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Silyl and Diphenylsilylene Derivatives of (η^5-C$_5$Me$_5$)(PMe$_3$)$_2$Ru. Evidence for the Base-Free Silylene Complex [(η^5-C$_5$Me$_5$)(PMe$_3$)$_2$Ru=SiPh$_2$]$^+$

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Abstract: The preparation, characterization, and properties of new ruthenium silyl and diphenylsilylene derivatives of Cp*(PMe$_3$)$_2$Ru (Cp* = η^5-C$_5$Me$_5$) are described. The silyl complexes Cp*(PMe$_3$)$_2$RuSiR$_3$ (SiR$_3$ = SiEt$_3$ (**1**), SiPh$_3$ (**2**), SiPh$_2$Me (**3**), SiPh$_2$Cl (**4**)) are obtained directly by reaction of Cp*(PMe$_3$)$_2$RuCH$_2$SiMe$_3$ with the appropriate silane HSiR$_3$ at 80–100 °C. Other conditions lead to loss of 1 equiv of PMe$_3$ to afford the ruthenium(IV) bis(silyl) species Cp*(PMe$_3$)Ru(SiR$_3$)$_2$H (SiR$_3$ = Si(OEt)$_3$ (**5**), SiPh$_2$Cl (**6**), SiMe$_2$OEt (**7**)). The nucleophilic reagents MeMgCl and LiAlH$_4$ displace chloride from **4** to afford **3** and Cp*(PMe$_3$)$_2$RuSiPh$_2$H (**8**), respectively. The triflate derivative Cp*(PMe$_3$)$_2$RuSiPh$_2$(OTf) (**9**, OTf = OSO$_2$CF$_3$) is obtained in high yield from reaction of **4** and Me$_3$SiOTf in dichloromethane. Solubility properties and solid-state infrared spectroscopy indicate that **9** possesses a covalent silicon–triflate interaction. Compound **9** exhibits a triplet resonance in the ^{29}Si NMR spectrum at δ 112.39 ($^2J_{PSi}$ = 33 Hz). In acetonitrile solution **9** exists mainly as the ionic silylene adduct [Cp*(PMe$_3$)$_2$RuSiPh$_2$(NCMe)]OTf, as determined by ^{1}H NMR spectroscopy, solution infrared spectroscopy, and conductivity measurements. Addition of NaBPh$_4$ to an acetonitrile solution of **9** allows isolation of the silylene adduct [Cp*(PMe$_3$)$_2$RuSiPh$_2$(NCMe)]BPh$_4$ (**10**) as a dichloromethane solvate. This procedure also produces significant quantities of [Cp*(PMe$_3$)$_2$Ru(NCMe)]BPh$_4$ (**11**) as byproduct. Compound **11** was prepared independently by reaction of Cp*(PMe$_3$)$_2$RuCl and AgBPh$_4$ in acetonitrile. Compound **10** exhibits a single broad resonance in its ^{29}Si NMR spectrum at δ 95.75. The thermal stability of **10** in solution and in the solid state is described. **10** reacts with water rapidly to give **11** and the disiloxane Ph$_2$HSiOSiHPh$_2$. It also reacts with LiAlH$_4$ to afford **8** in 37% yield. The acetonitrile of **10** is quite labile and exchanges rapidly with free acetonitrile in solution. A line-shape analysis of variable-temperature ^{1}H NMR spectra of **10** in the presence of 1 equiv of NCMe afforded activation parameters for this exchange process of $\Delta H^\ddagger$ = 14.5 ± 0.3 kcal mol^{-1} and $\Delta S^\ddagger$ = 14 ± 2 eu. This positive value for the entropy of activation is consistent with a dissociative mechanism and provides evidence for existence of the base-free silylene complex Cp*(PMe$_3$)$_2$Ru=SiPh$_2$$^+$ in solution. Structures of complexes **8**, **9**, and **10**·CH$_2$Cl$_2$ have been determined by single-crystal X-ray diffraction experiments. Crystals of **8** are triclinic, $P\bar{1}$, with a = 9.362 (1) Å, b = 9.748 (2) Å, c = 16.376 (3) Å, α = 98.18 (2)°, β = 103.71 (2)°, γ = 94.14 (2)°, V = 1428.4 (6) Å^3, Z = 2, R_F = 2.59%, and R_{wF} = 2.98%. Crystals of **9** are triclinic, $P\bar{1}$, with a = 10.171 (3) Å, b = 10.802 (3) Å, c = 16.880 (5) Å, α = 86.82 (2)°, β = 88.03 (2)°, γ = 64.00 (1)°, V = 1664.2 (7) Å^3, Z = 2, R_F = 4.39%, and R_{wF} = 5.61%. Crystals of **10**·CH$_2$Cl$_2$ are monoclinic, $P2_1/n$, with a = 21.565 (8) Å, b = 10.215 (4) Å, c = 25.59 (1) Å, β = 108.40 (3)°, V = 5349 (3) Å^3, Z = 4, R_F = 6.32%, and R_{wF} = 6.37%. The Ru–Si distances for these complexes are 2.387 (1) (**8**), 2.349 (2) (**9**), and 2.328 (2) Å (**10**·CH$_2$Cl$_2$). Whereas **8** and **9** exhibit similar staggered conformations with the Cp* and X (Cp*(PMe$_3$)$_2$RuSiPh$_2$X, X = H or OTf) groups in a gauche relationship, **10**·CH$_2$Cl$_2$ has a conformation that is skewed toward an eclipsed arrangement of substituents (Cp* centroid–Ru–Si–N dihedral angle = 38.0°). The Si–O distance in **9** is rather long, at 1.853 (5) Å. The Si–N distance in **10**·CH$_2$Cl$_2$, 1.932 (8) Å, is consistent with a dative interaction between nitrogen and silicon. Other geometrical parameters for these complexes are compared and discussed.

Carbenes,[1] germylenes,[2] stannylenes,[2] and plumbylenes[2] are well-established ligands for transition metals, but little is known about the coordination chemistry of silylenes (SiR$_2$). Although there are numerous examples of compounds with bridging silylene ligands,[3] evidence for terminal silylene complexes (L$_n$M=SiR$_2$) is scarce despite many attempts to prepare and isolate them. Interest in metal-bound silylene species has intensified over the past few years since they are postulated intermediates in a number of transition-metal-mediated processes, including Rochow's direct process,[4] catalytic redistribution of silanes.[5] various silylene-transfer reactions,[6] and dehydrogenative silane couplings.[7] Isolation and study of silylene complexes should, therefore, provide valuable information regarding important chemical transformations of silicon compounds. At present there is no direct evidence for involvement of silylene coordination complexes in any catalytic reactions that involve silylene transfer. Whether or not these species can participate extensively in reaction chemistry awaits discovery of suitable model systems and reactivity studies.

Terminal transition-metal silylene complexes have proven to be elusive synthetic targets, partly because many of the known preparative methods for congeneric carbon, germanium, tin, and lead compounds are not applicable to analogous silicon systems.[3a] For example, carbene complexes can be obtained by abstraction of a group bound to carbon with an electrophile.[8] Analogous attempts to prepare silylene complexes (eq 1) have failed, prin-

$$\mathrm{L}_n\mathrm{M{-}SiR_2X} + \mathrm{E^+Y^-} \rightarrow [\mathrm{L}_n\mathrm{M{=}SiR_2}]^+\mathrm{Y^-} + \mathrm{E^+X^-} \quad (1)$$

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cipally due to secondary reactions of the metal-bound silicon with the abstraction reagent.[9] For example, reaction of $Cp(CO)_2FeSiCl_3$ with 3 equiv of $AgBF_4$ led to fluorination of the silyl group and isolation of $Cp(CO)_2FeSiF_3$.[9b] A number of early reports of silylene complexes involve incomplete characterization or have subsequently been disproved.[3a] A substantial difficulty is that the presence of a M=Si double bond is difficult to establish by most spectroscopic methods.

In 1987, the first two reports of successful syntheses of donor-stabilized silylene complexes, with characterization by X-ray crystallography, appeared.[10a,11] Zybill and Müller published the syntheses of $(CO)_4FeSi(O^tBu)_2(S)$ (S = HMPA, THF) complexes via reaction of $Fe(CO)_4^{2-}$ with $(^tBuO)_2SiCl_2$.[10a] Subsequently this method has been applied to the syntheses of other solvent-complexed silylene derivatives of first-row transition-metal carbonyl fragments.[10b-d] We have briefly described characterization of $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]BPh_4$ (**10**, Cp* = η^5-C_5Me_5), synthesized via the abstraction reaction of eq 1.[11] Ogino and co-workers have reported examples of another type of donor-stabilized silylene complex, the diastereomers of $\overline{Cp^*(CO)FeSiMe(OMe)(\mu\text{-}OMe)SiMe_2}$, obtained from photolysis of $Cp^*(CO)_2FeSiMe_2SiMe(OMe)_2$.[12]

Here we describe in detail the synthesis of the donor-stabilized silylene complex **10** and some of its chemical and physical properties. For synthesis of silylene complexes by abstraction of a group from the ligated silicon atom (eq 1), our attention focused initially on electron-rich ruthenium silyl complexes derived from the $Cp^*(PMe_3)_2Ru-$ group.[13] An electron-rich transition-metal center was chosen to stabilize the adjacent electron-deficient, three-coordinate silicon atom. Additionally, the stability of ruthenium silylene complexes $[Cp^*(PMe_3)_2Ru{=}SiR_2]Y$ should be influenced by the steric and electronic nature of the substituents R, as well as on the reactivity and coordinating ability of the counteranion Y^-. Our efforts have, therefore, involved use of the tetraphenylborate anion, which appears to be relatively inert toward the silicon center of $[Cp^*(PMe_3)_2Ru{=}SiR_2]Y$ complexes. An indication of the stability of the silylene ligand in **10** is provided by dynamic NMR studies, which show that in solution **10** is in equilibrium with $[Cp^*(PMe_3)_2Ru{=}SiPh_2]BPh_4$. These results therefore represent the first direct evidence for a base-free silylene complex. The approach outlined above requires ruthenium(II) silyl complexes $Cp^*(PMe_3)_2RuSiR_2X$, where X is a leaving group, and herein we also describe the synthesis and characterization of new ruthenium silyl complexes of this type.

