

Synthesis and Study of the Ruthenium-Silene Complexes (η^5 -C₅Me₅)(PR₃)RuH(η^2 -CH₂=SiR'₂) (R = ⁱPr, Cy; R' = Me, Ph)

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Abstract: The silene complexes Cp*(PR₃)RuH(η^2 -CH₂=SiR'₂) (Cp* = η^5 -C₅Me₅; 3: R = ⁱPr, R' = Me; 4: R = Cy (cyclohexyl), R' = Me; 5: R = ⁱPr, R' = Ph; 6: R = Cy, R' = Ph) have been obtained by reaction of the appropriate ClMgCH₂SiHR'₂ reagent with Cp*(PR₃)RuCl. Chemical and physical properties for these compounds are reported, including the X-ray structure for 5, which reveals geometric parameters (Ru-Si = 1.78(2) Å; sum of angles about Si = 344°) that are consistent with significant sp² character at silicon. Compound 5 thermally decomposes in solution

to the cyclometalated product Cp*Ru[ⁱPr₂P(CMeH)CH₂](H)(SiMePh₂), isolated as a 7:1 mixture of diastereomers (7a and 7b). The crystal structure of 7a was determined. Compounds 4 and 6 undergo thermolysis to the dicyclohexyl-(cyclohexenyl)phosphine complex Cp*RuH[Cy₂P(η^2 -C₆H₉)] (8), with elimination of HSiMeR₂ (R = Me or Ph). A kinetic and mechanistic study of the conversion of 5 to 7 indicates that the rate-limiting step is rotation of the silene fragment, to place the silene carbon atom near the migrating hydride ligand, and that the rotation and migration steps are irreversible. Compound 5 reacts with PMe₂R (R = Me, Ph) via hydride migration to the silene carbon atom and phosphine exchange to afford Cp*(PMe₂R)₂RuSiMePh₂ (9, R = Me; 10, R = Ph). Mechanistic studies show that this reaction occurs via two pathways, involving irreversible migration of hydride to the silene carbon atom and reversible migration of hydride to silicon. The latter process appears to lead to Cp*(PMe₃)RuH(η^2 -CH₂=SiPh₂), which rearranges rapidly to Cp*(PMe₃)RuSiMePh₂. Thus, Cp*(PMe₃)₂RuCH₂SiHPh₂ (11) is not a kinetic product of the reaction, as demonstrated by its independent synthesis and study. The reaction of 5 with carbon monoxide proceeds in a similar manner, via both hydrogen-migration manifolds, to Cp*(PⁱPr₃)(CO)RuCH₂SiHPh₂ (12) and Cp*(PⁱPr₃)(CO)RuSiMePh₂ (13). The reaction of 5 with hydrogen can also be explained by a mechanism involving two hydride-migration pathways, to give Cp*(PⁱPr₃)RuH₃ (14) and HSiMePh₂ (via trapping of Cp*(PⁱPr₃)RuCH₂SiHPh₂), and Cp*(PⁱPr₃)RuH₂(SiMePh₂) (15, via trapping of Cp*(PⁱPr₃)RuSiMePh₂). Compound 15 may also be obtained by hydrogenation of 7. The reaction of 5 with COS leads to cleavage of the C-S bond and formation of Cp*(PⁱPr₃)(CO)RuSSiMePh₂ (16). Electrophiles Me₃SnCl and HCl appear to react with 5 via initial electrophilic attack at ruthenium, but different migration processes are observed to occur. Thus, the reaction with Me₃SnCl gives principally Cp*(PⁱPr₃)RuCl and Me₃SnCH₂SiHPh₂. The reaction with HCl produces ClSiMePh₂, 7, Cp*(PⁱPr₃)RuCl, and 14. Mechanisms for the above reactions are discussed.

Silenes (R₂C=SiR'₂) are inherently reactive species that play an important role in organosilicon chemistry.¹⁻⁴ The first compelling evidence for the existence of a silene was presented by Flowers and Guse'lnikov, who were able to trap transient H₂C=SiMe₂ after its formation by pyrolysis of 1,1-dimethylsilacyclobutane.² A more recent resurgence of interest in silenes has been stimulated by the isolation of compounds such as (Me₃-Si)₂Si=C(OSiMe₃)(1-adamantyl)³ and Me₂Si=C(SiMe^tBu₂)-(SiMe₃),⁴ which are stabilized toward dimerization by steric protection of the reactive C=Si double bond.

Given the well-established ability of transition-metal fragments to stabilize and modify the chemistry of species via coordination, transition-metal-silene complexes seem to offer rich possibilities for new reaction pathways involving organosilicon compounds. In fact, silene complexes have often been invoked to explain metal-mediated reactions of organosilicon species.^{5,6} Of particular note is the recent report by Procopio and Berry that ruthenium complexes catalyze the dehydrocoupling of Me₃SiH to oligomeric polycarbosilanes, probably via intermediate silene complexes.⁷ A transition-metal-silene complex was first suggested by Pannell

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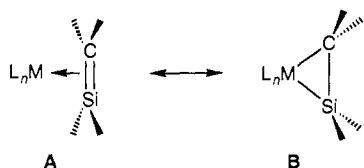
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to explain the reaction of $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SiHMe}_2$ with PPh_3 , to give $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeSiMe}_3$.^{6a} More recently, Randolph and Wrighton have reported spectroscopic evidence for the existence of $\text{Cp}^*(\text{CO})\text{FeH}(\eta^2\text{-CH}_2\text{=SiMe}_2)$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) at low temperature. The latter species, obtained by near-UV photolysis of $\text{Cp}^*(\text{CO})_2\text{FeCH}_2\text{SiHMe}_2$ in the presence of L (L = CO or PPh_3), was stable to 225 K but was transformed at higher temperatures to $\text{Cp}^*(\text{CO})(\text{L})\text{FeSiMe}_3$.⁸

The investigations cited above strongly indicated that silenes might be stabilized significantly by coordination to a metal fragment. This stability would appear to result from reduction of the Si=C bond order via π -backbonding to the silene π^* orbital, as described by resonance form B. We have therefore concen-

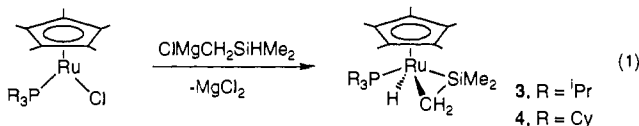


trated on electron-rich (strongly π -donating) metal fragments such as $\text{Cp}^*(\text{PR}_3)(\text{H})\text{Ru}$ and $\text{Cp}^*(\text{PMe}_3)\text{Ir}$, in attempts to synthesize stable silene complexes that can be thoroughly investigated. We have previously communicated use of β -hydrogen transfer in $\text{M-CH}_2\text{SiHR}_2$ complexes for the preparation of stable silene complexes of both fragments.^{9,10} The synthesis and structure of a tungsten-silene complex, $\text{Cp}_2\text{W}(\eta^2\text{-CH}_2\text{=SiMe}_2)$, has also been reported by Berry.¹¹ More recently, Ando and co-workers have reported stable η^4 -silyltrimethylenemethane complexes $[\eta^4\text{-Mes}_2\text{SiC}(\text{CH}_2)_3\text{CH}^t\text{Bu}]\text{M}(\text{CO})_3$ (M = Fe, Ru; Mes = mesityl).¹² Here we describe studies on the synthesis and reactivity of ruthenium silene complexes $\text{Cp}^*(\text{PR}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiR}'_2)$ (R = ⁱPr, Cy (cyclohexyl); R' = Me, Ph).

Results and Discussion

Preparation and Characterization of η^2 -Silene Complexes.

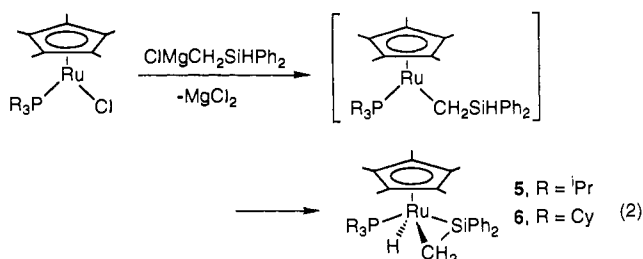
Reactions of the coordinatively unsaturated complexes $\text{Cp}^*(\text{PR}_3)\text{RuCl}$ (**1**, R = ⁱPr; **2**, R = Cy)¹³ with $\text{ClMgCH}_2\text{SiHMe}_2$ in diethyl ether were initiated at -78°C and then allowed to warm to room temperature. Rapid workup afforded the yellow crystalline products **3** and **4**, which exhibit similar ¹H NMR spectra that are consistent with the η^2 -silene structures shown in eq 1. These spectra contain peaks assigned to Cp^* , PR_3 , hydride,



and inequivalent methylene hydrogens and methyl groups for the silene ligand. Further characterization of these compounds was hindered by their thermal instability. Complex **3** rapidly decomposes in benzene-*d*₆ solution (*t*_{1/2} = ca. 50 min at 23 °C). Complex **4** exhibits a similar rate of decomposition in solution and completely decomposes in the solid state within 1 week.

More stable silene complexes are obtained via introduction of the diphenylsilylmethyl group. Diethyl ether solutions of

$\text{ClMgCH}_2\text{SiHPh}_2$ and $\text{Cp}^*(\text{PR}_3)\text{RuCl}$ were combined at -78°C , and the resulting mixtures were allowed to warm to room temperature to afford silene complexes $\text{Cp}^*(\text{PR}_3)\text{Ru}(\text{H})(\eta^2\text{-CH}_2\text{-SiPh}_2)$ (**5**, R = ⁱPr; **6**, R = Cy), isolated as yellow crystals in ca. 75% yield. Compounds **5** and **6** are stable under nitrogen in the solid state for months. Apparently, these reactions proceed via 16-electron alkyl complexes, which undergo rapid β -hydrogen elimination to give the observed silene complexes. Monitoring the formation of **5** by variable-temperature ³¹P NMR spectroscopy (in toluene-*d*₈) revealed the presence of a transient resonance at δ 43.26, which slowly gave way to product at -30°C . We assign this resonance to the intermediate alkyl complex shown in eq 2 (for R = ⁱPr).



As expected, the ¹H NMR spectra for **5** and **6** contain resonances for inequivalent phenyl groups. The methyl groups of the P^iPr_3 ligand of **5** give rise to two resonances, due to chirality at the ruthenium center. A characteristic feature of the ¹H NMR spectra for **3-6** is the ABX spin pattern exhibited by the inequivalent methylene hydrogens of the silene ligand. For **5**, these hydrogens appear as multiplets of equal intensity at δ 0.22 (H_a) and 0.42 (H_b) (Figure 1a). A computer simulation of this region of the spectrum (Figure 1b) provided the coupling constants ²*J*_{HaHb} = -9.81, ³*J*_{PHa} = -0.08, and ³*J*_{PHb} = 9.93 Hz. Therefore, as described previously for complexes of the type $\text{Cp}(\text{CO})(\text{PPh}_3)\text{-FeCH}_2\text{R}$,¹⁴ two different H-C-M-P dihedral angles result in one large and one very small ³*J*_{PH} coupling constant. The observed ²*J*_{HH} coupling constant in **5** is nearly identical in magnitude to that of 10 Hz reported for $\text{Cp}^*(\text{CO})\text{FeH}(\eta^2\text{-CH}_2\text{SiMe}_2)$.⁸

The ¹³C chemical shift for the silene carbon atom (δ -29.04) is considerably upfield compared to shifts for olefinic carbon atoms in the analogous complexes $\text{Cp}(\text{PPh}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=CH}_2)$ (δ 20.73)¹⁵ and $[(\eta^6\text{-C}_6\text{Me}_6)(\text{PPh}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=CH}_2)]^+$ (δ 41.55).¹⁶ This chemical shift difference may be attributed largely to the influence of silicon substitution, which gives rise to resonances at higher field. This effect is demonstrated by comparing the ¹³C chemical shifts for the ruthenium-bound carbon atoms in $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{CMe}_3$ (δ 19.6) and $\text{Cp}^*(\text{PMe}_3)_2\text{-RuCH}_2\text{SiMe}_3$ (δ -22.8).¹⁷ The ¹*J*_{CH} coupling constant for the coordinated =CH₂ group of **5** (143.3 Hz) is intermediate between values for free ethylene (156.2 Hz) and methane (125.0 Hz),¹⁸ which suggests significant sp² character for the silene carbon atom. For comparison, the ethylene complex $\text{Cp}^*(\eta^2\text{-CH}_2\text{=CH}_2)\text{Ru}(\mu\text{-}\eta^1,\eta^2\text{-CH=CH}_2)_2\text{RuCp}^*$ exhibits ¹*J*_{CH} coupling constants of 157 and 151 Hz.¹⁹ Structural and NMR parameters for the three crystallographically characterized η^2 -silene complexes are collected in Table I.

