37.61, 38.30, 44.83 (Cy carbons), 95.06 (C_5Me_5). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ 3.20. ^{29}Si NMR (dichloromethane-d_2): δ 67.57 (t, $^2J_{SiP} = 40$ Hz). IR: 1300 w, 1278 m, 1255 w, 1203 w, 1025 w, 993 m, 959 s, 942 s, 882 w, 856 w, 842 w, 744 m, 710 m, 673 w, 665 s, 483 m, 453 s, 420 m.

$Cp^*(Me_3P)_2RuSi(SMes)_2Cl$ (7). Toluene (6 mL) was added to $Cp^*(Me_3P)_2RuCH_2SiMe_3$ (1.02 g, 2.15 mmol) and a 4:1 $HSi(SMes)_3/HSi(SMes)_2Cl$ mixture (1.01 g, 2.26 mmol of the chloride), and the resulting mixture was heated (115 °C) in a closed flask for 5 h. After removing the volatile material in vacuo and washing with pentane (3 × 20 mL), the product was crystallized from a 1:1 dichloromethane/diethyl ether mixture at −78 °C. Yield: 35% (0.57 g). Anal. Calcd for $C_{34}H_{55}ClP_2RuS_2Si$: C, 54.1; H, 7.35; Cl, 4.70. Found: C, 53.6; H, 7.37; Cl, 4.56. Mp: 232−234 °C, dec ^1H NMR (dichloromethane-d_2): δ 1.47 (virtual t, 18 H, PMe_3), 1.95 (s, 15 H, Cp*), 2.18 (s, 6 H, $SC_6Me_2H_2\mathit{Me}$), 2.28 (s, 12 H, $SC_6\mathit{Me}_2H_2Me$), 6.75 (s, 4 H, $SC_6Me_2\mathit{H}_2Me$). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ 3.96. IR: 1298 m, 1279 m, 1048 w, 1023 w, 955 s, 940 s, 849 s, 710 m, 675 w, 665 w, 458 s.

$Cp^*(Me_3P)_2RuSi(SEt)_2OTf$ (8). To a solution of **3** (2.80 g, 4.67 mmol) in pentane (20 mL) was added Me_3SiOTf (0.85 mL, 4.67 mmol). This mixture was stirred for 8 h, during which time the product precipitated as yellow microcrystals. The supernatant was removed by filtration and the product was washed with pentane (5 mL) to afford 2.91 g of **8** (91% yield; mp 173−179 °C dec). Anal. Calcd for $C_{21}H_{43}F_3O_3P_2RuS_3Si$: C, 36.7; H, 6.30. Found: C, 36.7; H, 6.54. ^1H NMR (dichloromethane-d_2): δ 1.26 (t, $J = 7$ Hz, 6 H, $SCH_2C\mathit{H}_3$), 1.46 (virtual t, 18 H, PMe_3), 1.80 (s, 15 H, Cp*), 2.88 (q, $J = 7$ Hz, 4 H, $SC\mathit{H}_2CH_3$). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 11.52 ($C_5\mathit{Me}_5$), 17.50 ($SCH_2\mathit{C}H_3$), 23.87 (t, $J_{CP} = 15$ Hz, PMe_3), 26.28 ($S\mathit{C}H_2CH_3$), 94.26 (C_5Me_5). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ 2.07. ^{29}Si NMR (−80 °C, dichloromethane-d_2): δ 86.05 (t, $J_{SiP} = 37$ Hz). IR: 1358 s, 1281 w, 1235 m, 1208 s, 1172 s, 1152 m, 955 s, 938 s, 850 w, 712 w, 664 w, 628 s. Equivalent conductance = 12 Ω^{-1} cm^2 equiv^{-1} (0.0018 M at 23 °C in dichloromethane).

$Cp^*(Me_3P)_2RuSi(NMe_2)_2(OTf)$ (13) and $Cp^*(Me_3P)_2RuSi(NMe_2)(OTf)_2$ (14). Trimethylsilyl triflate (0.12 mL, 0.7 mmol) was added to a cold (−78 °C) pentane solution (100 mL) of $Cp^*(Me_3P)_2RuSi(NMe_2)_3$ (0.61 g, 1.1 mmol), the resulting solution was allowed to slowly warm to 23 °C, and then stirring was continued for 12 h. The resulting precipitate was isolated by filtration and washed with pentane (3 mL) to give 0.12 g (17%) of product that contained a small amount of contamination by **14**. Anal. Calcd for $C_{21}H_{45}F_3P_2RuN_2O_3SSi$: C, 38.6; H, 6.94; N, 4.28. Found: C, 37.9; H, 6.29; N, 2.86. ^1H NMR (dichloromethane-d_2): δ 1.50 (vir t, 18 H, $P\mathit{Me}_3$), 1.84 (t, $J_{HP} = 1$ Hz, 15 H, $C_5\mathit{Me}_5$), 2.72 (s, 12 H, NMe_2). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 11.31 ($C_5\mathit{Me}_5$), 24.17 (vir t, $P\mathit{Me}_3$), 40.06 (NMe_2), 94.79 (C_5Me_5). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ −1.38. IR: 1365 m, 1265 s, 1188 m, 1139 s, 1029 s, 992 m, 978 m, 936 m, 720 m, 666 w, 633 s. To the filtrate from above, more trimethylsilyl triflate (0.36 mL, 2.1 mmol) was added, and the solution was then stirred for an additional 12 h. The resulting precipitate (0.55 g) was isolated and then crystallized from a 1:1 dichloromethane/diethyl ether mixture at −35 °C to give yellow crystals of **14**. Yield = 0.18 g (22%). Anal. Calcd for $C_{21}H_{45}F_3P_2RuN_2O_3SSi$: C, 31.7; H, 5.18; N, 1.85. Found: C, 31.3; H, 5.38; N, 2.23. ^1H NMR (dichloromethane-d_2): δ 1.46 (vir t, 18 H, $P\mathit{Me}_3$), 1.77 (t, $J_{HP} = 1$ Hz, 15 H, $C_5\mathit{Me}_5$), 2.66 (s, 6 H, NMe_2). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 11.13 ($C_5\mathit{Me}_5$), 23.68 (vir t, $P\mathit{Me}_3$), 39.34 (NMe_2), 95.21 (C_5Me_5). $^{31}P\{^1H\}$ NMR (dichloromethane-d_2): δ −0.03. $^{29}Si\{^1H\}$ NMR (dichloromethane-d_2): δ 37.88 (t, $^2J_{SiP} = 41$ Hz). IR: 1360 s $\nu(SO_3)$, 1286 m 1240 m, 1195 s, 1150 m, 1002 s, 972 m, 955 m, 924 m, 850 w, 712 w, 672 m, 629 s, 460 m.