Results and Discussion

Preparation and Properties of New Ruthenium(II) and Ruthenium(IV) Silyl Complexes. Ruthenium(II) silyl complexes **1–4** are readily obtained by heating the alkyl $Cp^*(PMe_3)_2RuCH_2SiMe_3$ with the appropriate silane (eq 2).

$$Cp^*(PMe_3)_2RuCH_2SiMe_3 + HSiR_3 \xrightarrow{\Delta} Cp^*(PMe_3)_2RuSiR_3 + SiMe_4 \qquad (2)$$

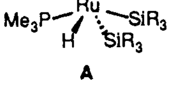
1, $SiR_3 = SiEt_3$
2, $SiR_3 = SiPh_3$
3, $SiR_3 = SiPh_2Me$
4, $SiR_3 = SiPh_2Cl$

Generally, higher yields of these products are obtained if the reaction is carried out in a closed system to prevent loss of PMe_3 (vide infra). The yellow, crystalline compounds are isolated in high yield and have been completely characterized by elemental analyses and NMR spectroscopy. As is typical for $Cp^*(PMe_3)_2RuX$ derivatives, the ^1H NMR spectra of **1–4** contain a virtual triplet pattern for the PMe_3 protons.[13] When $Cp^*(PMe_3)_2RuCH_2SiMe_3$ is heated with a large excess of $HSiCl_3$, two ruthenium(II) complexes are formed in roughly equal amounts. These pale yellow compounds cocrystallize from diethyl ether and appear to be $Cp^*(PMe_3)_2RuSiCl_3$ and $Cp^*(PMe_3)_2RuSiHCl_2$ on the basis of their ^1H NMR spectra. Sterically hindered silanes, such as $(Me_3Si)_3SiH$ and $^tBu_2SiHCl$, do not react with $Cp^*(PMe_3)_2RuCH_2SiMe_3$ at elevated temperatures (100 °C) over 16 h.

Under certain conditions ruthenium(IV) bis(silyl) complexes are obtained via loss of 1 equiv of PMe_3 (eq 3). Formation of these species is promoted by periodic exposure of the reaction solution to vacuum to remove PMe_3. Compounds **5** and **6** have been completely characterized and are unusual in exhibiting anomalously low $^2J_{PRuH}$ coupling constants (3 Hz). Generally, hydride complexes of $Cp(PR_3)_nRu$ and $Cp^*(PR_3)_nRu$ (n = 1 or 2) derivatives possess $^2J_{PRuH}$ coupling constants in the range 20–40 Hz.[13,14] Compound **7**, isolated in a slightly impure state, was obtained as a 6:1 mixture of two isomers that gave rise to resonances in the ^1H NMR spectrum at δ −13.25 ($^2J_{PRuH}$ = 3 Hz) and −12.60 ($^2J_{PRuH}$ = 33 Hz), respectively. The two isomers may correspond to cis and trans geometries (**A** and **B**), but the exceptionally low $^2J_{PRuH}$ coupling constant for the major isomer suggests the possibility of η^2-$HSiR_3$ structures.[15] Note that for

$$Cp^*(PMe_3)_2RuCH_2SiMe_3 + 2HSiR_3 \xrightarrow[-PMe_3]{\Delta} Cp^*(PMe_3)Ru(SiR_3)_2H + SiMe_4 \qquad (3)$$

5, $SiR_3 = Si(OEt)_3$
6, $SiR_3 = SiPh_2Cl$
7, $SiR_3 = SiMe_2OEt$



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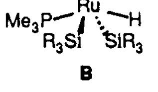

B

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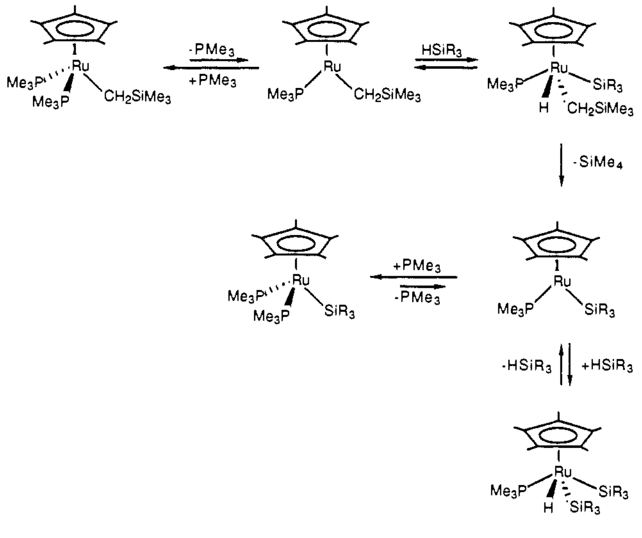
Scheme I. Proposed Mechanism for Formation of Ruthenium Silyl Complexes



trans-Cp(dmpe)RuH$_2{}^+$ ${}^2J_{PRuH}$ = 31 Hz, whereas for Cp(dmpe)Ru(η^2-H$_2$)$^+$ ${}^2J_{PRuH}$ = 3.6 Hz.[16] The major isomer, therefore, appears to correspond to the cis (or perhaps a η^2-HSiR$_3$) structure. We currently are attempting to more accurately establish the structures of these isomers with X-ray crystallography.

It is possible, then, to obtain both ruthenium(II) and ruthenium(IV) silyl complexes from reaction of Cp*(PMe$_3$)$_2$RuCH$_2$SiMe$_3$ with a silane. Reaction conditions can strongly influence the type of product(s) obtained, and it is sometimes difficult to adjust conditions to obtain a single ruthenium-containing product. For example, the procedure of eq 2 sometimes produces Cp*(PMe$_3$)$_2$RuSiPh$_2$Cl (**4**) that is contaminated by small amounts of the ruthenium(IV) product **6**. Fortunately, **6** is convienently converted to **4** by reaction with excess PMe$_3$ at elevated temperature in a sealed tube. For Cp*(PMe$_3$)$_2$RuSiPh$_2$H (**8**), the alternate procedure described below is preferred. It is interesting to note that the reaction of 8 equiv of HSi(OEt)$_3$ with Cp*(PMe$_3$)$_2$RuSH at 45 °C has been reported to give only the ruthenium(II) silyl Cp*(PMe$_3$)$_2$RuSi(OEt)$_3$.[17]

The reactions in eqs 2 and 3 require temperatures between 80 and 100 °C, a fact that is consistent with loss of PMe$_3$ from Cp*(PMe$_3$)$_2$RuCH$_2$SiMe$_3$ as the rate-limiting step.[18,19] The course of these reactions seems to be strongly influenced not only by reaction conditions but also by steric and electronic properties of the silane. Thus, small silanes with electronegative substituents appear to promote a second oxidative addition, as is observed in other systems.[3] The reaction with HSiCl$_3$ is anomalous and suggests that exceptionally electronegative silyl groups such as SiCl$_3$ inhibit phosphine dissociation, which is required for a second oxidative addition. These observations are consistent with the mechanism in Scheme I, which is analogous to that by which Cp*(PMe$_3$)$_2$RuR complexes activate arenes.[19]

The above methods are useful in some cases but are not always successful for preparation of desired ruthenium silyl starting materials. This can be due to complications arising from formation of both ruthenium(II) and ruthenium(IV) silyl species or from additional side reactions. We have, therefore, developed other

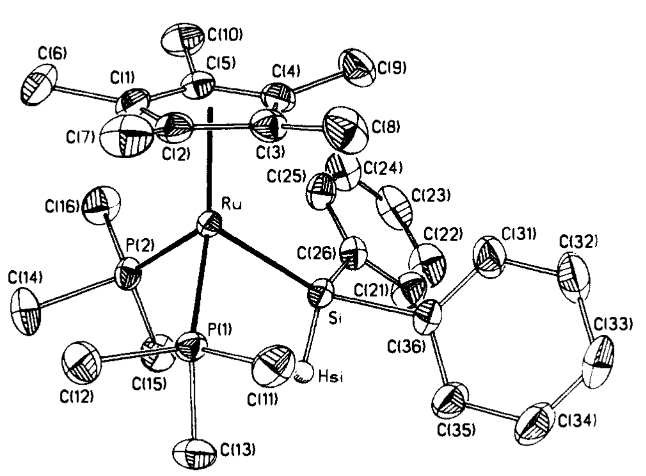
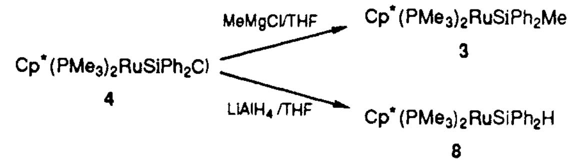


Figure 1. ORTEP view of Cp*(PMe$_3$)$_2$RuSiPh$_2$H (**8**) with atom-labeling scheme.

routes to new ruthenium silyl complexes involving exchange reactions at silicon.[3] Two examples utilizing nucleophilic reagents are shown in eq 4. Compound **3** was obtained in 90% yield by



$$\underset{\mathbf{4}}{Cp^*(PMe_3)_2RuSiPh_2Cl}\ \begin{cases}\xrightarrow{MeMgCl/THF} \underset{\mathbf{3}}{Cp^*(PMe_3)_2RuSiPh_2Me} \\ \xrightarrow{LiAlH_4/THF} \underset{\mathbf{8}}{Cp^*(PMe_3)_2RuSiPh_2H}\end{cases} \quad (4)$$

this method, and **8** was isolated in 53% yield after crystallization from toluene. An X-ray crystal structure determination for **8** provided a detailed description of the molecular structure (Figure 1), which is discussed below.