Absorptions for the Ru-H bonds of **3-6** were not observed in infrared spectra. Also, infrared stretches for the Ru-D bonds of $\text{Cp}^*(\text{PR}_3)\text{RuD}(\eta^2\text{-CH}_2\text{SiPh}_2)$ (**5-d**, R = ⁱPr; **6-d**, R = Cy) could

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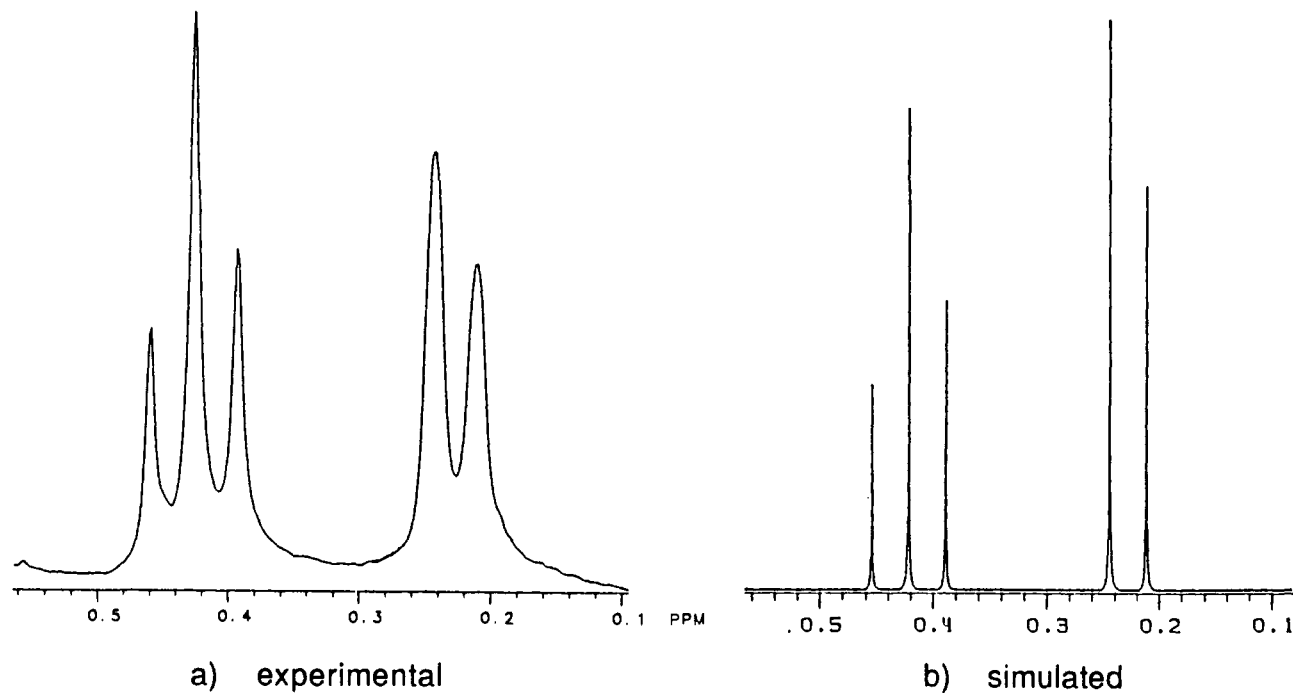


Figure 1. (a) Observed ^1H NMR resonance for the methylene group of **5**. (b) Simulated ^1H NMR resonance for the methylene group of **5**.

Table I. Comparison of Physical Properties for the Three Crystallographically Characterized Silene Complexes

| compd | ^{29}Si NMR, δ | ^{13}C NMR, δ (silene ligand) | $^1J_{\text{CH}}$ (Hz) (silene ligand) | $d(\text{C}-\text{Si})$, Å | $\Sigma(\angle\text{R}-\text{Si}-\text{R}')$, deg | ref |
|---|--------------------------------|---|--|-----------------------------|--|--------------|
| $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\eta^2\text{-CH}_2\text{SiPh}_2)$ | 6.14 | -29.04 | 143 | 1.78(2) | 343 | ^a |
| $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^2\text{-CH}_2\text{SiPh}_2)$ | -20.77 | -33.37 | 142 | 1.810(6) | 341 | 10 |
| $\text{Cp}_2\text{W}(\eta^2\text{-CH}_2\text{SiMe}_2)$ | -15.77 | -41.07 | 137 | 1.800(8) | 340 | 11 |

^a This work.

not be identified. Similar observations were made for $\text{Cp}^*(\text{CO})\text{-FeH}(\eta^2\text{-CH}_2\text{=SiMe}_2)$ by Wrighton and Randolph, who suggested that perhaps the $\nu(\text{FeH})$ absorption to the metal is incomplete.⁸ To address the latter possibility of an $\eta^2\text{-H-Si}$ structure (three-centered Ru-H-Si bonding interaction), a gated ^{29}Si NMR spectrum was obtained for **5**, since several studies have shown that $^2J_{\text{HMSi}}$ coupling constants for such structures fall within the 40–80-Hz range.⁵ This spectrum contains a multiplet centered at 6.14, which is intermediate between ^{29}Si chemical shift values found for stable silenes (δ 40–50)²⁰ and for silacyclopropanes (ca. δ -60).²¹ The largest apparent coupling constant (ca. 21 Hz) may be assigned as either $^2J_{\text{PSi}}$ or $^2J_{\text{HRuSi}}$. The iron–silyl complex $(\text{CO})_4\text{FeH}(\text{SiPh}_3)$, which does not have a direct Si-H bond, was found to have a $^2J_{\text{HFesi}}$ coupling constant of 20 Hz.²² Thus, it appears that little if any $\text{Si}\cdots\text{H}$ interaction exists in **5**.²³

An ORTEP view of one of the two enantiomers in the asymmetric unit of **5** is shown in Figure 2, and relevant geometric parameters are listed in Table II. Bond angles about Ru indicate that the hydride ligand is *cis* to the ligated silicon atom, as expected for β -hydrogen transfer from the Si-H group. Of particular interest are the Si-CH_2 distances in the silene ligand, 1.78(2) and 1.79(2) Å, which seem to reflect partial double bond character since Si-C single bond distances normally range from 1.87 to 1.91 Å.²⁴ As expected, these distances are somewhat longer than Si=C double bond distances observed for free silenes. The

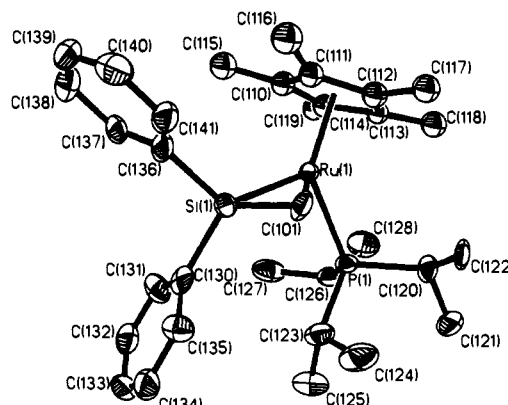


Figure 2. ORTEP view of $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiPh}_2)$ (**5**).

heteroatom-substituted silene $(\text{Me}_3\text{Si})_2\text{Si=C}(\text{OSiMe}_3)(1\text{-adamantyl})$ has a Si=C distance of 1.764(3) Å,^{3c} which is longer than values observed for both $\text{Me}_2\text{Si=C}(\text{SiMe}_3)(\text{SiMe}^t\text{Bu}_2)$ (1.702(5) Å)^{4d} and its tetrahydrofuran complex $(\text{THF})\text{Me}_2\text{Si=C}(\text{SiMe}_3)(\text{SiMe}^t\text{Bu}_2)$ (1.747(5) Å).^{4e} As shown by the data in Table I, the Si-C distances in all structurally characterized η^2 -silene complexes are comparable. The observed Ru-Si distances of 2.382(4) and 2.365(5) Å are relatively short and at the low end of the 2.34–2.51 Å range observed for other Ru-Si distances.⁵ Perhaps a better comparison is with the Ru-Si distance in $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiHPh}_2$, which is 2.387(1) Å.²⁵ The $\text{Ru-C}(1)$ distance

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(23) The structural similarities between **5** and $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\eta^2\text{-CH}_2\text{=SiPh}_2)$ (ref 10) further support this view.

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Table II. Selected Bond Distances and Angles for Cp*(PⁱPr₃)RuH(η²-CH₂=SiPh₂) (5)

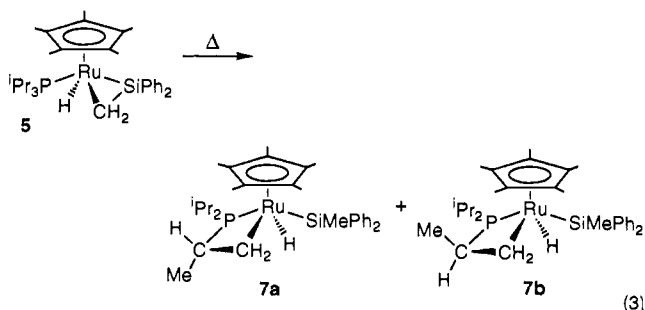
| | molecule A | molecule B |
|------------------------|------------|------------|
| (a) Bond Distances (Å) | | |
| Ru(1)–P(1) | 2.365(4) | 2.345(5) |
| Ru(1)–Si(1) | 2.382(4) | 2.365(5) |
| Ru(1)–C(101) | 2.25(2) | 2.26(1) |
| Si(1)–C(101) | 1.78(2) | 1.79(2) |
| Si(1)–C(136) | 1.88(2) | 1.90(2) |
| Si(1)–C(130) | 1.91(2) | 1.89(2) |
| (b) Bond Angles (deg) | | |
| Si(1)–Ru(1)–P(1) | 100.0(2) | 99.3(2) |
| C(101)–Ru(1)–P(1) | 90.9(4) | 91.3(4) |
| Si(1)–Ru(1)–C(101) | 45.2(5) | 45.4(4) |
| Si(1)–C(101)–Ru(1) | 71.3(7) | 70.2(5) |
| Ru(1)–Si(1)–C(101) | 63.5(5) | 64.3(5) |
| Ru(1)–Si(1)–C(130) | 124.3(5) | 127.9(5) |
| Ru(1)–Si(1)–C(136) | 120.8(6) | 119.1(6) |
| C(101)–Si(1)–C(130) | 120.7(8) | 119.7(8) |
| C(101)–Si(1)–C(136) | 119.3(10) | 119.5(7) |
| C(130)–Si(1)–C(136) | 104.6(8) | 103.4(7) |

in **5** (2.25(2) Å) is longer than comparable distances in the cationic ruthenium–ethylene complex (η⁶-C₆Me₆)(PPh₃)RuH(η²-CH₂-CH₂) (2.169(10) and 2.194(9) Å).¹⁶ The nonplanarity of the silene ligand (i.e., the bending back of the SiPh₂ fragment) can be described by the angle between the Si–C(101) bond and the Si, C(130), and C(136) plane, which is 36.2° (average for the two molecules). Another measure of silene character is the extent of pyramidalization at silicon, as described by the sum of the angles about silicon (344°), which falls between expected values for sp² (360°) and sp³ (329°) hybridization.

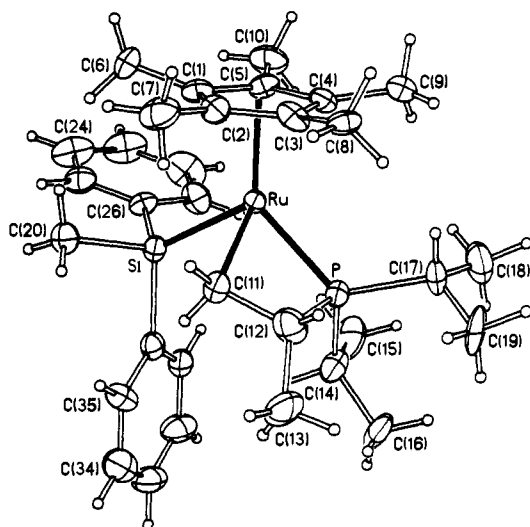
Thermolytic Decompositions of 3–6. In benzene-*d*₆ solution, the diphenylsilene complex **5** is considerably more stable (*t*_{1/2} = 5 h at 23 °C) than the analogous dimethylsilene complex **3** (*t*_{1/2} = 50 min at 23 °C). The thermal decomposition of **5** gives two products by ³¹P NMR spectroscopy (**7a**, δ 11.65; **7b**, δ 13.90) in a 7:1 ratio. This ratio is also observed for crystallized product, which gives a combustion analysis consistent with the formula for the starting silene complex.