$Cp^*(Me_3P)_2RuSi(SCH_2CH_2S)S\text{-}p\text{-}Tol)$ (16). The compounds **15** (0.900 g, 1.08 mmol) and $LiSCH_2CH_2SLi$ (0.266 g, 2.17 mmol) were stirred together in toluene (40 mL) for 11 days. The volatile materials were removed by vacuum distillation, and the resulting precipitate was then extracted with diethyl ether (2 × 25 mL). The combined ether extracts were cooled to −78 °C to obtain 0.116 g of product. After concentrating the solution, a second crop of crystals (0.095 g) was obtained. Total yield: 31%. Anal. Calcd for $C_{25}H_{44}P_2RuS_3Si$: C, 47.6; H, 7.03. Found: C, 47.9; H, 7.08. ^1H NMR (dichloromethane-d_2): δ 1.49 (vir t, 18 H, P*Me*$_3$), 1.91 (s, 15 H, C$_5$*Me*$_5$), 2.04 (m, 2 H, SC*H*$_2$C*H*$_2$S), 2.28 (s, 3 H, C$_6$H$_4$*Me*), 2.44 (m, 2 H, SC*H*$_2$SC*H*$_2$S), 6.98 (d, J = 8 Hz, 2 H, C$_6$*H*$_4$Me), 7.37 (d, 2 H, J = 8 Hz, C$_6$*H*$_4$Me). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 12.22 (C$_5$*Me*$_5$), 21.22 (C$_6$H$_4$*Me*), 23.33 (vir t, P*Me*$_3$), 37.17 (S*C*H$_2$*C*H$_2$S), 95.12 (*C*$_5$Me$_5$), 128.57, 134.55, 135.38, 135.98 (aryl carbons). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 3.63. ^{29}Si{^{1}H} NMR (dichloromethane-d_2): δ 71.71 (t, $^2J_{\mathrm{SiP}}$ = 34 Hz). IR: 1294 w, 1277 m, 1150 w, 1089 w, 1020 w, 957 s, 941 s, 845 m, 800 s, 710 br m, 668 m, 472 s, 420 m.

Cp*(Me$_3$P)$_2$RuSi(1,2,4-S$_2$MeC$_6$H$_3$)(S-*p*-Tol) (17). Benzene (30 mL) was added to a flask containing **15** (0.66 g, 0.79 mmol) and Li$_2$S$_2$MeC$_6$H$_3$ (0.17 g, 1.0 mmol), and the resulting heterogeneous mixture was stirred for 36 h. The reaction mixture was filtered to remove precipitated LiOTf, and the filtrate was evacuated to a solid, which was extracted into diethyl ether (3 × 15 mL). Upon cooling the combined extracts to −78 °C, precipitation of the product as a yellow powder occurred (0.12 g). After concentrating and cooling the solution further, a second crop (0.16 g) was obtained. Total yield: 51%. Anal. Calcd for C$_{30}$H$_{46}$P$_2$RuS$_3$Si: C, 51.9; H, 6.68. Found: C, 51.5; H, 6.98. ^{1}H NMR (benzene-d_6): δ 1.32 (vir t, 18 H, P*Me*$_3$), 1.82 (s, 15 H, C$_5$*Me*$_5$), 1.95 (s, 3 H), 1.98 (s, 3 H), 6.40 (d, J = 8 Hz, 1 H, S$_2$C$_6$*H*$_3$Me), 6.67 (d, J = 8 Hz, 2 H, SC$_6$*H*$_4$Me), 7.05 (s, 1 H, S$_2$C$_6$*H*$_3$Me), 7.14 (d, J = 8 Hz, 1 H, S$_2$C$_6$*H*$_3$Me), 7.69 (d, 2 H, J = 8 Hz, SC$_6$*H*$_4$Me). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 12.04, 12.44 (C$_5$*Me*$_5$), 20.61 (C$_6$H$_4$*Me*), 23.40 (vir t, P*Me*$_3$), 95.03 (*C*$_5$Me$_5$), 123.48, 125.35, 126.42, 127.80, 128.74, 132.28, 135.15, 135.34, 138.33, 141.63 (aryl carbons). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 3.63. ^{29}Si{^{1}H} NMR (dichloromethane-d_2): δ 69.12 (t, $^2J_{\mathrm{SiP}}$ = 33 Hz). IR: 1294 w, 1274 w, 1111 w, 1020 w, 955 s, 938 s, 845 w, 798 s, 712 m, 703 m, 665 m.

Reaction of Cp*(Me$_3$P)$_2$RuSi(SMes)$_2$Cl (7) with Me$_3$SiOTf. Me$_3$SiOTf (8 μL, 0.04 mmol) was syringed into a benzene-d_6 solution of **7** (0.03 g, 0.04 mmol), and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 8 h, two new products with spectroscopic characteristics consistent with Cp*(Me$_3$P)$_2$RuSi(SMes)Cl(OTf) (**19**) and Cp*(Me$_3$P)$_2$RuSi(SMes)$_2$OTf (**18**) were observed in a 2:1 ratio. NMR spectroscopic data for **18** are as follows: ^{1}H NMR (dichloromethane-d_2): δ 1.50 (virtual t, 18 H, PMe$_3$), 1.89 (s, 15 H, Cp*), 2.22 (s, 3 H, SC$_6$Me$_2$H$_2$*Me*), 2.36 (s, 6 H, SC$_6$*Me*$_2$H$_2$Me), 6.82 (s, 4 H, SC$_6$Me$_2$*H*$_2$Me). ^{31}P{^{1}H} NMR (benzene-d_6): δ 3.48 (s).