Preparation and Properties of Cp*(PMe$_3$)$_2$RuSiPh$_2$(OTf) (9). Initial attempts to carry out abstractions to produce silylene complexes by the method of eq 1 were unsuccessful. For example, reaction of **4** with AgBPh$_4$, carried out in dichloromethane at room temperature and in toluene at 60 °C, proceeded extremely slowly, and no identifiable products were observed. Our attention then turned to triflate-substituted silyl complexes in search of evidence for dissociation of the triflate group.

Reaction of **4** with Me$_3$SiOTf (OTf = OSO$_2$CF$_3$) in dichloromethane readily affords the triflate derivative Cp*(PMe$_3$)$_2$RuSiPh$_2$(OTf) (**9**, eq 5). Chemical and spectroscopic

$$\underset{\mathbf{4}}{Cp^*(PMe_3)_2RuSiPh_2Cl} + Me_3SiOTf \xrightarrow[-Me_3SiCl]{CH_2Cl_2} \underset{\mathbf{9}}{Cp^*(PMe_3)_2RuSiPh_2(OTf)} \quad (5)$$

properties for this yellow compound suggest the presence of a covalent Si–O bond. The compound is soluble in nonpolar aromatic hydrocarbons, and the infrared spectrum (Nujol mull) contains a band at 1360 cm^{-1} that we assign to the triflate group. Such an infrared stretch near 1380 cm^{-1} may be attributed to an SO$_3$ stretching mode for monodentate-bound triflate.[20] However, several results, including the molecular structure (vide infra), suggest that the triflate group of **9** is weakly bound to silicon. Similar observations have been made for Cp(NO)(PPh$_3$)ReGePh$_2$(OTf), which possesses a labile triflate group.[21]

The ^{29}Si NMR spectrum of **9** exhibits a triplet resonance at δ 112.39 (${}^2J_{PSi}$ = 33 Hz). Observation of downfield ^{29}Si shifts for compounds containing sp^2-hybridized silicon[22a] and arguments based on correlations between ^{13}C and ^{29}Si NMR data[22b] suggest that such downfield shifts might be expected for a silicon ligand with considerable silylene (or silylenium) character. However,

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Table I. ^{29}Si NMR and Structural Parameters for Donor-Complexed Silylene Complexes

compd	^{29}Si NMR shift, ppm	Si···X (donor) dist, Å	ref
$(CO)_4Fe{=}Si(O^tBu)_2(HMPA)$	7.1	1.730 (3)	10a,c
$(CO)_4Fe{=}Si(O^tBu)_2(THF)$	-9.4		
$(CO)_4Fe{=}Si(HMPA)_2{=}Fe(CO)_4$		1.745 (2), 1.748 (3)	10b
$(CO)_5Cr{=}Si(O^tBu)_2(HMPA)$	12.7	1.736 (2)	10c
$(CO)_4Fe{=}SiMe_2(HMPA)$	92.4	1.731 (4), 1.736 (4)	10d
$Cp^*(CO)FeSiMe_2(\mu\text{-}OMe)SiMe(OMe)$	93.9, 101.9, 121.1, 127.4[a]	1.793 (9), 1.799 (8)	12
$Cp^*(PMe_3)_2RuSiPh_2(OTf)$ (**9**)	112.39	1.853 (5)	this work
$[Cp^*(PMe_3)_2Ru{=}SiPh_2(NCMe)]BPh_4$ (**10**)	95.75	1.932 (8)	this work.

[a] Two isomers present in solution.

results reported so far for donor-stabilized silylene complexes are not entirely consistent with such a trend (Table I). Alkoxy-substituted complexes $(CO)_4FeSi(O^tBu)_2(S)$ (S = HMPA, THF) and $(CO)_5CrSi(O^tBu)_2(HMPA)$ exhibit ^{29}Si NMR shifts near 0 ppm, but it is possible that the oxygen substituents in these compounds cause the ^{29}Si NMR shifts to occur at higher field. Isomers of the iron silylene complexes $Cp^*(CO)FeSiMe(OMe)(\mu\text{-}OMe)SiMe_2$ possess ^{29}Si shifts at δ 93.9, 101.9, 121.1, and 127.4. Finally, the recently reported dimethylsilylene derivative $(CO)_4FeSiMe_2(HMPA)$ has a ^{29}Si chemical shift of δ 92.4. For comparison, typical ^{29}Si NMR shifts for transition-metal silyl compounds are in the range −30 to +70 ppm,[3a] and the corresponding value for **4** is 74.07 ($^2J_{PSi}$ = 30 Hz).

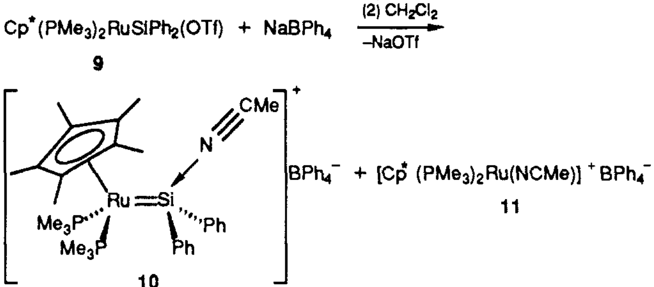
Triflate complex **9** is stable for long periods in the solid state under nitrogen, but decomposes slowly (over ca. 2 weeks) in acetonitrile solution at room temperature. Heating an acetonitrile-d_3 solution of **9** at 110 °C resulted in quantitative conversion to $[Cp^*(PMe_3)_2Ru(NCCD_3)]OTf$ (38% conversion after 18 h), identified by comparison of ^{1}H NMR spectra with those of independently prepared $[Cp^*(PMe_3)_2Ru(NCMe)]BPh_4$ (**11**) (vide infra). The silicon-containing product from this decomposition reaction gave rise to an unidentified, broad peak in the phenyl region of the ^{1}H NMR spectrum. This reaction involving loss of the silylene fragment is currently under investigation.

Preparation and Properties of $Cp^*(PMe_3)_2RuSiPh_2(NCMe)^+$. Results indicate that in acetonitrile solution **9** is converted extensively to the ionic silylene adduct $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]OTf$. The infrared spectrum of **9** in acetonitrile does not contain a peak near 1360 cm^{-1} that can be assigned to covalently bound triflate, but it does have a peak at 1275 cm^{-1} that is not present in the spectrum of a mulled sample. The latter peak may be assigned to a $\nu(SO_3)$ vibrational mode for ionic triflate.[20] In addition, ^{1}H NMR resonances for **9** in acetonitrile-d_3 solution correspond very closely to those observed for isolated silylene adduct $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]BPh_4$ (**10**) (vide infra). Mixtures of compounds **9** and **10** in acetonitrile-d_3 or dichloromethane-d_2 exhibit only one set of peaks for the Cp*, PMe$_3$, and Ph groups, indicating that at room temperature triflate and acetonitrile are exchanging rapidly between the silylene ligands. In dichloromethane-d_2, separate sets of peaks for **9** and **10** are observed below −25 °C. Though **9** is solvated in acetonitrile solution, it can be recovered in unsolvated form by removal of solvent under vacuum. This manipulation, however, leads to some decomposition of **9** to $[Cp^*(PMe_3)_2Ru(NCMe)]OTf$.

Conductivity measurements in acetonitrile also shed light on the ionic nature of **9**. The equivalent conductance of **9**, measured for a 0.003 25 M solution at 24 °C, is 133 mho cm^2 equiv^{-1}. For comparison, the equivalent conductances for $Cp^*(PMe_3)_2RuSiPh_2Cl$ (**4**), $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]BPh_4\cdot CH_2Cl_2$ (**10**·CH_2Cl_2), and $[Cp^*(PMe_3)_2Ru(NCMe)]BPh_4$ (**11**) at the same concentration and temperature are 7.72, 98.3, and 95.7 mho cm^2 equiv^{-1}, respectively.

Given the lability of the triflate group in **9**, attempts were made to prepare silylene complexes by exchange of triflate for the potentially less coordinating anion tetraphenylborate. Reaction of **9** with NaBPh$_4$ in dichloromethane allowed crystallization of a single pure product as yellow-orange prisms (30% yield). This hydride complex has no diphenylsilylene group, and on the basis of comparison of ^{1}H and ^{31}P NMR data to that of previously reported $[Cp^*(PMe_3)_2Ru(H)Cl]PF_6$,[13] we formulate this complex as $[Cp^*(PMe_3)_2Ru(H)Cl]BPh_4$.

If this reaction is carried out in acetonitrile (or in dichloromethane in the presence of a few equivalents of added acetonitrile), a yellow crystalline material may be isolated by removal of solvent. Careful fractional crystallization from a dichloromethane–diethyl ether mixture allows isolation of **10** as a dichloromethane solvate (eq 6). This reaction also produces 30–40% of compound **11** as byproduct. An X-ray crystal structure determination for **10**·CH_2Cl_2 (vide infra) established the presence of one molecule of dichloromethane per formula unit, but by ^{1}H NMR spectroscopy the amount of solvent present is seen to vary from sample to sample, depending upon workup and storage conditions. As is common for nitrile coordination complexes,[23] two ν(CN) stretching frequencies are observed for **10**, at 2291 (m) and 2315 (w) cm^{-1}. These values are only slightly greater than the ν(CN) stretching frequency for free acetonitrile (2260 cm^{-1}), indicating rather weak complexation to the silylene silicon.[23] In close analogy to other donor-complexed silylene complexes (those without alkoxy substituents), the ^{29}Si NMR chemical shift for **10** is at δ 95.75 (see Table I).



(6)

In dichloromethane solution complex **10** decomposes slowly to **11** (10% decomposition after 8.5 days at room temperature, by ^{1}H NMR spectroscopy). It is much less stable in acetonitrile and decomposes with a half-life of 1.5–2 days at room temperature to three major products that have not been identified. Heating solid samples of **10** at 130 °C for 5 h results in decomposition to one major product, $Cp^*(PMe_3)_2RuSiPh_3$ (**2**) (83% isolated yield). The latter decomposition, therefore, involves transfer of a phenyl group from BPh_4^- to the silylene complex, but free BPh$_3$ was not present in the decomposition mixture (by ^{1}H NMR spectroscopy).