Complexes **7a** and **7b** exhibit similar resonances in their NMR spectra. For the major product **7a**, three distinct methine PCH multiplets (δ 0.32, 1.97, and 2.69) could be distinguished for the phosphine ligand. The presence of a cyclometalated phosphine ligand was suggested by resonances for **7a** in the ¹³C NMR spectrum at δ –3.15 and 45.47. The related cyclometalated

complex (η⁶-C₆H₆)RuH[ⁱPr₂P(CMeH)CH₂], isolated as a 70:30 mixture of two diastereomers, exhibits similar ¹³C NMR resonances at δ –10.74 (RuCH₂) and 42.80 (PCHMe).²⁶ We therefore formulate **7a** and **7b** as the diastereomeric pair shown in eq 3.



These compounds, which appear to be in equilibrium, may be regarded as examples of alkyl/hydride/silyl complexes, which are exceedingly rare and of interest as intermediates in transition-

(26) Kletzin, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 873.**Figure 3.** ORTEP view of Cp*RuH(CH₂CHMePⁱPr₂)(SiMePh₂) (**7a**).**Table III.** Selected Bond Distances and Angles for Cp*RuH(CH₂CHMePⁱPr₂)(SiMePh₂) (**7a**)

| | molecule A | molecule B |
|------------------------|------------|------------|
| (a) Bond Distances (Å) | | |
| Ru–CNT ^a | 1.923(9) | 1.906(9) |
| Ru–P | 2.296(4) | 2.311(4) |
| Ru–Si | 2.403(4) | 2.396(4) |
| Ru–C(11) | 2.179(10) | 2.190(13) |
| C(11)–C(12) | 1.52(2) | 1.57(2) |
| C(12)–P | 1.821(13) | 1.818(12) |
| (b) Bond Angles (deg) | | |
| CNT–Ru–P | 131.1(4) | 130.3(4) |
| CNT–Ru–Si | 121.3(4) | 122.1(4) |
| CNT–Ru–C(11) | 121.3(5) | 121.5(5) |
| P–Ru–Si | 107.6(1) | 107.6(1) |
| P–Ru–C(11) | 66.5(4) | 66.7(4) |
| Si–Ru–C(11) | 78.6(4) | 77.8(4) |
| Ru–P–C(12) | 89.3(5) | 91.0(5) |
| P–C(12)–C(11) | 94.1(8) | 93.6(8) |
| Ru–C(11)–C(12) | 102.5(8) | 102.9(8) |

^a CNT is the centroid of the Cp* ring.

metal catalyzed hydrosilylation.²⁷ Heating a solution of the **7a**/**7b** equilibrium mixture above 70 °C resulted in further decomposition to a mixture of products including HSiMePh₂ (¹H NMR spectroscopy).

An X-ray structure determination definitively defined the structure of **7a** (Figure 3). Relevant distances and angles are collected in Table III. The structural parameters for this molecule are in general comparable to those for related molecules.^{5,25} The Ru–Si bond length of 2.40 Å (average) is only slightly longer than the Ru–Si bond length in **5**.

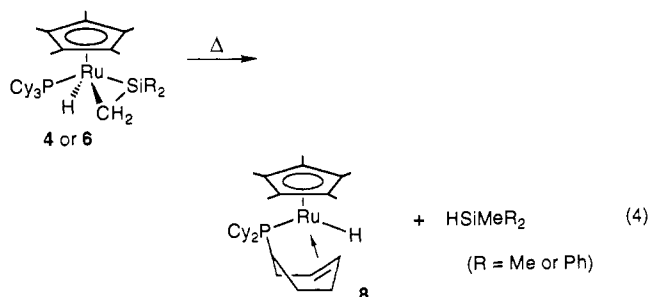
Complex **6** exhibits enhanced thermal stability with respect to **4** in benzene-*d*₆ solution (60% decomposition after 19 h at room temperature). Compounds **4** and **6** cleanly decompose to the same ruthenium hydride species (**8**), with elimination of HSiMe₃

(27) (a) Harrod, J. F.; Chalk, A. J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York 1977; Vol. 2, p 673. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *85*, 16. (d) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *85*, 1133. (e) Sietz, F.; Wrighton, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (f) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345. (g) Ruiz, J.; Bentz, P. O.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2709. (h) Duckett, S. B.; Haddleton, D. M.; Jackson, S. A.; Perutz, R. N.; Poliakoff, M.; Upmacis, R. K. *Organometallics* **1988**, *7*, 1526. (i) Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056. (j) Caseri, W.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 259. (k) Fernandez, M. J.; Esteruelas, M. A.; Oro, L. A.; Apreda, M.-C.; Focus-Focus, C.; Cano, F. H. *Organometallics* **1987**, *6*, 1751. (l) Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1372.

Table IV. Crystal and Refinement Data for **5** and **7a**

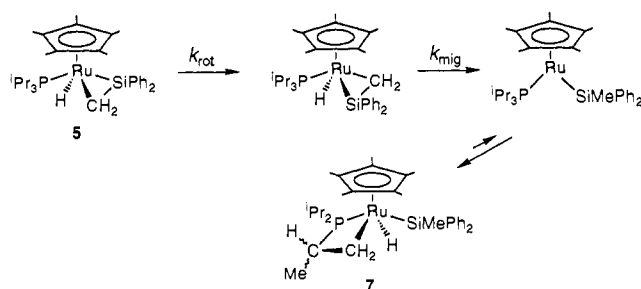
| | 5 | 7a |
|---|--|---------------------------------------|
| (a) Crystal Parameters | | |
| formula | C ₃₂ H ₄₉ PRuSi | C ₃₂ H ₄₉ PRuSi |
| formula weight | 593.87 | 593.87 |
| space group | P2 ₁ /c | P $\bar{1}$ |
| a, Å | 10.298(5) | 10.936(2) |
| b, Å | 41.51(2) | 16.193(3) |
| c, Å | 14.901(10) | 19.482(4) |
| α , deg | | 107.21(1) |
| β , deg | 108.29(5) | 93.012(1) |
| γ , deg | | 106.04(1) |
| V, Å ³ | 6047(6) | 3133.2(10) |
| Z | 8 | 4 |
| cryst dimens, mm | 0.4 × 0.4 × 0.5 | 0.26 × 0.28 × 0.42 |
| cryst color | yellow | pale yellow |
| D(calc), g cm ⁻³ | 1.305 | 1.259 |
| temp, K | 194 | 294 |
| (b) Data Collection | | |
| diffractometer | Nicolet R3m/V | Nicolet R3m |
| monochromator | graphite | graphite |
| radiation | MoK α (λ = 0.71073 Å) | MoK α (λ = 0.71073 Å) |
| 2 θ scan range, deg | 3–50 | 4–45 |
| data collected | 0 to 12, –1 to 49, (h, k, l) –17 to 16 | ±12, ±18, +21 |
| rflns collected | 10825 | 8447 |
| indpt rflns | 9815 | 8157 |
| R(merg), % | 11 | 2 |
| indpt obsvd rflns, F _o > σ (F _o) | 5086 (n = 6) | 5609 (n = 4) |
| std rflns | 3 std/50 data | 3 std/197 data |
| var in stds | <1 | <1 |
| (c) Refinement | | |
| R(F), % | 9.79 | 7.12 |
| R(wF), % | 12.19 | 7.94 |
| Δ/σ (max) | 0.04 | 0.09 |
| $\Delta(\rho)$, e Å ⁻³ | 1.7 | 2.1 |
| N _o /N _v | 9.6 | 9.7 |
| GOF | 2.45 | 1.65 |

and HSiMePh₂, respectively (eq 4). Colorless crystals of **8** from pentane gave spectroscopic and combustion analyses consistent with the formula Cp*₂Ru(H)P(C₆H₁₁)₂(C₆H₉). The ¹H NMR



spectrum of **8** contains a Ru–H resonance (δ –12.56) which appears as a doublet of doublets with ²J_{PH} = 39 Hz and J = 2 Hz (the latter coupling constant is possibly due to coupling with a vinylic hydrogen²⁸). This ²J_{PH} coupling constant is similar to ²J_{PH} values found for Cp(PPh₃)RuH(CH₂=CRR') complexes (37–39 Hz).¹⁵ The structural assignment for **8** as a dicyclohexyl-(cyclohexenyl)phosphine complex is based largely on the gated ¹³C NMR spectrum (benzene-*d*₆), which revealed doublet resonances for the phosphine ligand at δ 52.29 (¹J_{CH} = 156.5 Hz) and δ 43.32 (¹J_{CH} = 150.5 Hz). Clearly, these large coupling constants correspond to carbon atoms that possess considerable sp² character, which are identified as coordinated olefinic carbon atoms.^{28,29} The recently reported complex [Cp*₂Ru{(η²-C₆H₉)P(C₆H₁₁)₂}]⁺BF₄[–] contains a similarly dehydrogenated cyclohexyl group.²⁸

Scheme I



We were unable to observe an intermediate analogous to complex **7** during the formation of **8**. Presumably, the greater steric bulk of the PCy₃ ligand effectively promotes reductive elimination of silane from an intermediate Cp*{P(C₆H₁₀)(C₆H₁₁)₂}Ru(H)SiMePh₂ complex. The instability of the latter intermediate could also be explained by the facility with which a second intramolecular C–H activation can occur for the cyclohexyl groups of **4** and **6**.

The above thermolyses occur via migration of hydrogen from ruthenium to the methylene carbon of the silene ligand, as determined by deuterium-labeling experiments. The deuterides Cp*(PⁱPr₃)RuD(η²-CH₂SiPh₂) (**5-d**) and Cp*(PCy₃)RuD(η²-CH₂SiPh₂) (**6-d**) were prepared by reaction of the appropriate ruthenium chlorides with ClMgCH₂SiDPh₂. After 3 h at 90 °C (benzene-*d*₆), **6-d** decomposed cleanly to **8** and HSi(CD₂)Ph₂, as determined by ¹H and ²H NMR spectroscopy. Under similar conditions, **5-d** decomposes to Cp*{PⁱPr₂PCHMeCH₂}RuH[Si(CH₂D)Ph₂].

The thermal decomposition of complexes **3–6** therefore appears to involve migration of hydride to produce 16-electron intermediate silyl complexes Cp*(PR₃)RuSiMeR'₂, which then undergo cyclometalation to the final product, as depicted in Scheme I for **5**. Furthermore, since the hydride ligand and the silene carbon atom are *trans* to one another in the starting silene complexes, the hydrogen migration must be preceded by molecular motion that places these two atoms in neighboring (*cis*) positions. This motion (*k*_{rot}) could primarily involve rotation about the ruthenium–silene bond or a “pseudorotation” about ruthenium. For reasons given below, we propose that this rotation (or pseudorotation) is the rate-determining step in the thermal decomposition of **5** and that this step and the following hydride migration are essentially irreversible.

The rate of disappearance of **5** was monitored by ¹H NMR spectroscopy in benzene-*d*₆ at temperatures between 23 and 57 °C. These data established a first-order rate law for each temperature (Figure 4) and provided the activation parameters ΔH^\ddagger = 18(1) kcal/mol and ΔS^\ddagger = –17(3) eu (Figure 5). The thermolysis rates for **5-d** at 50 and 57 °C provided an isotope effect of 1.00.

If formation of the intermediate Cp*(PⁱPr₃)RuSiMePh₂ were reversible, exchange between the Ru–H and CH₂ hydrogens of the silene complex would be observed. However, NMR magnetization-transfer experiments failed to provide evidence for exchange between these sites. In search of a slower exchange process, we monitored a solution of **5-d** (benzene-*d*₆) to determine the degree to which deuterium label “washes” into the methylene position. After 24 h at 0 °C, followed by 1 h at 23 °C, a small amount of **7** had formed, but no Ru–H resonance could be detected. These two experiments lead us to conclude that during the thermal decomposition of **5** rapid hydrogen exchange between Ru–H and CH₂ does not occur and that hydrogen migration from ruthenium to carbon is irreversible. Furthermore, the lack of an isotope effect for the thermolysis is most consistent with *k*_{rot} as the rate-limiting step.