Cp*(Me$_3$P)$_2$RuSi(SMes)(OTf)Cl (19). Me$_3$SiOTf (0.11 mL, 1.5 mmol) was added to a dichloromethane (5 mL) solution of **7** (0.22 g, 0.75 mmol), and the resulting solution was stirred for 1 h. After the volatile materials were removed in vacuo, the resulting solid was washed with pentane (3 × 20 mL) and the product was crystallized from a 1:1 dichloromethane/diethyl ether mixture at −10 °C. Yield: 49% (0.11 g). Anal. Calcd for C$_{26}$H$_{44}$ClF$_3$O$_3$P$_2$RuS$_2$Si: C, 41.5; H, 5.90; Cl, 4.71. Found: C, 41.6; H, 5.90; Cl, 5.10. ^{1}H NMR (benzene-d_6): δ 1.24 (virtual t, 18 H, PMe$_3$), 1.70 (s, 15 H, C$_5$Me$_5$), 2.12 (s, 3 H, SC$_6$Me$_2$H$_2$*Me*), 2.82 (s, 6 H, SC$_6$*Me*$_2$H$_2$Me), 6.95 (s, 4 H, SC$_6$Me$_2$*H*$_2$Me). ^{31}P{^{1}H} NMR (benzene-d_6): δ 0.52 (d, J_{PP} = 39 Hz, 1 P, PMe$_3$), 2.06 (d, J_{PP} = 39 Hz, 1 P, PMe$_3$). IR: 1362 s ν(SO$_3$), 1233 m, 1208 s, 1189 s, 1146 m, 950 br s, 850 w, 715 w, 619 m, 488 m, 418 m.

[Cp*(Me$_3$P)$_2$RuSi(SEt)$_2$][BPh$_4$] (20). Compound **20** was prepared from **8** in 48% yield by the method used to obtain **21**. Anal. Calcd for C$_{44}$H$_{63}$BP$_2$RuS$_2$Si: C, 61.6; H, 7.40; Cl, 0.00. Found: C, 61.7; H, 7.11; Cl, 0.12. ^{1}H NMR (dichloromethane-d_2): δ 1.45 (t, J = 8 Hz, 6 H, SCH$_2$C*H*$_3$), 1.54 (virtual t, 18 H, PMe$_3$), 1.85 (s, 15 H, C$_5$Me$_5$), 3.14 (q, J = 8 Hz, 4 H, SC*H*$_2$CH$_3$), 6.88 (t, J = 7 Hz, 4 H, BPh), 7.04 (t, J = 7 Hz, 8 H, BPh), 7.32 (br s, 8 H, BPh). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 11.01 (C$_5$*Me*$_5$), 18.80 (SCH$_2$*C*H$_3$), 20.88 (t, J_{CP} = 15 Hz, PMe$_3$), 30.45 (S*C*H$_2$CH$_3$), 93.17 (*C*$_5$Me$_5$), 122.07, 126.00, 136.26 (BPh$_4$). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ −2.22. ^{29}Si NMR (−60 °C, dichloromethane-d_2): δ 264.4 br. IR: 1577 w, 1422 w, 1288 w, 1252 m, 1192 m, 1148 w, 1067 w, 1028 w, 958 s, 935 s, 852 m, 841 m, 750 w, 731 s, 704 s, 669 w, 664 w, 609 s, 561 s, 510 m. Equivalent conductance = 30 Ω^{-1} cm^2 equiv^{-1} (0.0018 M at 23 °C in dichloromethane). Attempts to measure the molecular weight in dichloromethane were hindered by decomposition of the compound.

[Cp*(Me$_3$P)$_2$RuSi(S-*p*-Tol)$_2$][BPh$_4$] (21). Compound **11** (3.00 g, 3.69 mmol), NaBPh$_4$ (1.50 g, 4.43 mmol), and dichloromethane (20 mL) were stirred in a reaction flask for 2 h. The solution was then filtered to remove the precipitate of NaOTf. The resulting solution was then concentrated, and diethyl ether was added to precipitate **21** as yellow microcrystals in 58% yield (2.1 g; mp 91−95 °C dec). Anal. Calcd for C$_{54}$H$_{67}$BP$_2$RuS$_2$Si: C, 66.0; H, 6.87; S, 6.52. Found: C, 66.7; H, 7.11; S, 6.36. ^{1}H NMR (dichloromethane-d_2): δ 1.37 (virtual t, 18 H, PMe$_3$), 1.91 (s, 15 H, Cp*), 2.34 (s, 6 H, SC$_6$H$_4$*Me*), 6.89 (t, J = 7 Hz, 4 H, BPh), 7.04 (t, J = 7 Hz, 8 H, BPh), 7.14 (d, J = 8 Hz, 4 H, SC$_6$*H*$_4$Me), 7.21 (d, J = 8 Hz, 4 H, SC$_6$*H*$_4$Me), 7.31 (br s, 8 H, BPh). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 11.59 (s, C$_5$*Me*$_5$), 21.58 (s, SC$_6$H$_4$*Me*), 24.12 (t, J_{CP} = 16 Hz, PMe$_3$), 96.70 (s, *C*$_5$Me$_5$), 122.08, 125.98, 128.68, 130.79, 134.54, 136.30, 140.00 (aryl carbons). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ −2.86. ^{29}Si NMR (dichloromethane-d_2): δ 250.6 br. At −80 °C: δ 259.4 (t, J_{SiP} = 34 Hz). IR: 1288 w, 1013 w, 952 m, 938 m, 808 w, 740 m, 739 s, 730 s, 704 s, 603 w. Equivalent conductance = 31 Ω^{-1} cm^2 equiv^{-1} (0.0037 M at 23 °C in dichloromethane). Mol wt in dichloromethane (isopiestic method): 990 (calcd 982 for ion pair).