The acetonitrile of **10** is remarkably labile and exchanges with free acetonitrile in solution rapidly on the NMR time scale. The chemical shift for the acetonitrile protons in **10** is quite temperature dependent, varying steadily from δ 0.53 at −75 °C to δ 1.13 at 25 °C. At −75 °C a dichloromethane-d_2 solution of **10** in the presence of 1 equiv of added acetonitrile gives rise to two separate peaks for free and bound acetonitrile. As the sample is warmed, these resonances broaden and coalesce (coalescence temperature

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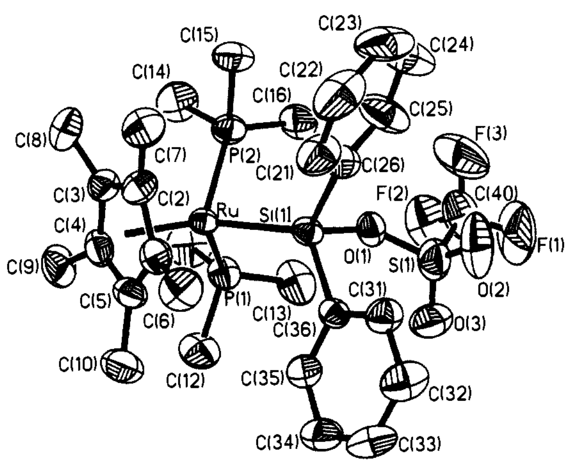

Figure 2. ORTEP view of $Cp^*(PMe_3)_2RuSiPh_2OTf$ (**9**) with atom-labeling scheme.

ca. −30 °C), and at room temperature there is only one peak that can be assigned to acetonitrile protons. A line-shape analysis of spectra taken over the temperature range −75 °C to +15 °C afforded activation parameters of $\Delta H^{\ddagger} = 14.5 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 14 \pm 2$ eu. The positive value for the entropy of activation indicates that acetonitrile exchange occurs via a dissociative mechanism (eq 7). This was confirmed by monitoring

$$Cp^*(PMe_3)_2RuSiPh_2(NCMe)^+ \rightleftarrows Cp^*(PMe_3)_2Ru{=}SiPh_2^+ + NCMe \quad (7)$$

the peak for bound acetonitrile in the slow-exchange region (−55 °C, line width due to exchange 12.7 Hz) as a function of added acetonitrile. Under these conditions the width of this peak at half-height did not increase over a 10-fold increase in acetonitrile concentration. Therefore, the exchange reaction is zero order in acetonitrile. A dissociative mechanism for exchange is also consistent with the observed reactivity of **10**, since reactions involving the silylene ligand (such as the reaction with water described below) are much slower in acetonitrile than in dichloromethane. Therefore, in solution, **10** is a convenient source of the base-free diphenylsilylene complex $[Cp^*(PMe_3)_2Ru{=}SiPh_2]BPh_4$.

Reactions of silylene complex **10** reflect the presence of an electrophilic silicon center. Acetonitrile is displaced from **10** by $LiAlH_4$ in tetrahydrofuran to afford **8** in 37% yield by ^1H NMR spectroscopy. The sensitivity of **10** to moisture is demonstrated by the rapid, quantitative reaction with water according to eq 8.

$$2Cp^*(PMe_3)_2RuSiPh_2(NCMe)^+ \xrightarrow{H_2O} \underset{\mathbf{11}}{2Cp^*(PMe_3)_2Ru(NCMe)^+} + Ph_2Si(H)OSi(H)Ph_2 \quad (8)$$

The complex $[Cp^*(PMe_3)_2Ru(NCMe)]BPh_4$ (**11**) was identified by comparison to an authentic sample, prepared by reaction of $Cp^*(PMe_3)_2RuCl$ with $AgBPh_4$ in acetonitrile. The disiloxane was prepared independently by reaction of Ph_2SiHCl with 0.5 equiv of water.

Because silylene complexes have been proposed as intermediates in transition-metal-mediated coupling reactions of unsaturated hydrocarbons with silylene fragments, we have conducted a preliminary survey of the reactivity of **10** with ethylene, acetylene, and phenylacetylene. In dichloromethane-d_2 no reactions were observed under the following relatively mild conditions: ethylene, room temperature, 1 equiv, 2 h; acetylene, room temperature. 1 equiv, 2 h; phenylacetylene, 50 °C, 1 equiv, 20 min.

Structural Studies. To investigate structure and bonding effects in related silyl and silylene derivatives of ruthenium, single-crystal X-ray diffraction studies were carried out on **8**, **9**, and **10**·CH_2Cl_2. Comparison of these $[Cp^*(PMe_3)_2RuSiPh_2Y]^{0/+}$ (Y = H, OTf, NCMe) structures provides information on the influence of silylene character on bond distances and angles. ORTEP views and atom-labeling schemes for these compounds are provided in Figures 1–3 and relevant geometrical parameters are listed in Tables III–V.

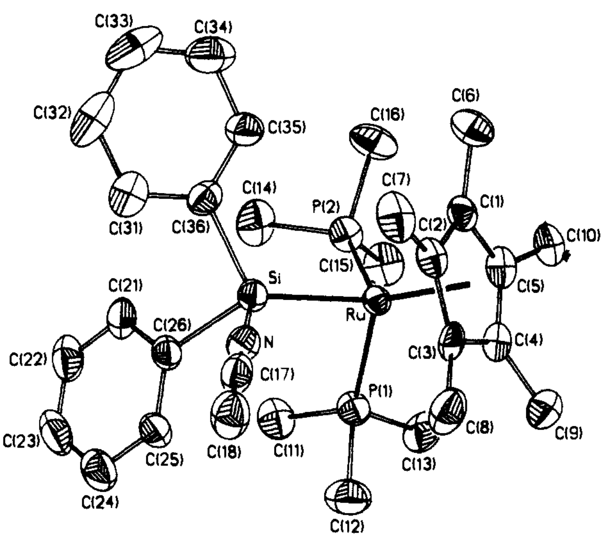

Figure 3. ORTEP view of the cation in $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]$-$BPh_4{\cdot}CH_2Cl_2$ (**10**·CH_2Cl_2) with atom-labeling scheme.

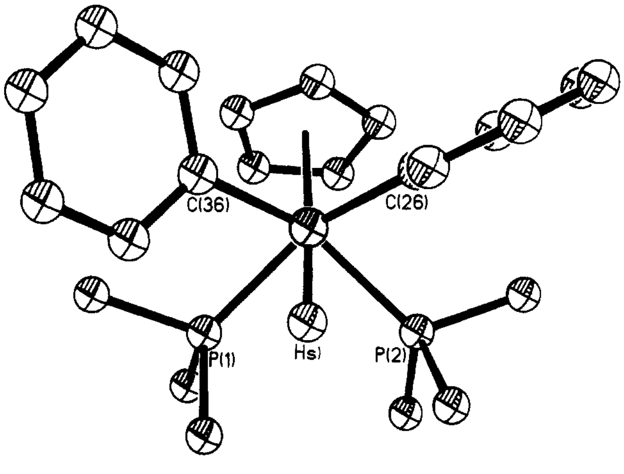

Figure 4. Newman projection down the Si–Ru bond of **8**. Torsion angles (deg): CNT-Ru-Si-C(26) 65.2; C(26)-Si-Ru-P(2) 70.6; P(2)-Ru-Si-Hsi 47.5; Hsi-Si-Ru-P(1) 45.0; P(1)-Ru-Si-C(36) 69.7; C(36)-Si-Ru-CNT 62.1; CNT-Ru-Si-Hsi 176.7. Cp* methyl groups are omitted for clarity.

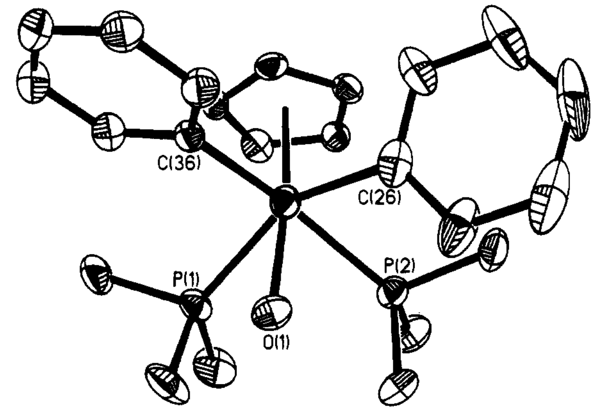

Figure 5. Newman projection down the Si–Ru bond of **9**. Torsion angles (deg): CNT-Ru-Si-C(26) 72.3; C(26)-Si-Ru-P(2) 58.6; P(2)-Ru-Si-O(1) 57.3; O(1)-Si-Ru-P(1) 35.3; P(1)-Ru-Si-C(36) 81.8; C-(36)-Si-Ru-CNT 54.6; CNT-Ru-Si-O(1) 171.8. Cp* methyl and SO_2CF_3 groups are omitted for clarity.