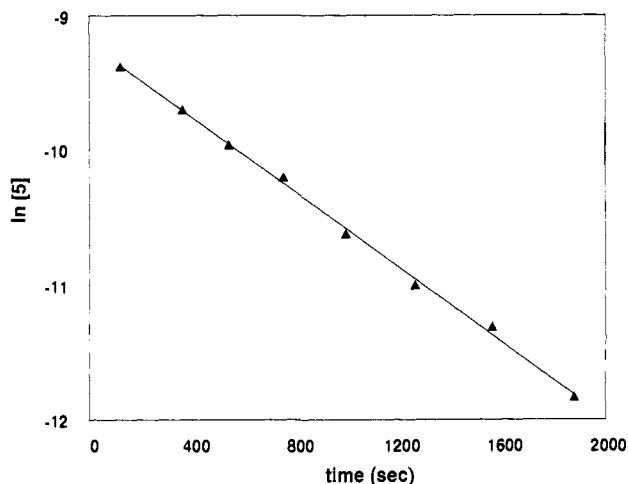


Figure 4. Representative kinetics plot for the thermolysis of **5** at 57 °C ($k = 1.4 (1) \times 10^{-3} \text{ s}^{-1}$). Other rate constants (s^{-1}): $k(24 \text{ °C}) = 6 (2) \times 10^{-5}$; $k(35 \text{ °C}) = 1.6 (2) \times 10^{-4}$; $k(45 \text{ °C}) = 4.8 (3) \times 10^{-4}$; $k(50 \text{ °C}) = 7.0 (7) \times 10^{-4}$.

In summary, the thermolysis reactions are best described as involving a rate limiting rotation, followed by relatively rapid migration and cyclization steps. The conversion of **5** to **7** therefore obeys a rate law that can be written as

$$\text{rate} = k_{\text{rot}}[\mathbf{5}]$$

This picture is supported by the observed stabilities of ruthenium-silene complexes, which parallel the expected barriers to rotation imposed by steric constraints. Thus, the diphenylsilene complexes **5** and **6** are much more stable than the corresponding dimethylsilene complexes **3** and **4**. In addition, **6** is more stable than **5**, and the analogous complex $\text{Cp}^*(\text{PMe}_3)\text{RuH}(\eta^2\text{-CH}_2=\text{SiPh}_2)$ is quite unstable (vide infra). The cyclization step in Scheme I must be rather rapid, since buildup of the intermediate $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$ during the formation of **7** is not observed (^1H NMR spectroscopy). However, the latter 16-electron silyl complex is in equilibrium with **7**, as indicated by reactions in which **7** serves as a synthetic equivalent for $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$ (vide infra).

Reactions of 5 with Phosphines PMe_2R ($\text{R} = \text{Me, Ph}$). Addition of excess PMe_2R ($\text{R} = \text{Me, Ph}$) to benzene- d_6 solutions of complex **5** results in quantitative conversion to the previously reported silyl $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiMePh}_2$ ²⁵ (**9**) and the new complex $\text{Cp}^*(\text{PMe}_2\text{Ph})_2\text{RuSiMePh}_2$ (**10**), respectively, with concomitant formation of free P^iPr_3 . Reaction rates were determined at 24 °C by ^{31}P NMR spectroscopy under pseudo-first-order conditions of excess PMe_2R (in benzene- d_6 solution). As expected, first-order dependence in **5** was established for both reactions (Figure 6), and for the reaction of **5-d** with PMe_3 . Slower rates for the latter reaction, compared to those for the corresponding reaction with **5**, result from a small isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.2$ for reactions with 30 equiv of PMe_3).

It seemed likely that these reactions occur via the unimolecular, rate-determining transformation of **5** to $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$, which is then trapped by the incoming phosphine. However, the kinetic behavior of these reactions is different from that of the thermolysis, and to our surprise the rates proved to be dependent on the initial phosphine concentration. For all three reactions, plots of $[\text{PMe}_2\text{R}]$ vs observed rate constants k_{obs} were linear, but did not intercept the origin (Figure 7). Therefore simple uni- or bimolecular processes are not operating, and the kinetic behavior of these reactions is consistent with competing first- and second-order pathways, where the first-order rate constant is given by the intercept ($[\text{PMe}_2\text{R}] = 0$) in Figure 7.³⁰ This intercept, at $9(1) \times 10^{-5} \text{ s}^{-1}$, is similar to the first-order rate constant for thermal decomposition of **5**, $6(2) \times 10^{-5} \text{ s}^{-1}$ (k_{rot}). The intercepts

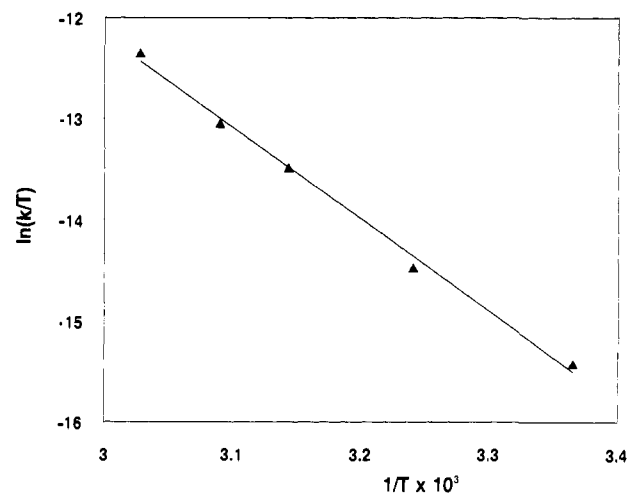


Figure 5. Eyring plot of the rate data for the thermolysis of **5**.

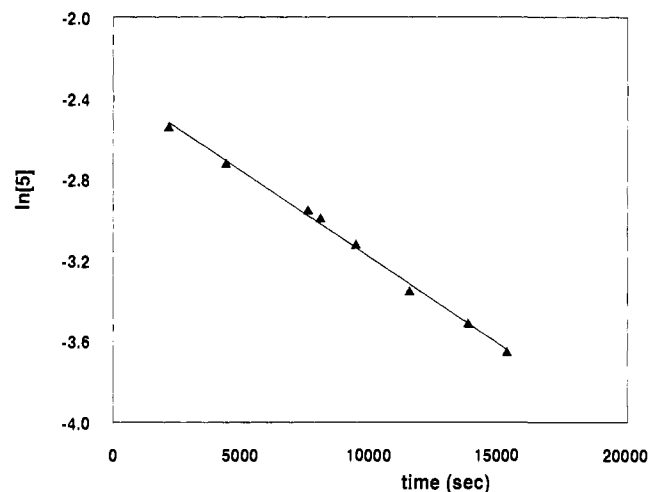


Figure 6. Representative kinetics plot for the reaction of **5** with PMe_2R . For this plot, $[\mathbf{5}]_0 = 0.098 \text{ M}$, $[\text{PMe}_2\text{Ph}] = 1.21 \text{ M}$, and temp = 24 °C.

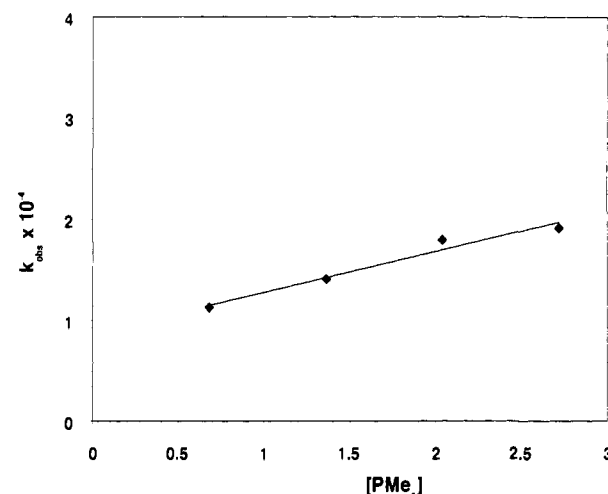
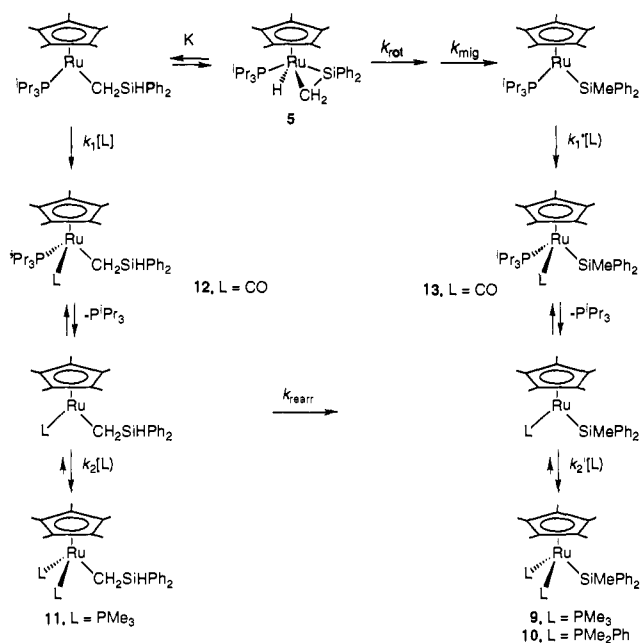


Figure 7. Plot of observed rate constants vs PMe_3 concentration for the reaction of **5** with PMe_3 .

from plots of k_{obs} vs $[\text{PMe}_2\text{R}]$ for all three reactions are similar, and average to $7(2) \times 10^{-5} \text{ s}^{-1}$.

Scheme II presents a mechanism that describes how **5** could react with an incoming ligand via competing first- and second-order pathways. This mechanism is based on two hydride-migration manifolds, via the 16-electron intermediates $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCH}_2\text{SiHPh}_2$ and $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$. The second-order behavior is explained by a preequilibrium involving

Scheme II

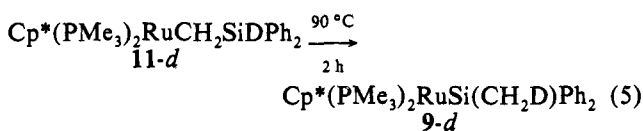


migration of hydride to the silene silicon. This could lead to a second-order rate term and a rate law of the form

$$\text{rate} = k_{\text{rot}}[\mathbf{5}] + Kk_1[\text{PMe}_2\text{R}][\mathbf{5}]$$

Of course, these reaction pathways give rise to two different products (e.g., alkyl **11** and silyl **9**), which is inconsistent with the results described above since only $\text{Cp}^*(\text{PMe}_2\text{R})_2\text{RuSiMePh}_2$ (**9** or **10**) were observed to form. Therefore, this scheme can account for the results only if an $\text{Ru}-\text{CH}_2\text{SiHPh}_2$ derivative along the reaction pathway rapidly rearranges to the corresponding $\text{Ru}-\text{SiMePh}_2$ silyl. Such a process would seem to be most facile for the sterically unhindered species $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiHPh}_2$, which could rearrange to $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiMePh}_2$ (k_{rearr} in Scheme II) via the silene hydride intermediate $\text{Cp}^*(\text{PMe}_3)_2\text{RuH}(\eta^2-\text{CH}_2=\text{SiPh}_2)$. Alternatively, $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiHPh}_2$ (**11**) is unstable and undergoes rapid conversion to **9** after it is formed.

To evaluate the stability of **11** at room temperature, we synthesized $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiDPh}_2$ (**11-d**) via the reaction of $\text{ClMgCH}_2\text{SiDPh}_2$ with $\text{Cp}^*(\text{PMe}_3)_2\text{RuCl}$, which gave the thermally stable product as analytically pure, yellow crystals from diethyl ether. Compound **11-d** is stable indefinitely at room temperature, but heating to 90°C in benzene- d_6 for 2 h results in clean rearrangement to $\text{Cp}^*(\text{PMe}_3)_2\text{RuSi}(\text{CH}_2\text{D})\text{Ph}_2$ (**9-d**, eq 5).



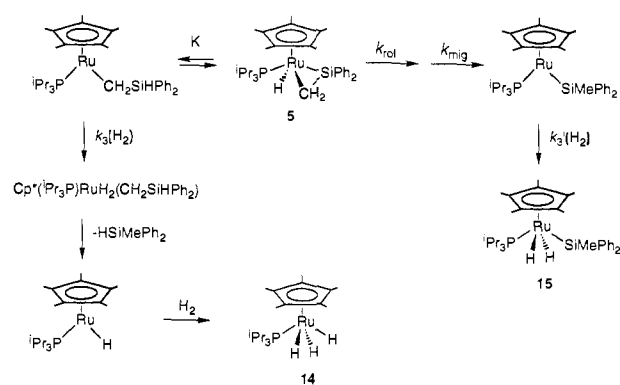
The conditions required for this reaction suggest dissociation of PMe_3 as the rate-determining step, in accordance with previous studies of the $\text{Cp}^*(\text{PMe}_3)_2\text{RuX}$ system.³¹ Therefore **11** is a stable compound and does not form kinetically in reactions of **5** with PMe_2R (at phosphine concentrations up to 3 M; 42 equiv). The absence of detectable quantities of **11** during the reaction of **5** with PMe_3 therefore appears to be due to rapid rearrangement of $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiHPh}_2$ to the corresponding silene hydride under the reaction conditions employed (that is, $k_{\text{rearr}} \gg$

(29) Hietkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347.