[Cp*(Me$_3$P)$_2$RuSi(SCy)$_2$][BPh$_4$] (22). Dichloromethane (20 mL) was added to Cp*(Me$_3$P)$_2$RuSi(SCy)$_2$Cl (0.41 g, 0.60 mmol) and NaBPh$_4$ (0.31 g, 0.90 mmol), and the resulting solution was stirred for 1.5 days. This yellow-orange solution was filtered to remove NaCl, and then all volatile components were removed in vacuo. Yield: 95%. Anal. Calcd for C$_{50}$H$_{28}$BP$_2$RuS$_2$Si: C, 63.7; H, 8.02. Found: C, 63.6; H, 7.65. Mp: 89−96 °C, dec. ^{1}H NMR (dichloromethane-d_2): δ 1.4−1.8 (m, 16 H, Cy) 1.55 (vir t, 18 H, P*Me*$_3$), 1.86 (s, 15 H, C$_5$*Me*$_5$), 2.04 (br m, 4 H, Cy), 3.63 (br m, 2 H, Cy), 6.88 (t, J = 8 Hz, 4 H, BPh$_4$), 7.04 (t, J = 8 Hz, 8 H, BPh$_4$), 7.32 (br m, 4 H, BPh$_4$). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 11.48 (C$_5$*Me*$_5$), 24.35 (vir t, P*Me*$_3$), 25.40, 26.64, 37.05, 48.32 (Cy carbons), 95.84 (*C*$_5$Me$_5$), 122.03, 125.94, 136.21, 164.38 (q, J_{CB} = 49 Hz, ipso carbon of BPh$_4$). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ −2.47. ^{29}Si NMR (dichloromethane-d_2): δ 268.67 (t, $^2J_{\mathrm{SiP}}$ = 35 Hz). IR: 1577 w, 1284 w, 1258 m, 1022 br m, 952 s, 938 s, 848 w, 800 w, 730 s, 701 s, 679 w, 610 m, 598 w, 561 m, 528 m.

[Cp*(Me$_3$P)$_2$RuSi(S-2-Naph)$_2$][B(C$_6$F$_6$)$_3$(S-2-Naph)] (23). B(C$_6$F$_6$)$_3$ (0.075 g, 0.15 mmol) and **4** (0.12 g, 0.13 mmol) were combined in an NMR tube with 0.7 mL of dichloromethane-d_2, and the tube was shaken to dissolve the contents. After 20 min, ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy revealed the formation of a single product (**23**). Afterward, *n*-butyl ether was added to the sample, and upon concentrating the solution, crystals formed (0.080 g). These crystals were analyzed (by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis) as the starting material **4**. Data for **23**. ^{1}H NMR (dichloromethane-d_2): δ 1.37 (vir t, 18 H, P*Me*$_3$), 1.91 (t, J_{HP} = 1 Hz, 15 H, C$_5$Me$_5$), 7.22−7.75 (m, 21 H, Naph). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 11.47 (C$_5$*Me*$_5$), 23.92 (vir t, P*Me*$_3$), 96.95 (*C*$_5$Me$_5$), 124.22, 125.68, 126.29, 126.67, 127.52, 127.55, 127.64, 128.05, 129.44, 129.54, 130.84, 130.93, 131.81, 133.08, 133.78, 133.83, 134.05 (Naph aryl carbons), 136.95 (d of mult, J_{CF} = 235 Hz, (S-2-Naph)B(*C*$_6$F$_5$)$_3$), 138.85 (d of mult, J_{CF} = 253 Hz, (S-2-Naph)B(*C*$_6$F$_5$)$_3$), 184.43 (d of mult, J_{CF} = 245 Hz, (S-2-Naph)B(*C*$_6$F$_5$)$_3$). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ −2.65. ^{29}Si{^{1}H} NMR (dichloromethane-d_2): δ 260.51 (t, J_{SiP} = 33 Hz).

[Cp*(Me$_3$P)$_2$Ru=SiMe$_2$][B(C$_6$F$_5$)$_4$] (24). LiB(C$_6$F$_5$)$_4$·Et$_2$O (0.12 g, 0.16 mmol) and Cp*(Me$_3$P)$_2$RuSiMe$_2$OTf (0.090 g, 0.15 mmol) were combined in an NMR tube, which was then cooled to −78 °C. Dichloromethane-d_2 (0.6 mL) was then added, and the tube was shaken to mix the reagents. The tube was warmed to 0 °C, and NMR spectra at this temperature indicated 90% conversion to one ruthenium product. X-ray quality crystals were grown by addition of a ^{n}Bu$_2$O solution (0.5 mL) of LiB$(C_6F_5)_4\cdot Et_2O$ (0.050 g, 0.066 mmol) to a dichlorobenzene solution (1 mL) of Cp*$(Me_3P)_2$RuSiMe$_2$OTf (0.040 g, 0.066 mmol) at 23 °C. Over the course of 5 min, ^{n}Bu$_2$O (2.5 mL) was added slowly until crystals began to form. The solution was left undisturbed for 18 h before the crystals were isolated by filtration. Yield: 0.028 g/38%. Anal. Calcd for $C_{42}H_{39}BF_{20}P_2RuSi$: C, 44.8; H, 3.49. Found: C, 44.7; H, 3.42. ^{1}H NMR (0 °C, dichloromethane-d_2): δ 0.99 (s, 6 H, SiMe$_2$), 1.44 (vir t, 18 H, PMe$_3$), 1.81 (t, J_{HP} = 1 Hz, 15 H, C$_5$Me$_5$). ^{31}P{^{1}H} NMR (0 °C, dichloromethane-d_2): δ 2.29. ^{29}Si{^{1}H} NMR (0 °C, dichloromethane-d_2): δ 311.41 (br s).