Many of the corresponding distances and angles for these structures are similar, particularly those that describe the coordination environments about the ruthenium atoms (see Tables III–V). There are significant differences, however, in conformations about the Ru–Si bonds of **8**, **9**, and **10**·CH_2Cl_2 in the

Table II. Crystal, Data Collection, and Refinement Parameters for **8**, **9**, and **10**·CH_2Cl_2

	8	**9**	**10**·CH_2Cl_2
	Crystal Parameters		
formula	$C_{28}H_{44}P_2RuSi$	$C_{29}H_{43}F_3O_3P_2RuSi$	$C_{55}H_{68}BCl_2NP_2RuSi$
crystal size, mm	0.25 × 0.33 × 0.38	0.06 × 0.36 × 0.40	0.30 × 0.30 × 0.35
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	9.362 (1)	10.171 (3)	21.565 (8)
b, Å	9.748 (2)	10.802 (3)	10.215 (4)
c, Å	16.376 (3)	16.880 (5)	25.59 (1)
α, deg	98.18 (2)	86.82 (2)	
β, deg	103.71 (2)	88.03 (2)	108.40 (3)
γ, deg	94.14 (2)	64.00 (1)	
V, Å^3	1428.4 (6)	1664.2 (7)	5349 (3)
Z	2	2	4
ρ (calcd), g cm^{-3}	1.339	1.436	1.26
μ (Mo Kα), cm^{-1}	7.0	7.0	5.1
	Data Collection		
diffractometer	Nicolet R3m	Nicolet R3m/V	Nicolet R3m/μ
radiation	Mo Kα	Mo Kα	Mo Kα
temp, °C	25	23	23
scan limits, deg	$4 \le 2\theta \le 55$	$3 \le 2\theta \le 45$	$4 \le 2\theta \le 48$
reflcns collected	6791	4642	7735
indpdt reflcns	6560	4342	7050
R (merge), %	1.2	1.8	2.3
obs reflcns	5824 ($3\sigma F_o$)	3004 ($6\sigma F_o$)	4288 ($3\sigma F_o$)
std reflcns	3 std/197 data	3 std/67 data	3 std/197 data
decay, %	≤ 1	2	<1
	Refinement		
R_F, %	2.59	4.39	6.32
R_{wF}, %	2.98	5.61	6.37
GOF	0.94	1.03	1.44
Δ/σ (final)	0.09	0.00	0.13
$\Delta(\rho)$, e Å^{-3}	0.33	0.93	1.14 (near Cl(1))
N_o/N_v	12.5	8.9	8.4

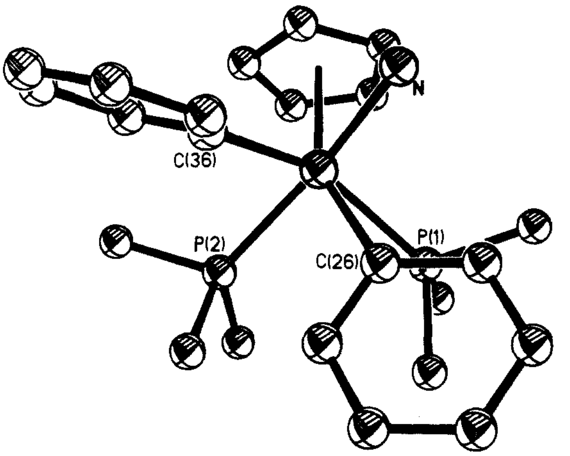

Figure 6. Newman projection down the Si-Ru bond of **10**·CH_2Cl_2. Torsion angles (deg): CNT-Ru-Si-N 38.0; N-Si-Ru-P(1) 94.2; P(1)-Ru-Si-C(26) 15.1; C(26)-Si-Ru-P(2) 76.5; P(2)-Ru-Si-C(36) 65.7; C(36)-Si-Ru-CNT 70.4. Cp* methyl and CMe(nitrile) groups are omitted for clarity.

solid-state structures, as demonstrated by Newman projections down the Si-Ru bonds (Figures 4–6). Complex **8** possesses a symmetric, staggered conformation that reflects steric hindrance between the Cp* and PMe_3 ligands (see torsion angles, Figure 4). The hydrogen substituent on silicon and the Cp* ligand adopt a nearly perfect anti relationship (Cp* centroid-Ru-Si-H torsion angle = 176.7°). Apparently this allows the phenyl groups to nestle into the spaces between the Cp* and PMe_3 ligands. Triflate derivative **9** exhibits a similar structure with the phenyl groups in a gauche relationship to the Cp* ligand, but skewed somewhat away from a perfectly staggered conformation (Figure 5). Finally, **10**·CH_2Cl_2 exists in a quite different conformation, with a nearly eclipsed P-Ru-Si-C(phenyl) arrangement (15.1°) and a surprisingly small Cp* centroid-Ru-Si-N dihedral angle (38.0°) (Figure 6). Presently it is difficult to provide a definitive explanation for these differences, but it seems likely that barriers to rotation about the Ru-Si bonds in these compounds are relatively small. Also, it is not clear that there should be an electronic preference for the conformation displayed by **10**·CH_2Cl_2. since the silylene π-acceptor orbital is utilized in bonding to the acetonitrile.

The most direct probe of Ru-Si multiple-bond character is perhaps the Ru-Si bond length, which decreases on going from **8** (2.387 (1) Å) to **9** (2.349 (2) Å) to **10**·CH_2Cl_2 (2.328 (2) Å). The value for **10**·CH_2Cl_2 represents the shortest Ru-Si bond yet reported, which is consistent with some silylene character at silicon. However, this distance is only 0.06 Å shorter than that found for **8**, and other reported Ru-Si distances range between 2.34 and 2.51 Å, with a mean of 2.44 Å.[24] A difficulty in making these comparisons is that often M-Si "single-bond" distances for late-transition-metal silyl complexes are shorter than expected on the basis of covalent radii, possibly due to π-bonding interactions resulting from donation of d-electron density to empty orbitals on silicon.[3]

Available structural data for germylene and stannylene complexes $L_nMM'X_2$ (M' = Ge, Sn) show planar $MM'X_2$ arrangements that are consistent with sp^2 hybridization at M'.[2] These

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Table III. Selected Bond Distances (Å) and Angles (deg) for **8**

Bond Distances			
Ru-CNT[a]	1.934	Ru-Hsi	1.39 (2)
Ru-Si	2.387 (1)	Si-C (26)	1.916 (2)
Ru-P(1)	2.265 (1)	Si-C (36)	1.928 (2)
Ru-P(2)	2.277 (1)		
Bond Angles			
CNT-Ru-Si	125.8	Hsi-Si-Ru	112.9 (9)
CNT-Ru-P(1)	124.5	Hsi-Si-C(26)	100.8
CNT-Ru-P(2)	126.4	Hsi-Si-C(36)	96.7
Si-Ru-P(1)	87.4 (1)	C(26)-Si-C(36)	100.5 (1)
Si-Ru-P(2)	88.9 (1)	Ru-Si-C(26)	119.4 (1)
P(1)-Ru-P(2)	92.4 (1)	Ru-Si-C(36)	122.4 (1)

[a] CNT = Cp* ring centroid.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **9**

Bond Distances			
Ru-CNT[a]	1.941	Si-O(1)	1.853 (5)
Ru-Si	2.349 (2)	Si-C(26)	1.935 (8)
Ru-P(1)	2.308 (3)	Si-C(36)	1.928 (5)
Ru-P(2)	2.290 (2)		
Bond Angles			
CNT-Ru-Si	122.1	O(1)-Si-Ru	118.2 (2)
CNT-Ru-P(1)	123.8	O(1)-Si-C(26)	96.7 (3)
CNT-Ru-P(2)	123.2	O(1)-Si-C(36)	97.1 (2)
Si-Ru-P(1)	95.8 (1)	C(26)-Si-C(36)	103.7 (2)
Si-Ru-P(2)	90.8 (1)	Ru-Si-C(26)	118.1 (2)
P(1)-Ru-P(2)	92.5 (1)	Ru-Si-C(36)	118.8 (2)

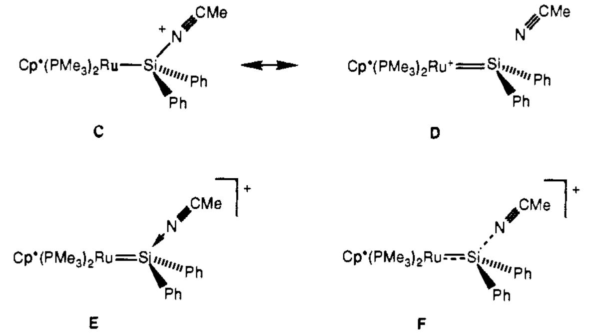
[a] CNT = Cp* ring centroid.

Table V. Selected Bond Distances (Å) and Angles (deg) for **10**·CH_2Cl_2

Bond Distances			
Ru-CNT[a]	1.927	Si-C(26)	1.930 (6)
Ru-Si	2.328 (2)	Si-C(36)	1.916 (8)
Ru-P(1)	2.291 (3)	N-C(17)	1.132 (12)
Ru-P(2)	2.300 (3)	C(17)-C(18)	1.434 (14)
Si-N	1.932 (8)		
Bond Angles			
CNT-Ru-Si	125.7	N-Si-C(26)	91.3 (3)
CNT-Ru-P(1)	122.9	N-Si-C(36)	93.8 (3)
CNT-Ru-P(2)	124.7	C(26)-Si-C(36)	102.2 (3)
Si-Ru-P(1)	92.5 (1)	Ru-Si-C(26)	128.2 (2)
Si-Ru-P(2)	93.9 (1)	Ru-Si-C(36)	121.2 (2)
P(1)-Ru-P(2)	91.5 (1)	Si-N-C(17)	178.9 (7)
N-Si-Ru	110.9 (2)	N-C(17)-C(18)	178.7 (8)

[a] CNT = Cp* ring centroid.

Chart I



structures also exhibit rather acute X-M′-X angles (ca. 100°), which suggest that considerable s character is concentrated into the M-M′ bonds. For example, acute X-M′-X angles have been observed for $(CO)_5CrGe(SMes)_2$ (102.4 (2)°),[25] $(CO)_5CrGe[CH(SiMe_3)_2]_2$ (102.8 (2)°),[26] and $(CO)_5CrSn[CH(SiMe_3)_2]_2$ (98°).[27] It has also been noted that addition of a Lewis base to the M′ center leads to some pyramidalization but does not change the geometry at M′ to the degree that might have been expected.[2] Thus, $(CO)_5CrSn^tBu_2(pyr)$ has a C-Sn-C angle of 109.5 (7)°, and the tin atom lies only 0.44 Å above the plane defined by the chromium and carbon substituents. Also in the latter structure, the Cr-Sn-C angles of 119.6 (4)° and 120.8 (5)° are greater than the Cr-Sn-N angle of 107.8 (3)°.[28] Similar distortions from tetrahedral geometry at silicon have been reported for base-complexed silylene derivatives $(CO)_4FeSi(O^tBu)_2(HMPA)$,[10a] $(CO)_5CrSi(O^tBu)_2(HMPA)$,[10c] and $(CO)_4FeSiMe_2(HMPA)$;[10d] for Lewis base adducts of silaimines $(Me_2Si(THF)NSi^tBu_3$[29] and $^tBu_2Si(O{=}CPh_2)NSi^tBu_3$[30]); and for a silene $(Me_2Si(THF)C(SiMe_3)SiMe^tBu_2)$.[31] In all of these adducts, the angle between the formal double bond and the bond to the Lewis base donor atom is in the range 106–112°. The other bond angles involving the Lewis base (base–M′–X) are 97–104°, and angles between the formal double bond and the M′ substituents X are ca. 116–124°.