(30) Schneider, K. J.; van Eldik, R. *Organometallics* **1990**, *9*, 92 and references therein.

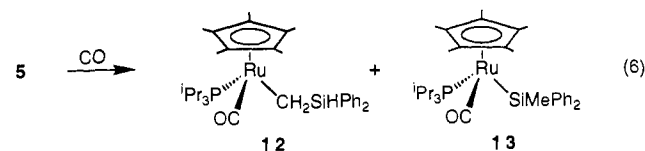
(31) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

Scheme III



$k_2[\text{PMe}_3]$). Consistent with this, **5** is converted in neat PMe_3 to both **9** and **11** in a 4:1 ratio. Thus, only at extremely high concentrations of PMe_3 is the trapping of $\text{Cp}^*(\text{PMe}_3)_2\text{RuCH}_2\text{SiHPh}_2$ (to give **11**) competitive with rearrangement to $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiMePh}_2$. Our inability to observe $\text{Cp}^*(\text{PMe}_3)_2\text{RuH}(\eta^2-\text{CH}_2=\text{SiPh}_2)$ during these reactions further illustrates the increased stability imparted to **3–6** by sterically bulky phosphine ligands.

Reaction of 5 with Carbon Monoxide. Complex **5** reacts with CO to give both $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{CO})\text{RuCH}_2\text{SiHPh}_2$ (**12**) and $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{CO})\text{RuSiMePh}_2$ (**13**) (eq 6). The inequivalent methylene



protons for **12** appear in the ^1H NMR spectrum (benzene- d_6) at $\delta -0.37$ (m) and -0.02 (m), and the Si–H hydrogen resonates at $\delta 5.40$ (m). Chirality at the metal center of **13** is reflected in diastereotopic methyl groups for the P^iPr_3 ligand and in inequivalent ortho phenyl protons. The carbonyl carbon atoms for **12** and **13** resonate at $\delta 212.34$ (d, $^2J_{\text{PC}} = 20.7$ Hz) and $\delta 213.88$ (d, $^2J_{\text{PC}} = 16.4$ Hz), respectively, in the ^{13}C NMR spectrum.

The ratio of the two products depends on the reaction conditions employed, in accordance with Scheme II. For example, addition of a slight excess of CO to a benzene- d_6 solution of **5** produced a 1:2 product ratio (**12**:**13**), with complete reaction within 24 h. Thus, even at low concentrations of CO, both hydrogen-migration products form competitively. When a diethyl ether solution of **5** was pressurized with CO (80 psi, $t_{1/2} = \text{ca. } 30$ min) for 1.5 h, a product ratio of 5:1 was observed. Therefore consistent with Scheme II, higher concentrations of CO favor formation of **12**.

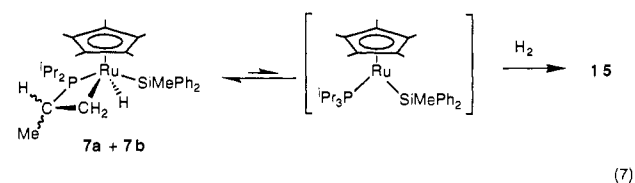
Neither product could be isolated in pure form via fractional crystallization. An attempt to independently synthesize **12** by reaction of $\text{ClMgCH}_2\text{SiHPh}_2$ with $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{CO})\text{RuCl}$ ¹³ resulted mainly in formation of the known ruthenium hydride $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{CO})\text{RuH}$ (90%),³² along with some **12** (ca. 5%) and two unidentified products (by ^1H and ^{31}P NMR spectroscopy). Thermolysis of **12** results in clean, quantitative formation of **13** (100°C ; $t_{1/2} = \text{ca. } 20$ min), presumably via the silene intermediate $\text{Cp}^*(\text{CO})\text{RuH}(\eta^2-\text{CH}_2\text{SiPh}_2)$. Complex **13** may also be prepared by reaction of **7** with CO.

Reaction of 5 with Hydrogen. The reaction of **5** with hydrogen also leads to formation of two ruthenium-containing products (Scheme III). Higher hydrogen pressures favor formation of the trihydride $\text{Cp}^*(\text{P}^i\text{Pr}_3)_2\text{RuH}_3$,³² presumably via trapping of the alkyl $\text{Cp}^*(\text{P}^i\text{Pr}_3)_2\text{RuCH}_2\text{SiHPh}_2$. Thus, after stirring a solution of **5** under a hydrogen atmosphere of 50 psi for 1.5 h, a 10:1 mixture of **14** to **15** was obtained. With a hydrogen pressure of

(32) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

10 psi, this product ratio decreased to 3:2. Exposure of the isolated product mixtures to more hydrogen does not change the product ratio, indicating that **15** is stable to further hydrogenation and that **14** and **15** are formed via different reaction pathways. Furthermore, hydrogenation (1 atm) of $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuD}(\eta^2\text{-CH}_2\text{-SiPh}_2)$ (**5-d**) revealed only ^2H NMR resonances for DSiMePh_2 and $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_2[\text{Si}(\text{CH}_2\text{D})\text{Ph}_2]$ (**15-d**) (benzene/benzene- d_6). No evidence was found for the formation of $\text{HSi}(\text{CDH}_2)\text{-Ph}_2$. Therefore, as might be expected, C–H reductive elimination from the presumed intermediate $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_2(\text{CH}_2\text{SiHPh}_2)$ is more facile than Si–H reductive elimination from **15**.

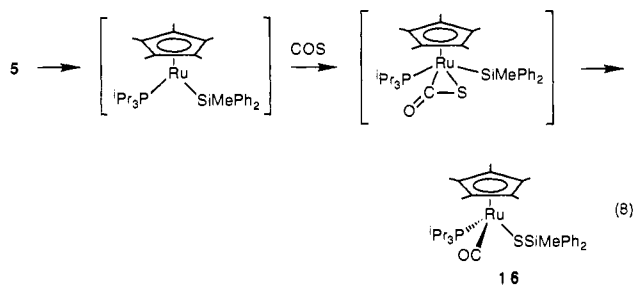
Hydrogenation of a **7a/7b** mixture gave only **15**, isolated in 76% yield as colorless crystals from diethyl ether/acetonitrile (eq 7; quantitative by NMR). The presence of a single Ru–H



resonance at $\delta = 12.17$ (d, $^2J_{\text{PH}} = 28.2$ Hz) for equivalent ruthenium hydride ligands suggests a *trans* piano-stool geometry for **15**, which presumably results from a pseudorotation process following oxidative addition of H_2 .

Reaction of 5 with Heterocumulenes. Upon prolonged stirring of **5** in diethyl ether under an atmosphere of CO_2 (40 psi), only the decomposition products of **5** (**7a** and **7b**) were isolated as product. On the other hand, the reaction of **5** with CS_2 (benzene- d_6) is quite rapid and produces a red solution containing five products which could not be characterized (by ^1H and ^{31}P NMR spectroscopy). A much cleaner reaction is observed between **5** and carbonyl sulfide. By ^1H and ^{31}P NMR spectroscopy, the reaction of 1 equiv of COS (g) with **5** (benzene- d_6) is complete within 24 h and quantitatively gives one product. Preparative scale reactions allow isolation of red-orange crystals from pentane. This new product contains a carbonyl ligand ($\nu_{\text{CO}} = 1909$ cm^{-1} ; $\delta(^{13}\text{C}) = 211.81$, d, $^2J_{\text{PC}} = 37$ Hz), resulting from cleavage of the C=S bond in COS. Further spectroscopic and analytical data allow formulation of the product as $\text{Cp}^*(\text{P}^i\text{Pr}_3)(\text{CO})\text{RuSSiMePh}_2$ (**16**).

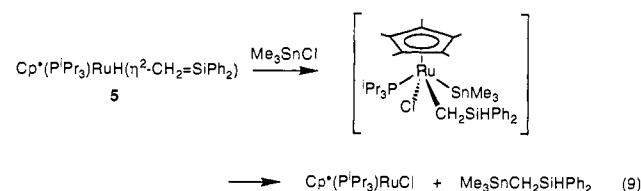
It therefore appears that COS selectively traps the hydrogen-migration product $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$ under these reaction conditions. Apparently, the latter intermediate binds COS to give $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{Ru}(\eta^2\text{-COS})\text{SiMePh}_2$, which undergoes C–S bond cleavage via migration of the silyl group to sulfur (eq 8). In this context, it is worth noting that Si–S bonds are ca. 7 kcal/mol stronger than C–S bonds³³ and that carbon–sulfur bond cleavage in $\eta^2\text{-COS}$ complexes is known to be facile.³⁴ The formation of **16** appears to represent the first example of COS insertion into a M–Si bond.



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Reaction of 5 with Electrophiles. Reactions of **5** with the electrophiles Me_3SnCl and HCl produce products resulting from migration of hydride to the silicon and carbon atoms of the silene ligand, respectively. With Me_3SnCl (1 equiv), the major products are $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCl}$ (**1**, isolated in 70% yield) and $\text{Me}_3\text{SnCH}_2\text{-SiHPh}_2$ (eq 9). The latter organotin compound was independently



synthesized from Me_3SnCl and $\text{ClMgCH}_2\text{SiHPh}_2$ and was characterized in solution by ^1H and ^{13}C NMR and IR spectroscopy. The Sn–C linkage is clearly evident from the ^1H NMR spectrum, in which the SnCH_2 protons appear as a doublet (δ 0.17, $^3J_{\text{HH}} = 4.8$ Hz) with Sn satellites ($^2J_{\text{SnH}} = 66$ Hz). For comparison, the $^2J_{\text{SnH}}$ coupling constant of the methylene protons in $\text{Me}_3\text{SnCH}_2\text{SnMe}_3$ is 63 Hz.³⁵

Baird and co-workers have characterized the reactions of electrophiles with $\text{Cp}^*(\text{CO})(\text{L})\text{OsR}$ (L = CO, PMe_2Ph ; R = Me, Et, ^iPr , CH_2Ph) and $\text{CpLL}'\text{RuR}$ (L, L' = CO, PPh_3 ; R = Me, CH_2Ph) complexes as proceeding via electrophilic attack at the metal and M^{IV} intermediates.³⁶ Similarly, stannylation of **5** could give $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCl}(\text{CH}_2\text{SiHPh}_2)(\text{SnMe}_3)$, possibly via the cationic complex $[\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiPh}_2)(\text{SnMe}_3)]^+\text{Cl}^-$, which could undergo migratory insertion to give the alkyl stannyl intermediate. Subsequent reductive elimination of $\text{Me}_3\text{SnCH}_2\text{SiHPh}_2$ would then produce **1**. No evidence for formation of $\text{ClCH}_2\text{SiHPh}_2$ was found.

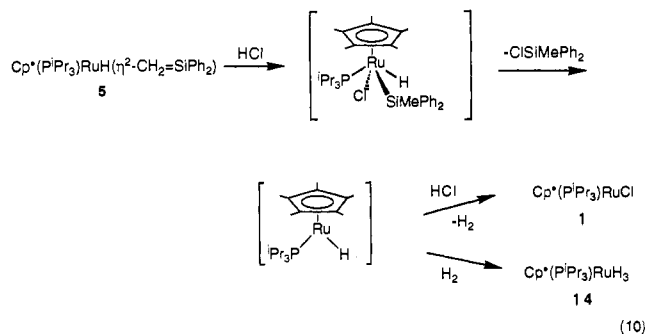
The reaction of HCl (2 equiv) with **5** is rapid (by ^1H and ^{31}P NMR spectroscopy; benzene- d_6), and gives ClSiMePh_2 , $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCl}$ (**1**), **7(a and b)**, $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_3$ (**14**) (roughly equal amounts of **1**, **7**, and **14**), and a small quantity of a ruthenium hydride complex that could not be identified (eq 10). The compounds HSiMePh_2 and $\text{ClCH}_2\text{SiHPh}_2$ were not detected in the reaction mixture. The products of Ru–Si bond cleavage (ClSiMePh_2 , **1**, and **14**) may be explained by a mechanism similar to that of eq 9 above, except that in this case migration of hydride to the methylene group occurs, to give $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\text{Cl})\text{-SiMePh}_2$. The formation of this intermediate would then be followed by rapid reductive elimination of ClSiMePh_2 to produce the highly reactive 16-electron ruthenium hydride intermediate. We have previously reported a related reductive elimination, of ClSiH_2Mes (Mes = 1,3,5- $\text{Me}_3\text{C}_6\text{H}_2$) from $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{-RuH}(\text{Cl})(\text{SiH}_2\text{Mes})$, which proceeds rapidly at room temperature. In contrast, $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\text{Cl})(\text{SiH}_2\text{Ph})$ does not lose $\text{ClSiH}_2\text{-Ph}$, even when heated at 90 °C for several hours.³⁷ This suggests that loss of chlorosilanes in this system is sterically driven. Oxidative addition of HCl to $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}$ could give the intermediate $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_2\text{Cl}$, which would rapidly lose H_2 to give **1**. Note that the reverse reaction, addition of H_2 to **1**, does not occur even under severe conditions (100 psi H_2).³⁸ The hydrogen generated by reductive elimination from $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_2\text{Cl}$ could then trap $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}$ to give $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}_3$.