X-ray Crystal Determination for 24. A yellow, blocklike crystal with approximate dimensions of 0.30 × 0.34 × 0.34 mm was mounted in a glass capillary. The mounted crystal was placed under a cold stream of nitrogen on a Siemens P4 diffractometer. Crystal quality was evaluated via measurement of intensities and inspection of peak scans. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. The 8444 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the systematic absences indicated uniquely space group $P2_1/n$. Removal of systematically absent and redundant data left 8128 unique data in the final data set. The structure was solved by direct methods and refined via standard least-squares and Fourier techniques. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.80 and −0.52 e Å^{-3}. The final residuals for 604 variables refined against the 4112 data were R = 5.78%, R_w = 7.46%, and GOF = 1.31.

[Cp*(Me$_3$P)$_2$Ru=SiPh$_2$][B(C$_6$F$_5$)$_4$]·0.1CH$_2$Cl$_2$ (25). LiB(C$_6$F$_5$)$_4$·Et$_2$O (0.13 g, 0.16 mmol) and Cp*(Me$_3$P)$_2$RuSiPh$_2$OTf (0.12 g, 0.15 mmol) were combined in an NMR tube, which was then cooled to −78 °C. Dichloromethane-d_2 (0.6 mL) was then added, and the tube was shaken to give an orange-red solution. The tube was warmed to −30 °C, and NMR spectra at this temperature revealed the presence of only one product. After acquiring a ^{29}Si NMR spectrum (−30 °C), the tube was cooled to −78 °C for 16 h to give orange-red crystals. The solvent was syringed out of the tube, and the tube was warmed to 23 °C. Under vacuum, the crystals desolvated and turned opaque. Yield: 0.042 g/22%. Anal. Calcd for $C_{52}H_{43}BF_{20}P_2RuSi\cdot(0.1CH_2Cl_2$: C, 49.7; H, 3.46; Cl, 0.53. Found: C, 49.1; H, 3.42; Cl, 0.4. ^{1}H NMR (−30 °C, dichloromethane-d_2): δ 1.50 (br s, 18 H, P*Me*$_3$), 1.91 (br s, 15 H, C$_5$*Me*$_5$), 7.53 (br s, 10 H, SiPh$_2$). ^{13}C{^{1}H} NMR (−30 °C, dichloromethane-d_2): δ 10.91 (C$_5$*Me*$_5$), 22.70 (vir t, P*Me*$_3$), 95.22 (*C*$_5$Me$_5$), 127.52, 131.02, 133.38, 147.05 (aryl carbons). ^{31}P{^{1}H} NMR (−30 °C, dichloromethane-d_2): δ 1.67. ^{29}Si{^{1}H} NMR (−30 °C, dichloromethane-d_2): δ 299 (t, J_{SiP} = 32 Hz).

Cp*(Me$_3$P)$_2$RuSi[S(Tol-*p*)]$_2$Ph (26). PhMgBr (0.10 mL of a 3.2 M solution, 0.31 mmol) was syringed into a benzene (20 mL) solution of Cp*(Me$_3$P)$_2$RuSi[S(Tol-*p*)]$_2$OTf (0.25 g, 0.31 mmol), and the resulting solution was stirred for 2 h while precipitation of MgBrOTf occurred. After the volatile material was removed in vacuo, the resulting residue was extracted with 2 × 20 mL of diethyl ether and the combined extracts were cooled to −35 °C to give a light yellow precipitate (0.041 g). Yield: 18%. ^{1}H NMR (dichloromethane-d_2): δ 1.51 (virtual t, 18 H, PMe$_3$), 1.77 (s, 15 H, Cp*), 2.09 (s, 6 H, SC$_6$H$_4$*Me*), 6.52 (d, J = 8 Hz, 4 H, SC$_6$*H*$_4$Me), 6.70 (d, J = 8 Hz, 4 H, SC$_6$*H*$_4$Me), 6.98 (m, 3 H, Ph), 7.75 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 12.14 (C$_5$*Me*$_5$), 20.86 (SC$_6$H$_4$*Me*), 24.04 (virtual t, PMe$_3$), 94.77 (*C*$_5$Me$_5$), 126.09, 126.77, 128.38, 133.81, 134.13, 135.36, 137.57, 144.67 (aryl carbons). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 3.24 (s).

Cp*(Me$_3$P)$_2$RuSiMe$_2$Ph (27). This compound was prepared from **11** by the same method used for **26**. Yield: 45%. Anal. Calcd for $C_{24}H_{44}P_2RuSi$: C, 55.0; H, 8.47. Found: C, 53.3; H, 8.34. ^{1}H NMR (dichloromethane-d_2): δ 0.30 (s, 6 H, SiMe$_2$), 1.40 (virtual t, 18 H, PMe$_3$), 1.60 (s, 15 H, C$_5$Me$_5$), 7.05−7.21 (m, 3 H, Ph), 7.54 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 10.41 (SiMe$_2$), 11.84 (C$_5$*Me*$_5$), 24.04 (virtual t, PMe$_3$), 93.13 (*C*$_5$Me$_5$), 125.48, 126.50, 134.99, 154.95 (aryl carbons). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 6.48. ^{29}Si{^{1}H} NMR (dichloromethane-d_2): δ 18.91 (t, J_{SiP} = 28 Hz).