The geometry of **10**·CH_2Cl_2 corresponds closely to the above trends. For example, the C-Si-C angle is rather small, at 102.2 (3)°. As might be expected for considerable silylene character, the Ru-Si-C angles, 121.2 (2) and 128.2 (2)°, are much larger than the Ru-Si-N angle of 110.9 (2)°, and the C-Si-N angles, 91.3 (3) and 93.8 (3)°, are close to 90°. Note, however, that bond angles about the silicon atoms of **8** and **9** also reflect considerable distortion from tetrahedral geometry, presumably for steric reasons. The silicon atom in **10**·CH_2Cl_2 is the least pyramidal, as can be seen for example by comparing the Ru-Si-Y angles of 110.9 (2)° (Y = NCMe), 112.9 (9)° (Y = H), and 118.2 (2)° (Y = OTf). In comparing these angles, one must also consider the differences in conformations about the Ru-Si bonds. In **8** and **9**, the Y group is anti to the bulky Cp* ligand, whereas in **10**·CH_2Cl_2 the Cp* and NCMe substituents are nearly eclipsed. The silicon atom in **10**·CH_2Cl_2 lies 0.34 Å above the plane defined by Ru, C(26), and C(36). The corresponding values for **8** and **9** are 0.51 and 0.53 Å, respectively.

The exceptionally long Si-O distance of 1.853 (5) Å for **9** may reflect stabilization of the diphenylsilylene group by the electron-rich $Cp^*(PMe_3)_2Ru$ fragment. For comparison, Si-O single bonds in compounds of tetrahedral silicon normally fall in the range 1.63–1.66 Å.[31b] This distance is also considerably longer than Si-O distances found in donor adducts of silylene complexes involving less electron-rich, first-row transition-metal carbonyl derivatives (see Table I). The Si-N distance in **10**·CH_2Cl_2, 1.932 (8) Å, is also quite long since typical Si-N single bonds to tetrahedral silicon range between 1.7 and 1.8 Å.[32] Other distances and angles within the coordinated acetonitrile are consistent with a dative interaction between nitrogen and silicon.[23b]

Conclusions

Silyl for alkyl ligand exchanges in reactions of $Cp^*(PMe_3)_2RuCH_2SiMe_3$ with silanes provide good synthetic routes to new ruthenium(II) and ruthenium(IV) silyl complexes. Silyl ligands in these complexes are readily modified via exchange reactions at silicon. The electron-rich $Cp^*(PMe_3)_2Ru$ fragment appears to bind strongly to silyl groups and helps stabilize the diphenylsilylene ligand. Evidence for this is seen in the solution behavior of **9**, which possesses a labile triflate group and ionizes in acetonitrile solution to give the acetonitrile-complexed silylene derivative $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]OTf$. The triflate group

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in this salt can be exchanged for tetraphenylborate, allowing isolation of the silylene complex **10**·CH_2Cl_2. The Si-O(triflate) distance in **9** and the Si-N(acetonitrile) distance in **10**·CH_2Cl_2 are quite long, indicating that the silylene group in these complexes is stabilized to a greater extent than those in less electron-rich, first-row transition-metal carbonyl derivatives (see Table I). As has been discussed previously for donor adducts of silenes,[22a,31a] the bonding in **10** is probably best described by a hybrid of two limiting formulations: **C** and the no-bond structure **D** (Chart I). This bonding model can be represented by either of the single structures **E** or **F**, and we have chosen to use the former representation (**E**) because it appears to reflect observed reactivity patterns.

Significantly, dynamic NMR studies show that exchange of acetonitrile in **10** with free acetonitrile occurs by a dissociative mechanism. This result represents the first direct evidence for a base-free silylene complex, $Cp^*(PMe_3)_2Ru{=}SiPh_2{}^+$. We therefore conclude that base-free silylene complexes are relatively stable and should be isolable under favorable circumstances. Efforts are underway to isolate such species.

Experimental Section

General Conditions. All manipulations were performed under an inert atmosphere of nitrogen or argon. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Galbraith Microanalytical Laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^1H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si) and on a Varian EM 390 instrument at 90 MHz. The $^{29}Si\{^1H\}$ NMR spectra were obtained with single-pulse techniques, with an $\approx 45°$ pulse angle and a 1.2-s delay between pulses. Conductivity measurements were obtained with a YSI Model 35 conductance meter. The compounds $HSi(OEt)_3$ (Aldrich), $HSiPh_3$ (Aldrich), $HSiPh_2Me$ (Aldrich), $Me_3SiOSO_2CF_3$ (Petrarch), and H_2SiPh_2 (Petrarch) were used as received. The silanes $HSiCl_3$ and $HSiPh_2Cl$ (Petrarch) were distilled before use, and $HSiEt_3$ (Petrarch) was stored over 4-Å molecular sieves. The complexes $Cp^*(PMe_3)_2RuCl$ and $Cp^*(PMe_3)_2RuCH_2SiMe_3$ were prepared according to the literature procedure.[13]

$Cp^*(PMe_3)_2RuSiEt_3$ (1). A solution of $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (0.60 g, 1.26 mmol) in $HSiEt_3$ (4 mL) was refluxed for 5 h. The resulting yellow solution was evacuated to dryness, giving a yellow crystalline solid that was shown to be reasonably pure **1** by ^1H NMR. The compound was dissolved in pentane, and concentration and cooling (−40 °C) of this solution gave one crop of analytically pure **1** in 68% yield (0.44 g). Anal. Calcd for $C_{22}H_{48}P_2RuSi$: C, 52.5; H, 9.61. Found: C, 52.4; H, 9.42. ^1H NMR (90 MHz, 34 °C, benzene-d_6): δ 1.15 (q, J = 7 Hz, 6 H, $SiC\mathit{H}_2CH_3$), 1.21 (virtual t, 18 H, PMe_3), 1.42 (t, J = 7 Hz, 9 H, $SiCH_2C\mathit{H}_3$), 1.71 (s, 15 H, Cp*).

$Cp^*(PMe_3)_2RuSiPh_3$ (2). Toluene (4 mL), $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (2.00 g, 4.20 mmol), and $HSiPh_3$ (1.15 g, 4.42 mmol) were combined in a reaction flask. The closed (Teflon stopcock) flask was heated at 100 °C for 6 h. After the solution was stored at room temperature for 2 h, large yellow crystals of the product formed. Cooling to −50 °C for 6 h resulted in further crystallization. The product was isolated by filtration and dried under vacuum to give **2** in 78% yield (2.13 g). Anal. Calcd for $C_{34}H_{48}P_2RuSi$: C, 63.0; H, 7.47. Found: C, 63.1; H, 7.36. ^1H NMR (90 MHz, 34 °C, benzene-d_6): δ 1.12 (virtual t, 18 H, PMe_3), 1.49 (t, J = 1 Hz, 15 H, Cp*), 7.20 (m, 6 H, Ph), 7.84 (m, 4 H, Ph).

$Cp^*(PMe_3)_2RuSiPh_2Me$ (3). A partially evacuated flask containing toluene (2 mL), $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (0.45 g, 0.95 mmol), and $HSiPh_2Me$ (0.19 mL, 0.96 mmol) was closed (Teflon stopcock), and the contents were heated to 90 °C for 9 h. All volatiles were then removed by vacuum transfer to give 0.51 g (92%) of yellow crystalline **3** of >95% purity by ^1H NMR. Analytically pure **3** was obtained by recrystallization from toluene. Anal. Calcd for $C_{29}H_{46}P_2RuSi$: C, 59.5; H, 7.92. Found: C, 59.7; H, 8.04. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 0.59 (s, 3 H, $SiCH_3$), 1.32 (virtual t, 18 H, PMe_3), 1.62 (s, 15 H, Cp*), 7.11 (m, 6 H, Ph), 7.41 (m, 4 H, Ph). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 9.82 (q, J = 117 Hz, $SiCH_3$), 12.08 (q, J = 126 Hz, $C_5\mathit{Me}_5$), 24.48 (qt, J_{CH} = 128 Hz, J_{CP} = 14 Hz, PMe_3), 93.37 (s, C_5Me_5), 125.83 (d, J = 158 Hz), 126.37 (d, J = 161 Hz), 136.50 (d, J = 153 Hz), 153.59 (s).

$Cp^*(PMe_3)_2RuSiPh_2Cl$ (4). (a) The procedure described below for **6** was followed with a closed system (tightly sealed Schlenk tube; no degassing of the reaction mixture during heating), and workup after 16 h gave **4** in near quantitative yield.