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Conclusions

Use of electron-rich $\text{Cp}^*(\text{PR}_3)\text{HRu}$ fragments has permitted isolation of the first examples of stable transition-metal–silene complexes, which have provided considerable structural and chemical information. Initially, we reasoned that an electron-rich metal center would help stabilize a $\text{Si}=\text{C}$ double bond by acting as a strong π -donor, to significantly reduce the $\text{Si}-\text{C}$ bond order. However, spectroscopic and crystallographic data suggest that the silene ligand possesses significant double bond character. The stability of $\text{Cp}^*(\text{PR}_3)\text{RuH}(\eta^2\text{-CH}_2\text{SiR}'_2)$ complexes is very much a function of the ligand environment, with steric factors being most important. Kinetic studies indicate that the rate-determining step in the decomposition of these silene complexes is rotation of the silene ligand. Thus, increased steric congestion about the ruthenium center dramatically increases the thermal stability of the silene complexes.

Metal–silene complexes are potentially very important as intermediates in metal-catalyzed transformations of organosilane species. Two recent reports by Berry emphasize this point by providing strong evidence for involvement of silene complexes in an osmium-catalyzed H/D exchange between benzene- d_6 and alkyl silanes^{6b} and in the ruthenium-catalyzed dehydrocoupling of Me_3SiH to oligomeric polycarbosilanes $\text{Me}_3\text{Si}(\text{CH}_2\text{SiMe}_2)_n\text{H}$.⁷ For future development of catalytic reactions, it is important to learn (1) how organosilanes might give rise to silene ligands upon interaction with a transition metal and (2) what reaction pathways are open to a silene ligand. Berry's work indicates that silenes may form via β -hydrogen elimination from a $\text{M}-\text{SiMe}_3$ derivative. Our studies, on the other hand, show that for $\text{Cp}^*(\text{PR}_3)\text{RuH}(\eta^2\text{-CH}_2\text{SiR}'_2)$ complexes under *relatively mild conditions*, migration of hydrogen from ruthenium to carbon is an important and irreversible decomposition mode for the silene complex.

The interaction of **5** with various substrates has been shown to proceed via two manifolds of reactivity. Thus, depending on the nature of the reactant and the reaction conditions, either 16-electron $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCH}_2\text{SiHPh}_2$ or $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuSiMePh}_2$ intermediates are trapped. Reactions of **5** with phosphines, CO, and H_2 are consistent with the bimodal mechanisms of Schemes II and III. Electrophilic attack on **5** also appears to give rise to both migration reactions, but this is based on two examples (Me_3SnCl and HCl), and little mechanistic information is available. We have recently reported the selective reactions of **5** with 2 equiv of primary silanes ArSiH_3 ($\text{Ar} = \text{Ph}, p\text{-MeC}_6\text{H}_4$), to produce $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\text{SiH}_2\text{Ar})_2$ and HSiMePh_2 .³⁷ Based on deuterium-labeling studies, these reactions appear to proceed exclusively via migration of hydrogen to the silene silicon, and therefore the ArSiH_3 silanes are very efficient traps for $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCH}_2\text{-SiHPh}_2$. This suggests that oxidative addition of these silanes to the 16-electron ruthenium complex is extremely rapid and faster than the oxidative addition of hydrogen.

Experimental Section

All manipulations were performed using rigorously anaerobic and anhydrous conditions. Elemental analyses were performed by Pascher Mikroanalytisches Labor. Infrared spectra were recorded on a Perkin-

Elmer 1330 infrared spectrometer. ^1H (300 MHz), ^{29}Si (59.6 MHz), ^{13}C (75.5 MHz), and ^{31}P (121.5 MHz) NMR spectra were recorded with a GE QE-300 NMR spectrometer. These spectra were recorded at room temperature for benzene- d_6 solutions, unless otherwise indicated. Mass Spectral analyses were performed at the U.C. Riverside Mass Spectrometry Laboratory. Hydrogen (Linde Specialty Gases), CO (Linde Specialty Gases), HCl (Matheson), COS (Matheson), PMe_2Ph (Aldrich), Me_3SnCl (Aldrich), CO_2 (Liquid Carbonics), and CS_2 (Aldrich) were used as received. The compounds $\text{Cp}^*(\text{PR}_3)\text{RuCl}$ (**1** and **2**), ^{13}C $\text{MgCH}_2\text{-SiHMe}_2$,^{6c} and $\text{ClCH}_2\text{SiHPh}_2$ ³⁹ were prepared as reported in the literature. The Grignard $\text{ClMgCH}_2\text{SiHPh}_2$ was prepared using the procedure for $\text{ClMgCH}_2\text{SiHMe}_2$, and $\text{ClCH}_2\text{SiDPh}_2$ was prepared from $\text{ClCH}_2\text{SiCIPh}_2$ and LiAlD_4 (Aldrich).

$\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiMe}_2)$ (3**)**. To $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCl}$ (0.186 g, 0.43 mmol) in cold (-78°C) diethyl ether (15 mL) was added $\text{ClMgCH}_2\text{-SiHMe}_2$ via syringe (0.54 mL, 0.8 M in diethyl ether, 0.43 mmol). The cold bath was removed, and the solution was warmed to room temperature. After filtration, the volatiles were removed to give the product as a spectroscopically pure yellow solid in 75% yield (0.151 g, 0.32 mmol): ^1H NMR δ -12.84 (d, 1 H, $^2J_{\text{PH}} = 18$ Hz, RuH), -0.25 (m, 1 H, RuCH_2), -0.18 (m, 1 H, RuCH_2), 0.43 (s, 3 H, SiMe), 0.55 (s, 3 H, SiMe), 1.09 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.13 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.72 (s, 15 H, Cp^*), 1.82 (m, 3 H, PCH); $^{13}\text{C}\{^1\text{H}\}$ NMR δ -22.42 (d, $^2J_{\text{PC}} = 4$ Hz, RuCH_2), 11.47 (Cp^*), 20.24 (PCCH_3), 20.81 (PCCH_3), 27.10 (d, $^1J_{\text{PC}} = 16.1$ Hz, PCCH_3), 89.62 (s, Cp^*); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 66.55.

$\text{Cp}^*(\text{PCy}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiMe}_2)$ (4**)**. The Grignard $\text{ClMgCH}_2\text{-SiHMe}_2$ (0.89 mL, 1.20 M in diethyl ether, 1.07 mmol) was added to a cold (-78°C) diethyl ether (25 mL) solution of $\text{Cp}^*(\text{PCy}_3)\text{RuCl}$ (0.592 g, 1.07 mmol). The slush bath was removed, and the solution was allowed to warm to room temperature, at which time the volatiles were promptly removed. The crude yellow solid was taken up in pentane (1×50 mL, 1×10 mL), and the resulting solution was concentrated and cooled (-40°C) to give the product as thermally unstable, bright yellow microcrystals (mp $166\text{--}168^\circ\text{C}$; yellow to bluish-white solid at $120\text{--}135^\circ\text{C}$) in 42.3% yield (0.267 g): IR (Nujol, CsI , cm^{-1}) 1236 m, 1169 w, 1120 w, 1062 w, 1022 m, 1001 m, 889 s, 850 m, 809 s, 761 w, 639 m, 610 w, 509 m, 490 w sh, 410 w, 390 w, 375 w, 305 m; ^1H NMR δ -12.82 (d, 1 H, $^2J_{\text{PH}} = 18$ Hz, RuH), -0.34 (m, 1 H, RuCH_2), -0.16 (m, 1 H, RuCH_2), 0.52 (s, 3 H, SiMe), 0.55 (s, 3 H, SiMe), 1.09 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.13 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.21–1.98 (multiplets, 33 H, PCy_3), 1.76 (s, 15 H, Cp^*).

$\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiPh}_2)$ (5**)**. To a royal-blue diethyl ether (50 mL) solution of $\text{Cp}^*(\text{P}^i\text{Pr}_3)\text{RuCl}$ (1.01 g, 2.30 mmol) at -78°C was added $\text{ClMgCH}_2\text{SiHPh}_2$ (3.4 mL, 0.50 M in diethyl ether, 2.3 mmol) via syringe, and the solution was then allowed to warm to room temperature. The volatiles were removed after stirring for 10 min more, and the yellow solid was extracted with diethyl ether (3×40 mL). The extracts were collected in a precooled (-78°C) flask, then concentrated, and cooled (-40°C) to give the product as yellow crystals (mp $126\text{--}128^\circ\text{C}$) in 70% yield (0.96 g; two successive crystallizations): IR (Nujol, CsI , cm^{-1}) 1427 s, 1362 m, 1240 w, 1104 s, 1062 w, 1050 w, 1022 m, 880 m, 852 m, 740 m, 732 w sh, 718 s, 702 s, 631 m, 522 m, 486 s, 460 m, 405 m; ^1H NMR δ -11.64 (d, 1 H, $^2J_{\text{PH}} = 18$ Hz, RuH), 0.23 (m, 1 H, RuCH_2), 0.42 (m, 1 H, RuCH_2), 0.94 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.02 (dd, 9 H, $^3J_{\text{PH}} = 12$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.57 (s, 15 H, Cp^*), 1.63 (m, 3 H, PCH), 6.94–7.11 (m, 6 H, SiPh_2), 7.87–7.95 (m, 4 H, SiPh_2); $^{13}\text{C}\{^1\text{H}\}$ NMR δ -29.04 (d, $^2J_{\text{PC}} = 5.4$ Hz, RuCH_2), 11.47 (Cp^*), 20.15 (PCCH_3), 21.05 (PCCH_3), 27.10 (d, $^1J_{\text{PC}} = 16.4$ Hz, PCCH_3), 90.36 (d, $^3J_{\text{PC}} = 1.6$ Hz, Cp^*), 127.32, 128.24, 136.06, 136.34, 139.14, 140.46 (SiPh_2); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 63.58. Anal. Calcd for $\text{C}_{32}\text{H}_{49}\text{P}_3\text{SiRu}$: C, 65.87; H, 8.21; P, 5.01. Found: C, 64.72; H, 8.32; P, 5.21.

$\text{Cp}^*(\text{PCy}_3)\text{RuH}(\eta^2\text{-CH}_2\text{=SiPh}_2)$ (6**)**. A synthetic procedure analogous to that used for **5** was employed. $\text{Cp}^*(\text{PCy}_3)\text{RuCl}$ (0.20 g, 0.36 mmol) and $\text{ClMgCH}_2\text{SiHPh}_2$ (1.70 mL, 0.23 M in diethyl ether, 0.36 mmol) gave the product as yellow microcrystals (mp $134\text{--}135^\circ\text{C}$) that were isolated from diethyl ether and washed with cold (-78°C) pentane (to remove traces of HSiMePh_2). This procedure gave an isolated yield of 74% (0.187 g): IR (Nujol, CsI , cm^{-1}) 1429 s, 1302 m, 1271 m, 1222 w, 1201 w, 1183 w, 1174 m, 1157 w, 1126 m, 1108 s, 1070 m, 1030 m, 1009 m, 919 w, 900 m, 892 sh, 853 s, 760 m, 744 s, 733 s, 720 s, 708 s, 676 m, 511 m, 490 s, 463 m, 410 s, 387 s; ^1H NMR δ -11.69 (d, 1 H, $^2J_{\text{PH}} = 19$ Hz, RuH), 0.29 (m, 1 H, RuCH_2), 0.41 (m, 1 H, RuCH_2),

1.06–1.98 (m, 33 H, PCy₃), 1.63 (s, 15 H, Cp*), 7.02–7.12 (m, 6 H, SiPh₂), 7.86 (m, 2 H, SiPh₂), 8.10 (m, 2 H, SiPh₂); ¹³C{¹H} NMR δ –29.68 (d, ²J_{PC} = 4.4 Hz, RuCH₂), 27.12, 27.78, 30.37, 31.42 (PCy₃), 37.20 (d, ¹J_{PC} = 15 Hz, PCH), 90.61 (d, ³J_{PC} = 1.6 Hz, Cp*), 127.25, 127.79, 128.11, 135.19, 136.20, 136.88, 139.70, 140.70 (SiPh₂); ³¹P{¹H} NMR δ 50.03. Anal. Calcd for C₄₁H₆₁PSiRu: C, 68.96; H, 8.61; P, 4.34. Found: C, 68.51; H, 8.22; P, 4.28.