Observation of [Cp*(Me$_3$P)$_2$RuSiMe$_2$(PMe$_3$)][B(C$_6$F$_5$)$_4$] (28). A solid mixture of Cp*(Me$_3$P)$_2$RuSiMe$_2$OTf (0.012 g, 0.020 mmol) and (Et$_2$O)LiB(C$_6$F$_5$)$_4$ (0.014 g, 0.020 mmol) was dissolved in 0.5 mL of dichloromethane-d_2 to generate the silylene complex **24**. The solution was then transferred to an NMR tube, which was sealed with a rubber septum. After cooling the tube to 0 °C, PMe$_3$ (3.1 μL, 0.030 mmol) was added via syringe, generating a yellow solution of **28**. ^{1}H NMR (dichloromethane-d_2): δ 0.52 (d, $^3J_{HP}$ = 4.5 Hz, 6 H, SiMe), 1.39 (vir t, 18 H, PMe$_3$), 1.42 (d, $^2J_{HP}$ = 9.1 Hz, 9 H, PMe$_3$), 1.78 (s, 15 H, C$_5$Me$_5$). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ −15.20 (s, 1 P), 2.87 (s, 2 P).

Observation of [Cp*(Me$_3$P)$_2$RuSiMe$_2$(PPh$_3$)][B(C$_6$F$_5$)$_4$] (29). A solution of **24** was generated in the same manner and on the same scale as described for **28**. PPh$_3$ (0.008 g, 0.030 mmol) was added to the solution of **24**, giving a dark yellow solution of **29**. ^{1}H NMR (dichloromethane-d_2): δ 0.45 (d, $^3J_{HP}$ = 4.5 Hz, 6 H, SiMe), 1.30 (vir t, 18 H, PMe$_3$), 1.79 (s, 15H, C$_5$Me$_5$), 7.34 (m, ArH), 7.65 (m, ArH). ^{31}P{^{1}H} NMR (dichloromethane-d_2): δ 5.34 (s, 2 P), 21.53 (s, 1 P).

[Cp*(Me$_3$P)$_3$Ru][OTf]. To a solution of [Cp*Ru(NCCH$_3$)$_3$]-OTf (0.300 g, 0.590 mmol) in 20 mL of dichloromethane was added PMe$_3$ (0.250 mL, 2.42 mmol) via syringe. After stirring this solution for 12 h, the volatile material was removed in vacuo and the residue was extracted with dichloromethane (2 × 10 mL). Concentration of the solution to 10 mL, addition of 5 mL of diethyl ether, and cooling to −78 °C gave crystals of the product. Yield: 90% (0.326 g). Anal. Calcd for $C_{20}H_{42}F_3O_3P_3RuS$: C, 39.15; H, 6.90. Found: C, 38.80; H, 7.15. Mp: 175−178 °C. ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 1.46 (vir t, 27 H, PMe$_3$), 1.76 (s, 15 H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (100 MHz, dichloromethane-d_2): δ 12.10 (s, Cp*), 23.24 (m, PMe$_3$), 96.36 (s, ring *C*$_5$Me$_5$). ^{31}P{^{1}H} NMR (121.5 MHz, dichloromethane-d_2): δ 1.98 (s). IR (KBr pellet): 2977 s, 2915 s, 1481 m, 1429 s, 1378 m, 1261 s, 1145 s, 1029 m, 962 s, 856 m, 715 m, 669, m, 636 s, 570 w, 516 m.

Observation of [Cp*(Me$_3$P)$_2$RuPPh$_3$][B(C$_6$F$_5$)$_4$] (31). A solution of **29** in dichloromethane-d_2, as generated above, was allowed to stand at room temperature for 2 days. ^{1}H and ^{31}P NMR spectroscopy indicated nearly quantitative conversion to the product. ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 1.47 (m, 18 H, PMe$_3$), 1.70 (s, 15 H, C$_5$Me$_5$), 7.45 (m, ArH), 7.74 (m, ArH). ^{31}P{^{1}H} NMR (161.98 MHz, dichloromethane-d_2): δ −4.88 (d, $^2J_{PP}$ = 35 Hz, 2 P), 53.12 (t, $^2J_{PP}$ = 35 Hz, 1 P).

[Cp*(Me$_3$P)$_2$RuSiMe$_2$(CH$_2$PPh$_3$)][B(C$_6$F$_5$)$_4$] (32a). A 50 mL round-bottom Schlenk flask was charged with Cp*(Me$_3$P)$_2$RuSiMe$_2$OTf (0.150 g, 0.252 mmol) and (Et$_2$O)LiB(C$_6$F$_5$)$_4$ (0.192 g, 0.252 mmol). Dichloromethane (5 mL) was added after cooling the flask to 0 °C, and the mixture was stirred until all reactants dissolved. A cloudy yellow solution formed within 30 s, indicating the formation of **24**. The solution was then filtered into a precooled (0 °C) flask containing CH$_2$PPh$_3$ (0.070 g, 0.253 mmol). The reaction mixture was stirred for 5 min, after which the volatile materials were removed under reduced pressure. The crude product was crystallized from 1:1 dichloromethane/diethyl ether (15 mL) at −78 °C. Yield: 80% (0.282 g). Anal. Calcd for $C_{61}H_{56}BF_{20}P_3RuSi$: C, 52.26; H, 4.03. Found: C, 52.01; H, 3.67. Mp: 180−183 °C. ^{1}H NMR (400 MHz, dichloromethane-d_2): δ −0.03 (s, 6 H, SiMe$_2$), 1.27 (vir t, 18 H, PMe$_3$), 1.84 (s, 15 H, C$_5$Me$_5$), 2.26 (d, $^2J_{HP}$ = 16 Hz, 2 H, CH$_2$), 7.68 (m, ArH), 7.78 (m, ArH). ^{13}C{^{1}H} NMR (100 MHz, dichloromethane-d_2): δ 1.26 (s, SiMe$_2$), 15.25 (s, C$_5$Me$_5$), 18.43 (d, $^1J_{CP}$ = 36 Hz, PMe$_3$), 41.41 (s, CH$_2$), 114.78 (s, ring

$\mathrm{C_5Me_5}$), 113.10 (m, $\mathrm{C_6F_5}$), 137.7 (dm, $^1J_{\mathrm{CF}} = 258$ Hz, $\mathrm{C_6F_5}$), 145.15 (dm, $^1J_{\mathrm{CF}} = 243$ Hz, $\mathrm{C_6F_5}$), 148.44 (dm, $^1J_{\mathrm{CF}} = 249$ Hz, $\mathrm{C_6F_5}$), 163.9 (dd, $^2J_{\mathrm{CP}cis} = 5.2$ Hz, $^2J_{\mathrm{CP}trans} = 49$ Hz). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121.5 MHz, dichloromethane-d_2): δ 5.85 (s, $\mathrm{PMe_3}$), 21.81 (s, $\mathrm{PPh_3}$). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ 35.24 (td, $_2J_{\mathrm{SiP}} = 32$ Hz, $^2J_{\mathrm{SiP}} = 15$ Hz). IR: 1278 s, 1251 m, 1202 m, 1095 w, 988 s, 791 m, 767 w, 743 m, 663 m, 585 m.