(b) A sealed tube containing **6** (1.20 g, 1.60 mmol), toluene (6 mL), and PMe_3 (1 mL, 9.4 mmol) was heated to 100–110 °C. Compound **6** slowly dissolved and eventually gave a yellow solution. The solution was heated at 100–110 °C for 36 h and was then cooled (at −40 °C for 5 h and then at −78 °C for 12 h) to give crystalline **4**, which was isolated by filtration and washed with cold (−78 °C) pentane (2 × 5 mL). The crystals were exposed to vacuum for 3 h at 40 °C to remove traces of the silane $HSiPh_2Cl$. Yield was 0.90 g (92%). Anal. Calcd for $C_{28}H_{43}ClP_2RuSi$: C, 55.1; H, 7.15; Cl, 5.85. Found: C, 55.3; H, 7.25; Cl, 5.64. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 1.41 (virtual t, 18 H, PMe_3), 1.65 (s, 15 H, Cp*), 7.20 (m, 6 H, Ph), 7.60 (m, 4 H, Ph). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 11.81 (q, J = 126 Hz, $C_5\mathit{Me}_5$), 24.02 (qt, J_{CH} = 126 Hz, J_{CP} = 15 Hz, PMe_3), 94.14 (s, C_5Me_5), 126.52 (d, J = 156 Hz), 126.90 (d, J = 159 Hz), 135.76 (d, J = 156 Hz), 150.76 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, 20 °C, dichloromethane-d_2): δ 3.27. $^{29}Si\{^1H\}$ NMR (59.6 MHz, 23 °C, dichloromethane-d_2): δ 74.07 (t, $^2J_{PSi}$ = 30 Hz). IR (Nujol, CsI, cm^{-1}): 1300 m, 1278 w, 1136 w, 1104 w, 1080 m, 1021 w, 952 m, 938 m, 850 m, 734 m, 722 m, 705 m, 666 w, 502 m, 473 w, 440 w, 423 w, 402 w.

Reaction of $Cp^*(PMe_3)_2RuCH_2SiMe_3$ with $HSiCl_3$. $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (0.31 g, 0.65 mmol), $HSiCl_3$ (excess, 10 mL), and dioxane (15 mL) were combined in a flask, and the mixture was heated at reflux for 3 h. Removal of all volatile material by vacuum transfer left a pale yellow residue that was insoluble in pentane. Extraction with diethyl ether (110 mL) gave a pale yellow solution that was concentrated (to ca. 60 mL) and cooled (to −40 °C) to afford 0.17 g of crystals. ^1H NMR spectroscopy showed that these crystals were a mixture of two compounds, probably $Cp^*(PMe_3)_2RuSiCl_3$ and $Cp^*(PMe_3)_2RuSiHCl_2$. ^1H NMR (90 MHz, 34 °C, benzene-d_6): δ 1.06–1.23 (two overlapping virtual triplets, PMe_3), 1.60 (t, J = 1.5 Hz, Cp* of $Cp^*(PMe_3)_2RuSiHCl_2$), 1.65 (t, J = 1.2 Hz, Cp* of $Cp^*(PMe_3)_2RuSiCl_3$), 6.89 (t, J = 3 Hz, $RuSiHCl_2$). IR (Nujol, CsI, cm^{-1}): ν(SiH) = 2060.

$Cp^*(PMe_3)Ru[Si(OEt)_3]_2H$ (5). A partially evacuated flask containing $HSi(OEt)_3$ (3 mL) and $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (0.83 g, 1.74 mmol) was closed (Teflon stopcock), and the contents were heated to 80 °C for 12 h. At this point the solution was pumped on briefly to remove some of the free PMe_3 that had formed. Heating of the solution was then continued at 80 °C for another 6 h. The resulting yellow solution was stripped down by evacuation to a waxy solid that was shown to be crude **5** by ^1H NMR (1.02 g, 92%). Recrystallization from acetone gave the analytically pure complex. Anal. Calcd for $C_{25}H_{55}O_3PRuSi_2$: C, 46.9; H, 8.66. Found: C, 46.7; H, 8.78. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ −13.47 (d, 1 H, J_{PH} = 3 Hz, RuH), 1.29 (t, J = 7 Hz, 18 H, $SiOCH_2C\mathit{H}_3$), 1.48 (d, J_{PH} = 9.6 Hz, 9 H, PMe_3), 1.90 (s, 15 H, Cp*), 3.98 (m, 12 H, $SiOC\mathit{H}_2CH_3$). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 11.01 (q, J = 127 Hz, $C_5\mathit{Me}_5$), 18.66 (q, J = 115 Hz, $SiOCH_2\mathit{C}H_3$), 22.0 (br m, PMe_3), 58.20 (t, J = 140 Hz, $SiO\mathit{C}H_2CH_3$), 97.02 (s, C_5Me_5).

$Cp^*(PMe_3)Ru(SiPh_2Cl)_2H$ (6). To $Cp^*(PMe_3)_2RuCH_2SiMe_3$ (1.12 g, 2.35 mmol) was added 2.2 mL (8.98 mmol) of $HSiPh_2Cl$. After this solution was heated to 110 °C with stirring, all the $Cp^*(PMe_3)_2RuCH_2SiMe_3$ dissolved to form an orange-yellow solution. Several minutes later, a yellow solid precipitated from solution. The solution was kept at 110 °C over 16 h, and during this time the solution was periodically evacuated briefly (ca. eight times) to remove PMe_3. The solution was cooled to room temperature, pentane (6 mL) was added, and the resulting mixture was cooled to −78 °C for 6 h. Pale yellow crystals of **6** (1.37 g, 78%) were isolated by filtration, washed with more cold (−78 °C) pentane (2 × 5 mL), and dried under vacuum. Anal. Calcd for $C_{37}H_{45}Cl_2PRuSi_2$: C, 59.3; H, 6.06; Cl, 9.47. Found: C, 58.4; H, 6.28; Cl, 9.26. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ −11.60 (d, 1 H, J_{PH} = 3 Hz, RuH), 1.06 (d, J_{PH} = 9 Hz, 9 H, PMe_3), 1.53 (s, 15 H, Cp*), 7.09 (m, 6 H, Ph), 7.28 (m, 4 H, Ph), 7.43 (m, 6 H, Ph), 8.06 (d, J = 7 Hz, 4 H, Ph). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 10.91 (q, J = 128 Hz, $C_5\mathit{Me}_5$), 22.10 (qd, J_{CH} = 124 Hz, J_{CP} = 32 Hz, PMe_3), 100.67 (s, C_5Me_5), 127.38 (d, J = 159 Hz), 127.51 (d, J = 159 Hz), 128.10 (d, J = 160 Hz), 128.58 (d, J = 160 Hz), 135.06 (d, J = 157 Hz), 145.68 (s), 146.73 (s). $^{29}Si\{^1H\}$ NMR (59.6 MHz, 23 °C, dichloromethane-d_2): δ 57.81 (d, $^2J_{PSi}$ = 23 Hz). IR (Nujol, CsI, cm^{-1}): 1918 w (ν(RuH)), 1087 m, 1023 w, 953 m, 934 w, 852 w, 737 m, 722 w, 701 s, 495 w, 475 m, 460 m, 408 m.

$Cp^*(PMe_3)_2RuSiPh_2H$ (8). To **4** (0.58 g, 0.96 mmol) and $LiAlH_4$ (0.20 g, 5.3 mmol) was added tetrahydrofuran (40 mL). After the reaction mixture was stirred at room temperature for 1 h, volatiles were removed and the product was extracted into toluene (50 mL). This solution was filtered, and concentration and cooling (−40 °C) gave **8** in 53% yield (0.29 g). Anal. Calcd for $C_{28}H_{44}P_2RuSi$: C, 58.8; H, 7.76. Found: C, 58.5; H, 7.72. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 1.35 (virtual t, 18 H, PMe_3), 1.71 (s, 15 H, Cp*), 5.19 (t, J = 7 Hz, 1 H, SiH), 7.17 (m, 6 H, Ph), 7.49 (m, 4 H, Ph). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 11.85 (q, J = 125 Hz, $C_5\mathit{Me}_5$), 23.29 (qt, J_{CH} = 125 Hz, J_{CP} = 14 Hz, PMe_3), 92.73 (s,

C_5Me_5), 126.28 (d, J = 158 Hz), 126.79 (d, J = 157 Hz), 136.79 (d, J = 154 Hz), 149.23 (s). IR (Nujol, CsI, cm^{-1}): 2028 m (ν(SiH)), 1299 m, 1278 m, 1168 w, 1151 w, 1082 m, 1062 w, 1023 m, 953 s, 938 s, 842 s, 724 s, 702 s, 667 m, 660 m.

$Cp^*(PMe_3)_2RuSiPh_2(OTf)$ (9). To an ice-cooled solution of **4** (3.36 g, 5.5 mmol) in dichloromethane (40 mL) was added Me_3SiOTf (2.0 mL, 10 mmol), causing a darker yellow color to develop. The reaction solution was stirred at 0 °C for 15 min and then for 1 h as it was allowed to warm to room temperature. Volatiles were removed, and the resulting yellow powder was recrystallized from a 1:1 mixture of dichloromethane and pentane to afford **9** in 89% yield (3.53 g). Anal. Calcd for $C_{29}H_{43}F_3O_3P_2RuSSi$: C, 48.4; H, 6.02. Found: C, 48.2; H, 5.93. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 1.40 (virtual t, 18 H, PMe_3), 1.58 (s, 15 H, Cp*), 7.30 (m, 6 H, Ph), 7.62 (m, 4 H, Ph). ^1H NMR (300 MHz, 20 °C, acetonitrile-d_3): δ 1.36 (virtual t, 18 H, PMe_3), 1.65 (s, 15 H, Cp*), 7.31 (m, 6 H, Ph), 7.47 (m, 4 H, Ph). ^{13}C NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 11.57 (q, J = 127 Hz, $C_5\mathit{Me}_5$), 23.91 (qt, J_{CH} = 125 Hz, J_{CP} = 14 Hz, PMe_3), 94.18 (s, C_5Me_5), 126.83 (d, J = 156 Hz), 128.38 (d, J = 159 Hz), 136.09 (d, J = 154 Hz), 145.39 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, 20 °C, dichloromethane-d_2): δ 2.16. $^{29}Si\{^1H\}$ NMR (59.6 MHz, 23 °C, dichloromethane-d_2): δ 112.39 (t, J_{PSi} = 33 Hz). IR (Nujol, CsI, cm^{-1}): 1360 s, 1310 w, 1300 w, 1290 w, 1280 w, 1226 m, 1182 s, 1160 m, 1087 m, 1026 w, 960 s, 943 s, 850 m, 742 m, 721 m, 709 m, 700 m, 670 m, 632 m, 517 m, 493 m, 448 w, 416 w.