Cp*₂RuH(CH₂CH(CH₃)PⁱPr₂)(SiMePh₂) (7). Complex **5-d** (0.155 g, 0.261 mmol) was dissolved in diethyl ether (30 mL), and the resulting yellow solution was stirred for 12 h, resulting in a pale blue solution. After removing the volatiles *in vacuo*, the resulting blue oily residue slowly deposited crystals. A blue impurity was washed away with cold (–78 °C) pentane, and the white solid left behind was then dissolved in pentane (25 mL). After filtration, the solution was concentrated and cooled (–30 °C) to give the product as beige crystals (mp 133–134 °C) in 25% yield (0.04 g). Increased yields were obtained when the thermolysis was conducted in the presence of CO₂ (40 psi, 36% isolated yield) or Me₃SiH (3 equiv, 48% isolated yield): IR (CaF₂, benzene-*d*₆, cm^{–1}) 2960 s, 2900 s, 2070 m, 1426 w, 1374 br w, 1236; ¹H NMR (7a) δ –9.27 (d, 1 H, ²J_{PH} = 22.5 Hz, RuH), 0.32 (m, 1 H, PCH), 0.80 (dd, 3 H, PCCH₃), 0.90 (s, 3 H, SiMe), 1.00 (m, 8 H, PCCH₃), 1.28 (dd, 3 H, PCCH₃), 1.53 (s, Cp*), 1.97 (m, 1 H, PCH), 2.70 (m, 1 H, PCH), 7.05, 7.28, 7.40, 7.81, 8.18 (m, 10 H, SiPh₂); ¹³C{¹H} NMR (7a) δ –3.15 (d, ²J_{PC} = 40.4 Hz, RuCH₂), 1.60 (SiMe), 10.29 (Cp*), 20.00, 20.99, 22.80, 23.63, 25.67, 32.69 (PⁱPr₂), 42.80 (d, ¹J_{PC} = 35.9 Hz, PCHMe), 94.48 (Cp*), 126.60, 127.10, 136.01, 136.64, 147.63, 151.15 (SiPh₂); ³¹P{¹H} NMR (7a) δ 11.65; ¹H NMR (7b) δ –9.71 (d, 1 H, ²J_{PH} = 25.5 Hz, RuH), 0.97 (s, 3 H, SiMe), 1.48 (s, Cp*), other peaks are obscured by those for the major product **7a**; ³¹P{¹H} NMR (7b) δ 13.89. Anal. Calcd for C₃₂H₅₀PSiRu: C, 64.61; H, 8.47. Found: C, 64.50; H, 8.38.

Cp*₂RuH(Cy₂PC₆H₉) (8). To a cold (–78 °C) diethyl ether (50 mL) solution of Cp*(PCy₃)RuCl (0.50 g, 0.90 mmol) was added ClMgCH₂SiHPh₂ (4.3 mL, 0.23 M in diethyl ether, 0.90 mmol) via syringe. After removal of the cold bath, the solution was allowed to warm to room temperature. After stirring for 10 min more, the volatiles were removed *in vacuo*, and the yellow solid residue was extracted into toluene (30 + 20 mL). Filtration of the clear yellow solution, followed by vigorous stirring of the solution for 24 h resulted in a color change to light blue. The toluene was removed, and the resulting blue oil was taken up in pentane (20 mL). The pentane solution was concentrated and cooled (–40 °C) to give the product as colorless crystals (mp 171–173 °C) in 52% yield (0.225 g): IR (Nujol, CsI, cm^{–1}) 2000 s, 1320 w, 1230 w, 1200 w, 1170 m, 1115 w, 1103 w, 1165 br w, 1020 m, 890 br m, 862 sh w, 852 m, 847 sh w, 815 m, 740 s, 682 m, 660 m, 550 br m, 395 m; ¹H NMR δ –12.57 (dd, 1 H, ²J_{PH} = 39 Hz, *J* = 3 Hz, RuH), 1.09–2.65 (m, 31 H, Cy₂PC₆H₉), 1.82 (s, 15 H, Cp*); ¹³C{¹H} NMR δ 11.31 (Cp*), 27.05 (s), 27.16 (s), 28.23 (m), 28.60 (d, *J* = 23 Hz), 28.61 (s), 29.67 (d, *J* = 26 Hz), 29.86 (dd, *J* = 25 Hz, *J* = 2 Hz), 30.27, 30.47, 31.34, 31.46, 32.32 (single lines), 37.74 (d, *J* = 10 Hz), 43.44 (s), 44.86 (d, *J* = 26 Hz), 52.29 (s), 92.36 (d, *J* = 2 Hz, Cp*); ³¹P{¹H} NMR δ –71.08. Anal. Calcd for C₂₈H₄₇PRu: C, 65.21; H, 9.18; P, 6.01. Found: C, 65.45; H, 9.29; P, 5.86.

Kinetic Study of the Thermal Decomposition of 5. Reactions were run in the probe of the NMR spectrometer, in septum-sealed 5-mm NMR tubes (benzene-*d*₆), at five different temperatures between 23 and 57 °C. Disappearance of **5** was followed by ¹H NMR spectroscopy, and integration values were periodically confirmed with ³¹P NMR spectra. Plots of ln[**5**] vs time were linear, establishing first-order dependence in **5**. Least-squares analysis gave correlation coefficients of >0.99 (with a minimum of eight data points). The activation parameters were determined (five data points) using the ACTPARM program written and kindly provided by Prof. William C. Troglor.

Cp*(PMe₂Ph)₂RuSiMePh₂ (10). The silene complex **5** (0.084 g, 0.141 mmol) was dissolved in benzene (4 mL), and PMe₂Ph (0.108 g, 0.846 mmol) was added. After stirring for 2 h, the volatiles were removed *in vacuo* at 55 °C (to remove excess PMe₂Ph) over 1 h. The crude yellow solid was dissolved in diethyl ether (15 mL), and the resulting solution was concentrated (5 mL) and cooled (–30 °C) to give the product as yellow prisms (mp 194–196 °C) in 80% yield (0.080 g): IR (Nujol, CsI, cm^{–1}) 1430 m, 1420 m, 1229 w, 1080 w, 1020 w, 933 m, 920 m, 902 s, 891 s, 829 w, 779 s, 761 s, 746 s, 699 s, 670 m, 642 w, 489 s, 405 s br; ¹H NMR δ 1.00 (s, 3 H, SiMe), 1.34 (pseudotriplet, 6 H, *J* = 3.9 Hz, PMe₂), 1.36 (s, 15 H, Cp*), 1.51 (pseudotriplet, 6 H, *J* = 2.7 Hz, PMe₂), 7.08, 7.23–7.38, 7.85 (m, 20 H, Ph); ¹³C{¹H} NMR δ 11.59 (Cp*), 12.00 (SiMe), 23.52 (pseudotriplet, *J* = 27.5, PMe₂), 24.15 (pseudotriplet, *J*

= 26.7, PMe₂), 93.37 (Cp*), 126.63, 127.37, 131.94 (m), 137.34, 137.42, 144.07, 144.29, 144.51, 152.37 (SiPh, PPh); ³¹P{¹H} NMR δ 17.87. Anal. Calcd for C₃₉H₅₀PSiRu: C, 65.98; H, 7.10; P, 8.73. Found: C, 66.10; H, 7.26; P, 8.79.

Kinetic Study of the Reaction of 5 with PMe₂R (R = Me, Ph). Reactions were run at 24 °C in the probe of the NMR spectrometer, in septum-sealed 5-mm NMR tubes (benzene-*d*₆). The rate of disappearance of **5** was determined by integration of ¹H NMR spectra. Pseudo-first-order conditions of excess phosphine were employed (10–50 equiv). Plots of ln[**5**] vs time were linear, and least-squares analysis gave correlation coefficients of >0.98 (with a minimum of 7 data points).

Cp*(PMe₃)₂RuCH₂SiDPh₂ (11-d). Toluene (20 mL) was added to a flask containing Cp*(PMe₃)₂RuCl (0.32 g, 0.76 mmol), and to the resulting solution was added ClMgCH₂SiDPh₂ (1.10 mL, 0.7 M in diethyl ether, 0.76 mmol) via syringe. After stirring for 5 h, the volatiles were removed, and the residue was dissolved in diethyl ether (35 mL). Concentration and cooling (–30 °C) of the ether solution gave the product as large, yellow crystals (mp 255–277 °C) in 22% yield (97 mg): IR (Nujol, CsI, cm^{–1}) 1522 w, 1426 m, 1297 w, 1278 w, 1102 m, 1026 m, 950 s, 932 s, 840 w, 798 w, 752 w, 740 m, 700 s, 660 m, 620 w, 601 m, 590 m sh, 479 w; ¹H NMR δ –0.58 (t, ³J_{PH} = 6.6 Hz, RuCH₂), 1.06 (pseudotriplet, 18 H, *J* = 7.2 Hz, PMe₃), 1.62 (s, 15 H, Cp*), 7.12–7.16, 7.21–7.21, 7.91 (m, 10 H, SiPh); ¹³C{¹H} NMR δ –33.79 (tt, ¹J_{CH} = 116 Hz, ²J_{PC} = 10 Hz, RuCH₂), 11.81 (q, ¹J_{CH} = 126 Hz, Cp*), 21.64 (q of m, ¹J_{CH} = 126 Hz, PMe₃), 127.81 (dd, ¹J_{CH} = 157 Hz, ²J_{CH} = 6.8 Hz, ortho C, SiPh), 128.19 (dt, ¹J_{CH} = 158 Hz, ²J_{CH} = 7.4 Hz, SiPh), 135.23 (dt, ¹J_{CH} = 156 Hz, ²J_{CH} = 7.4 Hz, SiPh), 144.36 (s, ipso C, SiPh); ³¹P{¹H} NMR δ 6.57. Anal. Calcd for C₂₉H₄₅DP₂SiRu: C, 59.36; H(D), 8.07; P, 10.56. Found: C, 58.52; H, 7.68; P, 10.20.

Thermolysis of 11-d. In a sealed NMR tube, **11-d** (25 mg) in benzene-*d*₆ (0.4 mL) was placed in an oven at 90 °C. Within 2 h, quantitative conversion to Cp*(PMe₃)₂RuSi(CH₂D)Ph₂ was observed (¹H and ³¹P NMR spectroscopy).

Reaction of 5 in Neat PMe₃. Complex **5** (24 mg) was placed in a 5-mm NMR tube, and PMe₃ was added (ca. 0.4 mL) in the glovebox. The reaction was allowed to proceed for 15 min, after which benzene-*d*₆ was added (0.2 mL). Free PⁱPr₃ was detected (³¹P NMR spectroscopy) as well as **11** and Cp*(PMe₃)₂RuSiMePh₂ (1:4 ratio).

Reaction of 5 with Carbon Monoxide. (a) To an NMR tube containing **5** (20 mg, 0.03 mmol) and benzene-*d*₆ (0.4 mL) was added CO via a 5-mL gas-tight syringe (ca. 5 mL, 1 atm). By ³¹P NMR spectroscopy, the reaction was nearly complete within 20 h, having formed Cp*(PⁱPr₃)(CO)RuCH₂SiHPh₂ (**12**) and Cp*(PⁱPr₃)(CO)RuSiMePh₂ (**13**) in a 1:2 ratio. (b) A diethyl ether (20 mL) solution of **5** (0.136 g) was pressurized with CO (80 psi) in a pressure bottle for 1.5 h, and then the volatiles were removed. The crude residue was shown to contain **12** and **13** in a 4:1 ratio, by ¹H and ³¹P NMR spectroscopy. Extraction with pentane (20 mL) gave a yellow solution, which was concentrated and cooled (–78 °C) to give a yellow solid, which became an oil upon warming to room temperature. This oil also contained **12** and **13** in a 4:1 ratio. Thermolysis of this sample in benzene (20 mL) at 100 °C for 3 h resulted in clean conversion to **13**. Anal. Calcd for C₃₃H₄₉OPSiRu: C, 63.74; H, 7.94. Found: C, 63.50; H, 7.90.