$[\mathrm{Cp^*(Me_3P)_2RuSiMe_2(CH_2PPh_3)}]\mathrm{OTf}$ (32b). $\mathrm{CH_2PPh_3}$ (0.070 g, 0.253 mmol) was dissolved in dichloromethane (5 mL), and the resulting solution was added via cannula to a solution of $\mathrm{Cp^*(Me_3P)_2RuSiMe_2OTf}$ (0.150 g, 0.252 mmol) in dichloromethane (5 mL). After stirring the reaction mixture for approximately 5 min, the volatile material was removed in vacuo to leave a bright yellow residue, which was crystallized from 1:1 dichloromethane/diethyl ether (15 mL) at −78 °C. Yield: 89% (0.196 g). Anal. Calcd for $\mathrm{C_{38}H_{56}F_3O_3P_3RuSSi}$: C, 52.34; H, 6.47. Found: C, 52.04; H, 6.10. Mp: 129−133 °C. The ^{1}H and ^{31}P NMR spectra were identical to those for **32a**. IR: 1268 m, 1249 s, 1210 w, 1156 s, 1043 m, 943 w, 832 m, 812 m, 774 m, 715 w, 686 w, 602 w, 593 w, 574 w.

X-ray Crystal Determination for 32b·$\mathrm{CH_2Cl_2}$. A yellow trapezoidal crystal with approximate dimensions of 0.15 × 0.20 × 0.30 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. The mounted crystal was placed under a cold stream of nitrogen on the diffractometer. Data were collected using a Siemens SMART diffractometer with a CCD area detector. A preliminary orientation matrix and unit cell parameters were determined by collecting 60 10-s frames. A hemisphere of data was collected at a temperature of -116 ± 1 °C using ω scans of 0.30° and a collection time of 20 s per frame. Frame data were integrated using SAINT. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. The 9339 reflections that were integrated were averaged in point group $2/m$ to yield 3557 unique reflections ($R_{\mathrm{int}} = 0.032$). No decay correction was necessary. The space group was determined to be $P2_1$ (No. 4). The structure was solved using direct methods (SIR92) and refined by full-matrix least-squares methods using teXsan software. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were included at calculated positions but not refined. The number of variable parameters was 477, giving a data/parameter ratio of 7.25. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.93 and −1.01 e$^-$/Å^3: $R = 0.041$, $R_{\mathrm{w}} = 0.050$, GOF = 2.75.

Reaction of 20 with $\mathrm{H_2}$ and Isolation of $[\mathrm{Cp^*(Me_3P)_2RuH_2}][\mathrm{BPh_4}]$ (33). Compound **8** (0.500 g, 0.727 mmol) and $\mathrm{NaBPh_4}$ (0.498 g, 1.46 mmol) were stirred in dichloromethane for 2 h, and then the solution was filtered. Hydrogen gas was bubbled into the resulting solution of $[\mathrm{Cp^*(Me_3P)_2Ru{=}Si(SEt)_2}][\mathrm{BPh_4}]$, the reaction flask was closed, and then the reaction mixture was stirred for 3.5 days. The volatile material was removed under reduced pressure to yield a light green oil. The oil was washed with pentane (3 × 10 mL), leaving a solid, which was purified by crystallizing from a 1:1 dichloromethane/diethyl ether mixture at −40 °C. Yield: 38% (0.198 g). Anal. Calcd for $\mathrm{C_{40}H_{55}RuP_2B}$: C, 67.70; H, 7.81. Found: C, 67.96; H, 7.48. Mp: 190 °C (dec). ^{1}H NMR (dichloromethane-d_2): δ −10.04 (t, $J_{\mathrm{PH}} = 33$ Hz, 1 H, RuH), 1.51 (vir t, 18 H, PMe_3), 1.94 (s, 15 H, $\mathrm{C_5}Me_5$), 6.96 (t, $J = 7$ Hz, 4 H, $\mathrm{BPh_4}$), 7.11 (t, $J = 7$ Hz, 8 H, $\mathrm{BPh_4}$), 7.41 (br s, 8 H, $\mathrm{BPh_4}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ 11.56 ($\mathrm{C_5}Me_5$), 24.70 (m, $\mathrm{PMe_3}$), 100.33 ($C_5\mathrm{Me_5}$), 122.04, 125.94, 136.28, (aryl carbons), 164.33 (q, $J_{\mathrm{CB}} = 49$ Hz, ipso carbon of $\mathrm{BPh_4}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ 10.10. IR (KBr pellet): 3052 s, 2996 s, 2910 m, 2138 m, 1961 m, 1941 m, 1579 w, 1479 m, 1427 m, 1288 m. 1147 w, 1068 w, 1029 m, 943 s, 854 m, 732 s, 703 s, 605 m.