$[Cp^*(PMe_3)_2RuSiPh_2(NCMe)]BPh_4\cdot CH_2Cl_2$ ($10\cdot CH_2Cl_2$). Compound **9** (2.01 g, 2.8 mmol), $NaBPh_4$ (1.16 g, 3.4 mmol), and acetonitrile (25 mL) were combined in a flask at 0 °C. After the mixture was stirred for 10 min, the ice bath was removed and the mixture allowed to stir for an additional period of 1 h. All volatiles were removed by extended (16 h) application of vacuum (10^{-3} mmHg). The residue was extracted with dichloromethane (15 mL), and this solution was then concentrated to ca. 5 mL. Slow addition of 3 mL of diethyl ether with stirring, followed by cooling to −40 °C, resulted in formation of yellow crystals of the product (1.08 g, 38%). The crude reaction mixture obtained by this procedure contains 30–40% of compound **11** as byproduct. Compound **10** may also be obtained in comparable yield by an analogous procedure with, as solvent, dichloromethane with 5 equiv of added acetonitrile. With this procedure it is easier to obtain product free of excess acetonitrile after a single crystallization. The elemental analysis obtained for this compound corresponds to a formula with only a small portion of dichloromethane solvate, implying that dichloromethane is readily lost from the crystals. Anal. Calcd for $C_{54}H_{66}BNP_2RuSi$ (no CH_2Cl_2): C, 69.7; H, 7.15. Anal. Calcd for $C_{54.5}H_{67}BClNP_2RuSi$ ($^1/_2$ CH_2Cl_2): C, 67.2; H, 6.94. Found: C, 68.9; H, 7.77. ^1H NMR (300 MHz, 23 °C, dichloromethane-d_2): δ 1.22 (s, 3 H, CH_3CN), 1.33 (virtual t, 18 H, PMe_3), 1.65 (t, J = 3 Hz, 15 H, Cp*), 5.35 (s, 2 H, free CH_2Cl_2), 6.85 (t, J = 8 Hz, 4 H, Ph), 7.00 (t, J = 8 Hz, 8 H, Ph), 7.37 (br m, 18 H, Ph). ^1H NMR (300 MHz, 20 °C, acetonitrile-d_3): δ 1.36 (virtual t, 18 H, PMe_3), 1.66 (s, 15 H, Cp*), 6.81 (t, J = 7 Hz, 4 H, $B(p\text{-}C_6H_5)_4$), 6.98 (t, J = 7 Hz, 8 H, $B(m\text{-}C_6H_5)_4$), 7.26 (br m, 8 H, $B(o\text{-}C_6H_5)_4$), 7.31 (m, 6 H, $RuSi(m,p\text{-}C_6H_5)_2$), 7.47 (m, 4 H, $RuSi(o\text{-}C_6H_5)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 0.83 (CH_3CN), 11.55 ($C_5\mathit{Me}_5$), 23.88 (pseudotriplet, PMe_3), 94.64 (s, C_5Me_5), 122.11, 126.17, 127.88, 129.32, 135.55, 136.16, 143.43 (Ph), 164.46 (q, J_{BC} = 50 Hz, ipso carbons of BPh_4). $^{31}P\{^1H\}$ NMR (121.5 MHz, 20 °C, dichloromethane-d_2): δ 0.46. $^{29}Si\{^1H\}$ NMR (59.6 MHz, 23 °C, dichloromethane-d_2): δ 95.75 (br m). IR (Nujol, CsI, cm^{-1}): 2315 w, 2291 m (ν(CN)), 1575 m, 1425 s, 1304 m, 1281 m, 1262 m, 1180 w, 1148 w, 1089 m, 1062 w, 1038 w sh, 1030 m, 998 w, 952 s, 948 s, 850 m, 740 s, 709 s, 625 w, 614 w, 604 m, 595 w, 508 s, 475 m, 441 m, 378 m.

$[Cp^*(PMe_3)_2Ru(NCMe)]BPh_4$ (11). The complex $Cp^*(PMe_3)_2RuCl$ (0.436 g, 1.03 mmol) and $AgBPh_4$ (0.440 g, 1.03 mmol) were combined in a flask, and 8 mL of acetonitrile was added at room temperature. A greenish suspension resulted, and after 10 min of stirring the solution was filtered and evacuated to dryness. Crystallization of the residue from a diethyl ether–dichloromethane mixture (1:1, ca. 10 mL) at −40 °C resulted in isolation of 0.580 g (75%) of **11**. Anal. Calcd for $C_{42}H_{56}BNP_2Ru$: C, 67.4; H, 7.54; N, 1.87. Found: C, 67.0; H, 7.93; N, 1.73. ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 1.40 (virtual t, 18 H, PMe_3), 1.69 (t, J = 1.6 Hz, 15 H, Cp*), 2.03 (t, J = 1.6 Hz, CH_3CN), 6.90 (t, J = 8 Hz, 4 H, Ph), 7.05 (t, J = 8 Hz, 8 H, Ph), 7.34 (br m, 8 H, Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, 20 °C, dichloromethane-d_2): δ 4.15 (CH_3CN), 10.88 ($C_5\mathit{Me}_5$), 20.10 (t, J_{PC} = 15 Hz, PMe_3), 91.40 (s, C_5Me_5), 122.04, 125.96, 136.24 (Ph), 164.39 (q, J_{BC} = 49 Hz, ipso carbons of BPh_4). $^{31}P\{^1H\}$ NMR (121.5 MHz, 20 °C, dichloromethane-d_2): δ 0.98. IR (Nujol, CsI, cm^{-1}): 2257 w, ν(CN), 1578 m, 1426 s, 1305 w, 1285 m, 1180 w, 1145 w, 1115 w, 1065 w, 1030 m, 959 s, 940 s, 845 m, 740 w sh, 732 s, 708 s, 669 w, 625 w, 608 m, 598 w, 360 w.

$Ph_2HSiOSiHPh_2$. To Ph_2SiHCl (1 mL, 5.1 mmol) in acetonitrile (10 mL) was added H_2O (50 μL, 2.8 mmol), and the solution was stirred for 1 h. All volatiles were removed by evacuation, and the resulting residue was extracted with pentane (20 mL). Concentration and cooling of this solution (−78 °C) resulted in crystallization of the product in 76% yield (0.85 g). ^1H NMR (300 MHz, 20 °C, dichloromethane-d_2): δ 5.59 (s, 2 H, SiH), 7.40 (m, 6 H, Ph), 7.57 (dd, 4 H, Ph). IR (Nujol, CsI, cm^{-1}): 2121, ν(SiH). MS (EI): parent ion observed at m/e 382.

Dynamic NMR Studies. Samples were dissolved in dichloromethane-d_2, and ^1H NMR spectra (at 300 MHz) were recorded over the temperature range −75 to +30 °C. Rate constants for acetonitrile exchange were determined by comparison of experimental and theoretical spectra. Theoretical line shapes were calculated with a computer program written by E. R. Johnston.[33] The exchange rate was taken as that which produced a simulated spectrum that was visually superimposable with the experimental spectrum. The nonexchange condition was defined as the condition corresponding to the spectrum observed at −75 °C. Before coalescence, the valley to peak ratio was the characteristic feature that was matched to the simulated spectra. For the faster exchange rates, the full width at half-height of the coalesced peak was the feature matched to the simulated spectra. Since the chemical shift of the acetonitrile group of **10** is temperature dependent, chemical shifts used in the simulation were those taken from the variable-temperature spectra for pure **10**. Rate constants obtained from the simulation were then used to calculate activation parameters from the Eyring equation.

Collection and Solution of X-ray Diffraction Data. Parameters summarizing the collection and solution of diffraction data for **8**, **9**, and $\mathbf{10}\cdot CH_2Cl_2$ are contained in Table II. Crystals were mounted in glass capillary tubes in an inert-atmosphere glovebox and then flame-sealed. In all cases, no absorption correction was applied due to low absorption coefficients and/or regular crystal shape. Heavy-atom methods were used to solve the structures of **8** and $\mathbf{10}\cdot CH_2Cl_2$, and the structure of **9** was solved by direct methods. The remaining non-hydrogen atoms were found via Fourier difference maps and refined anisotropically with full-matrix least-squares methods (SHELXTL PLUS computer programs; Nicolet Instrument Corp., Madison, WI). All phenyl rings were fixed as rigid hexagons (d(C–C) = 1.395 Å). The structure determinations for **8** and $\mathbf{10}\cdot CH_2Cl_2$ were carried out at the University of Delaware, and the structure of **9** was solved at the University of California.

For **8**, photographic characterization revealed no symmetry higher than triclinic. The centrosymmetric alternative was chosen on the basis of the chemically reasonable structure found after refinement. All hydrogen atoms were isotropically refined.

The space group for **9** was also not distinguishable from systematic absences. However, satisfactory refinement was only obtainable for $P\bar{1}$. The hydrogen atoms were fixed in calculated, idealized positions (d(C–H) = 0.96 Å, isotropic thermal parameter approximately 1.2 times the thermal parameter for the carbon to which it was attached).

The space group for $\mathbf{10}\cdot CH_2Cl_2$ was uniquely determined from systematic absences. The hydrogen atoms were calculated and fixed in idealized positions (d(C–H) = 0.96 Å, $U = 1.2U_{iso}$ for the carbon to which it was attached). The molecule of CH_2Cl_2 contained in the asymmetric unit was disordered about an inversion center, with the two full-occupancy chlorines shared equally by two half-occupancy carbon atoms. The BPh_4 anion was ordered and well-behaved.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **8**, **9**, and $\mathbf{10}\cdot CH_2Cl_2$ (21 pages); listings of observed and calculated structure factors for **8**, **9**, and $\mathbf{10}\cdot CH_2Cl_2$ (81 pages). Ordering information is given on any current masthead page.

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