For **12**: ¹H NMR δ –0.37 (m, 1 H, RuCH₂), –0.02 (m, 1 H, RuCH₂), 0.93 (dd, ³J_{HH} = 13 Hz, ²J_{PH} = 7 Hz, 9 H, PCCH₃), 0.98 (dd, ³J_{HH} = 12 Hz, ²J_{PH} = 7 Hz, 9 H, PCCH₃), 1.62 (s, 15 H, Cp*), 1.95 (m, 3 H, PCH), 5.37 (m, 1 H, SiH), 7.17–7.28 (m, 6 H, SiPh₂), 7.94 (d, *J* = 6.6 Hz, 4 H, ortho H, SiPh₂); ¹³C{¹H} NMR δ –28.03 (t of m, ¹J_{CH} = 120 Hz, RuCH₂), 10.51 (q, ¹J_{CH} = 127 Hz, Cp*), 19.70 (q of m, ¹J_{CH} = 124 Hz, PCCH₃), 20.39 (q of m, ¹J_{CH} = 127 Hz, PCCH₃), 27.50 (dd, ¹J_{CH} = 126 Hz, ¹J_{PC} = 19 Hz, PCCH₃), 95.38 (s, Cp*), 127.71 (d of m, ¹J_{CH} = 154 Hz, SiPh₂), 135.50 (d of m, ¹J_{CH} = 157 Hz, SiPh₂), 136.13 (d of m, ¹J_{CH} = 157 Hz, SiPh₂), 141.50 (s, ipso C, SiPh₂), 143.47 (s, ipso C, SiPh₂), 212.34 (d, ²J_{PC} = 20.7 Hz, RuCO); ³¹P{¹H} NMR δ 63.25.

For **13**: ¹H NMR δ 0.93–1.05 (overlapping dd's for diastereotopic PCCH₃ groups, 18 H), 1.13 (s, 3 H, SiMe), 1.61 (s, 15 H, Cp*), 7.11–7.26 (m, 6 H, SiPh₂), 7.91 (d, *J* = 7 Hz, 2 H, ortho H, SiPh₂), 7.99 (d, *J* = 7 Hz, 2 H, ortho H, SiPh₂); ¹³C{¹H} NMR: δ 5.65 (q, ¹J_{CH} = 118 Hz, SiMe), 11.10 (q, ¹J_{CH} = 127 Hz, Cp*), 19.76 (q of m, ¹J_{CH} = 122 Hz, PCCH₃), 21.15 (q of m, ¹J_{CH} = 122 Hz, PCCH₃), 28.59 (dd, ¹J_{CH} = 128 Hz, ¹J_{PC} = 16 Hz, PCCH₃), 97.16 (s, Cp*), 126.94 (d of m, ¹J_{CH} = 151 Hz, SiPh₂), 135.64 (d of m, ¹J_{CH} = 157 Hz, SiPh₂), 136.03 (d of m, ¹J_{CH} = 156 Hz, SiPh₂), 150.19 (s, ipso C, SiPh₂), 150.53 (s, ipso C, SiPh₂), 213.88 (d, ²J_{PC} = 16.4 Hz, RuCO); ³¹P{¹H} NMR δ 61.33.

Cp*(PⁱPr₃)RuH₂(SiMePh₂) (15). Complex **7** (0.112 g, 0.188 mmol) was generated *in situ* by thermolysis of **5** in benzene (50 mL), and the

solution was transferred to a pressure bottle. Hydrogen (100 psi) was admitted, and the reaction was stirred for 75 min. The volatiles were removed in vacuo, and the resulting colorless oil was dissolved in pentane (40 mL). All attempts to obtain a crystalline product from this solvent were unsuccessful. However, the product was obtained as colorless crystals (mp 145–147 °C) from acetonitrile/diethyl ether (5:1) at –30 °C, in 76% yield (85 mg): IR (Nujol, CsI, cm^{-1}) 2006 m, 1986 m br, 1423 m, 1232 w, 1085 m, 1065 w, 1054 w, 1023 m, 881 w, 780 s, 745 s, 701 s, 653 s, 640 m, 578 w br, 523 w, 488 m, 409 m, br; $^1\text{H NMR}$ δ –12.17 (d, 2 H, $^2J_{\text{PH}} = 28.2$ Hz, RuH), 0.98 (dd, 18 H, $^3J_{\text{PH}} = 13$ Hz, $^3J_{\text{HH}} = 7$ Hz, PCCH_3), 1.12 (s, 3 H, SiMe), 1.62 (s, 15 H, Cp*), 7.17, 7.26, 7.94 (m, 10 H, SiPh₂); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 81.52. Anal. Calcd for $\text{C}_{32}\text{H}_{51}\text{PSiRu}$: C, 64.50; H, 8.63; P, 5.20. Found: C, 64.49; H, 8.61; P, 4.98.

Cp*(P⁺Pr₃)(CO)RuSSiMePh₂ (16). Benzene (20 mL) was added to complex **5** (0.113 g, 0.190 mmol), and the resulting yellow solution was freeze–pump–thawed twice on a high-vacuum line. COS (0.190 mmol) was admitted into a calibrated bulb and then condensed onto the frozen solution. The solution was then allowed to warm to room temperature and was then stirred for 8.5 h. The volatiles were removed in vacuo, and pentane (10 mL) was added to give an orange solution, which was filtered, concentrated, and cooled (–30 °C) to give the product as dark orange rosettes (mp 129–131 °C) in 45% yield (0.055 g): IR (CaF₂ solution cell, benzene-*d*₆, cm^{-1}) 3058 m, 3040 m, 2957 s, 2899 s, 1909 vs, 1462 br m, 1427 m, 1378 m, 1243 m, 1102 s, 1021 w; $^1\text{H NMR}$ δ 1.05 (dd, 18 H, $^3J_{\text{PH}} = 13$ Hz, $^3J_{\text{HH}} = 6$ Hz, PCCH_3), 1.07 (s, 3 H, SiMe), 1.52 (s, 15 H, Cp*), 2.27 (m, 1 H, PCH), 7.25 (m, SiPh₂), 8.03 (m, SiPh₂); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 3.14 (SiMe), 10.41 (Cp*), 19.89 (PCCH_3), 27.51 (PCCH_3), 96.02 (Cp*), 134.78, 143.67 (SiPh₂), 211.81 (RuCO); $^{31}\text{P}\{^1\text{H}\}$ NMR δ 56.79. Anal. Calcd for $\text{C}_{32}\text{H}_{49}\text{OPSSiRu}$: C, 59.87; H, 7.69; P, 4.83. Found: C, 59.89; H, 7.47; P, 4.52.

Reaction of 5 with Me₃SnCl. A diethyl ether (5 mL) solution of Me₃SnCl (0.035 g, 0.18 mmol) was added to a diethyl ether (5 mL) solution of **5** (0.10 g, 0.17 mmol), which had been cooled to –78 °C. After stirring for 2 h at –78 °C, the reaction mixture was allowed to warm to room temperature. Removal of volatiles and extraction with pentane (15 mL) gave a blue solution, which was concentrated and cooled to give **1** in 60% isolated yield. Monitoring this reaction in benzene-*d*₆ by $^1\text{H NMR}$ spectroscopy revealed formation of **1** and Me₃SnCH₂SiHPh₂, identified by its independent generation, as described below.

Me₃SnCH₂SiHPh₂. To Me₃SnCl (0.35 g, 1.75 mmol) in diethyl ether (15 mL) was added ClMgCH₂SiHPh₂ (3.5 mL of a 0.5 M solution), resulting in precipitation of MgCl₂. After stirring for 5 min, the volatiles were removed, the product was extracted into pentane (20 mL), and the mixture was filtered. Attempts to crystallize the product from pentane were unsuccessful, but removal of solvent produced 0.63 g of the product, contaminated only slightly with impurities: IR (solution cell) 2114 cm^{-1} (ν_{SiH}); $^1\text{H NMR}$ δ 0.01 (s, 9 H, $^2J_{\text{SnH}} = 52.8$ Hz, SnMe₃), 0.18 (dd, 2 H, $^2J_{\text{SnH}} = 66.0$ Hz, $^3J_{\text{HH}} = 4.8$ Hz, SnCH₂Si), 5.20 (t, 1 H, $^3J_{\text{HH}} = 4.8$ Hz, SiH), 7.15–7.17 (m, 6 H, SiPh₂), 7.55–7.57 (m, 4 H, SiPh₂); $^{13}\text{C}\{^1\text{H}\}$ NMR δ –10.27 (dt, $^1J_{\text{CH}} = 121$ Hz, $^3J_{\text{CH}} = 8.7$ Hz, CH₂), –8.38 (q, $^1J_{\text{CH}} = 128$ Hz, SnMe₃).

X-ray Structure Determinations of 5 and 7a. For **5**: A yellow crystal with dimensions 0.4 × 0.4 × 0.5 mm was mounted in a glass capillary and flame-sealed. Data was collected at –100 °C with a Nicolet R3m/V diffractometer. Unit cell parameters: $a = 10.298(5)$ Å, $b = 41.51(2)$

Å, $c = 14.901(10)$ Å, $\beta = 108.29(5)^\circ$, $V = 6047(6)$ Å³, $Z = 8$ ($P2_1/c$). Reflections (10825) were collected ($3^\circ \leq 2\theta \leq 50^\circ$) using ω scans and were corrected for absorption. Of these, 9815 reflections were unique ($R_{\text{int}} = 11.13\%$) and 5086 were considered observed ($F > 6.0\sigma(F)$). The large R_{int} is due to slight crystal twinning. Solution of the structure utilized direct methods, and the refinement was by full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet (Siemens) XRD, Madison, WI). All non-hydrogen atoms (except the carbon atoms of the pentamethylcyclopentadienyl rings) were refined anisotropically, and hydrogen atoms (except those of the SiCH₂Ru group) were refined isotropically in fixed and idealized positions. Neither the SiCH₂Ru nor the RuH hydrogens were located. The asymmetric unit contains both enantiomorphs: $R_F = 9.79$, $R_{wF} = 12.2$, data/parameter = 9.6, GOF = 2.45, largest $\delta/\sigma = 0.042$, largest peak = $1.74 \text{ e} \text{ \AA}^{-3}$ (0.92 Å from Ru(2)).

For **7a**: A pale yellow crystal (0.26 × 0.28 × 0.42 mm) mounted in a Lindemann capillary tube was found to belong to the $\bar{1}$ Laue group. All processing was confined to the centrosymmetric triclinic alternative. This decision was affirmed by the computationally stable refinement of the structure. An empirical correction for absorption was applied to the reflection data. The structure was solved by direct methods which revealed the positions of the two independent Ru atoms. Unit cell parameters: $a = 10.936(2)$ Å, $b = 16.193(3)$ Å, $c = 19.482(4)$ Å, $\alpha = 107.21(1)^\circ$, $\beta = 93.012(1)^\circ$, $\gamma = 106.04(1)^\circ$, $V = 3133.2(10)$ Å³, $Z = 4$ ($P\bar{1}$). Reflections (8447) were collected ($4^\circ \leq 2\theta \leq 45^\circ$) using ω scans and were corrected for absorption. Of these, 8157 reflections were unique, and 5609 were considered observed ($F > 4\sigma(F)$). The asymmetric unit was found to consist of two crystallographically independent, but chemically identical, molecules. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were assigned idealized locations. The phenyl rings were constrained as rigid hexagons. At convergence, there remained two peaks (both ca. $2.1 \text{ e} \text{ \AA}^{-3}$) of unassigned electron density, each near (ca. 1.5 Å) one of the Si atoms and located on the side opposite Ru. We are unable to propose a chemically plausible interpretation for these peaks; as the thermal parameters for the Si-bound methyl groups are normal, disorder in these groups can be rejected. All other unassigned peaks are at the background level ($< 0.5 \text{ e} \text{ \AA}^{-3}$). $R_F = 7.12$, $R_{wF} = 3.35$, GOF = 1.65, data/parameter = 9.7, largest $\Delta/\sigma = 0.09$. All computations used the SHELXTL (5.1) program library (Sheldrick, G. Nicolet (Siemens) XRD, Madison, WI), and data was collected with a Nicolet R3m diffractometer.

Supplementary Material Available: Tables of crystal data, data collection, and refinement parameters, and hydrogen atom coordinates for **5** and **7a** (21 pages); listings of observed and calculated structure factors for **5** and **7a** (53 pages). Ordering information is given on any current masthead page.

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