Reaction of 20 with $\mathrm{H_3SiSiPh_3}$ and Isolation of $[\mathrm{Cp^*(Me_3P)_2RuH(SiH_2SiPh_3)}][\mathrm{BPh_4}]$ (35). Complex **20** (0.796 g, 0.928 mmol) and $\mathrm{H_3SiSiPh_3}$ (0.282 g, 0.972 mmol) were stirred in dichloromethane (15 mL) for 7 days. Diethyl ether (15 mL) was added, and the solution was cooled to −35 °C to give crystals of **35**. A second crop was obtained upon addition of more diethyl ether and further cooling, to give a total yield of 0.225 g (24%). The filtrate was concentrated to 1 mL, and the volatile components of the mixture were vacuum transferred and analyzed by ^{1}H NMR and mass spectroscopy as consisting of primarily $\mathrm{HSi(SEt)_3}$. Anal. Calcd for $\mathrm{C_{58}H_{71}BP_2RuSi_2}$: C, 68.8; H, 7.17. Found: C, 68.1; H, 7.31. ^{1}H NMR (dichloromethane-d_2): δ −10.10 (t, $J_{\mathrm{PH}} = 9$ Hz, 1 H, RuH), 1.31 (vir t, 18 H, PMe_3), 1.61 (s, 15 H, $\mathrm{C_5}Me_5$), 3.77 (vir t, 2 H, $\mathrm{SiH_2Ph_3}$), 6.87 (t, $J = 7$ Hz, 4 H, $\mathrm{BPh_4}$), 7.03 (t, $J = 7$ Hz, 8 H, $\mathrm{BPh_4}$), 7.31 (br s, 8 H, $\mathrm{BPh_4}$), 7.42 (m, 9 H, $\mathrm{SiH_2Ph_3}$), 7.59 (m, 6 H, $\mathrm{SiH_2Ph_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ 10.69 ($\mathrm{C_5}Me_5$), 20.95 (vir t, $\mathrm{PMe_3}$), 99.65 ($C_5\mathrm{Me_5}$), 122.07, 125.98, 128.67, 130.14, 135.23, 136.26, 136.33 (aryl carbons), 164.33 (q, $J_{\mathrm{CB}} = 49$ Hz, ipso carbon of $\mathrm{BPh_4}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ −0.34 (s).

Reaction of 20 with $\mathrm{H_3SiMes}$. Compound **8** (0.875 g, 1.27 mmol) and $\mathrm{NaBPh_4}$ (0.800 g, 2.34 mmol) were stirred in dichloromethane (10 mL) for 5 h, and then the solution was filtered. $\mathrm{H_3SiMes}$ (1 equiv) was syringed into the resulting solution, and stirring was continued for 4 days. The reaction solution was concentrated to 0.5 mL and was then extracted with pentane (2 × 4 mL) to leave a light yellow powder which was crystallized from dichloromethane/diethyl ether to give $[\mathrm{Cp^*(Me_3P)_2RuHCl}][\mathrm{BPh_4}]$ (**34**). Addition of more diethyl ether and cooling (−35 °C) gave a second crop for a combined yield of 0.32 g (34%). The pentane extract from above was cooled to −35 °C, to give white crystals of $\mathrm{BPh_3}$ (0.075 g, 24% yield; by ^{1}H NMR spectroscopy). The pentane filtrate was concentrated further to an oil, and then this residue was vacuum-transferred (10 h at 35 °C and 0.001 Torr). Analysis by ^{1}H, ^{13}C, ^{29}Si NMR and mass spectrometry revealed the presence of $\mathrm{H_3SiMes}$ and the new product $\mathrm{H_2SiMes(SEt)}$. The identity of the latter product was confirmed by an independent synthesis, involving reaction of $\mathrm{H_3SiMes}$ with $\mathrm{Ph_3CCl}$ to form $\mathrm{H_2SiMes(Cl)}$, which was then reacted with LiSEt to form $\mathrm{H_2SiMes(SEt)}$.[41] GC/MS (EI) parent ion: m/e 210. ^{1}H NMR (dichloromethane-d_2): δ 1.34 (t, $J = 8$ Hz, 3 H, $\mathrm{SCH_2C}H_3$), 2.34 (s, 3 H, Mes), 2.60, (s, 6 H, Mes), 2.66 (q, $J = 8$ Hz, 2 H, $\mathrm{SC}H_2\mathrm{CH_3}$), 5.22 (s, 1 H, SiH), 6.95 (s, 2 H, Mes). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ 18.18 ($\mathrm{SCH_2}C\mathrm{H_3}$), 21.40 ($\mathrm{S}C\mathrm{H_2CH_3}$), 23.50 (Mes), 23.68 (Mes), 128.79, 141.10, 145.29 (aryl carbons). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ −37.35 (s).

$[\mathrm{Cp^*(Me_3P)_2RuH(SiH_2Mes)}][\mathrm{BPh_4}]$ (36). $[\mathrm{Cp^*(Me_3P)_2Ru(NCMe)}][\mathrm{BPh_4}]$ (0.020 g, 0.027 mmol) was combined with $\mathrm{H_3SiMes}$ (0.005 mL, 0.029 mmol) in dichloromethane-d_2, and a small amount of new product was observed (8% by ^{1}H and ^{31}P NMR spectroscopy, 2 h) with spectroscopic characteristics consistent with **36**. ^{1}H NMR (dichloromethane-d_2): δ −11.23 (t, $J_{\mathrm{PH}} = 9$ Hz, 1 H, RuH), 1.48 (vir t, 18 H, PMe_3), 1.66 (s, 15 H, $\mathrm{C_5}Me_5$), 2.49 (s, 3 H, Mes), 2.49 (s, 6 H, Mes), 4.69 (t, $J = 8$ Hz, 2 H, SiH_2Mes). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (dichloromethane-d_2): δ −0.50. The silane $\mathrm{HSi(SEt)_3}$ was added to the reaction above (0.011 g, 0.060 mmol), and after 6 days the reaction mixture was found to contain $\mathrm{H_2SiMes(SEt)}$ as the main SiH- and mesityl-containing product (90%, by ^{1}H and ^{29}Si NMR spectroscopy).

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Supporting Information Available: Crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **24** and **32b**·$\mathrm{CH_2Cl_2}$ (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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