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(η^1-Pentamethylcyclopentadienyl)silyl Complexes of Ruthenium. Preparation, Reactivity, and X-ray Crystal Structure of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$

Frederick R. Lemke*

Department of Chemistry, Ohio University, Athens, Ohio 45701-2979

Richard S. Simons and Wiley J. Youngs[†]

Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

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The reaction of $Cp(PMe_3)_2RuCH_2SiMe_3$ (**1**) with $(\eta^1\text{-}Cp^*)SiHCl_2$ in refluxing toluene produces silyl $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ (**2**) in good yields; $Cp(PMe_3)_2RuSiCl_3$ (**3**) is a minor product of this reaction. The Cp* group in **2** is σ-bound to the silicon and is "static" on the NMR time scale at room temperature. The η^1-Cp* configuration in **2** was confirmed by a single-crystal X-ray diffraction study. In the structure of **2**, a "three-legged piano stool" geometry is observed around ruthenium whereas the silicon adopts a distorted tetrahedral geometry. The η^1-Cp* group on silicon is in an *anti* relationship with one of the phosphines on ruthenium (dihedral angle = 179.5(3)°). Complex **2** exhibits reactions involving chloride substitution, Si−Cp* bond cleavage, and Ru−Si bond cleavage. The reaction of **2** with $LiAlH_4$ produces $Cp(PMe_3)_2RuSiH_2(\eta^1\text{-}Cp^*)$ (**6**) in which the η^1-Cp* group is more mobile compared to **2**. The Si−Cp* bond of **2** is readily cleaved by acid (*i.e* HCl(g), pyridinium chloride) to give **3** and pentamethylcyclopentadiene. Methanolysis of **2** cleaves the Ru−Si bond and gives the dihydride $[Cp(PMe_3)_2RuH_2]Cl$ in nearly quantitative yields.

Introduction

The chemistry of transition metal silyl complexes continues to receive considerable attention.[1−9] The impetus for this interest has been the similarities, as well as the differences, between carbon and silicon chemistry, transition metal catalyzed reactions such as hydrosilylation, and the advent of metal−silicon multiple bonding. In a large number of these silyl derivatives, the metal centers are stabilized by the ubiquitous π-bound cyclopentadienyl (C_5H_5, Cp) and pentamethylcyclopentadienyl (C_5Me_5, Cp*) groups. The Cp and Cp* groups also have been used to prepare a variety of main group element derivatives.[10−12] In contrast to related transition metal derivatives, the Cp and Cp* groups usually adopt an η^1-configuration when attached to a main group element. Furthermore, main group element compounds containing the Cp* group are generally more stable than the corresponding Cp derivatives; this is particularly true for silicon. For example, the η^1-Cp compounds $CpSiX_3$ and Cp_2SiX_2 (X = H, Cl) slowly decompose at room temperature,[13,14] whereas the related η^1-Cp* compounds Cp^*SiX_3 and $Cp^*_2SiX_2$ can be obtained as distillable liquids or sublimable solids and are stable at room temperature for months.[15,16]

Despite this considerable interest and activity in the cyclopentadienyl chemistry of transition metals and main group elements, the use of a cyclopentadienyl group as a substituent on silicon in a transition metal silyl complex has received very little attention. Jutzi and Möhrke[17] reported the formation of a gold silylene from the reaction of decamethylsilicocene with carbonyl gold(I) chloride (eq 1), in which one Cp* group is σ-bound while the other is π-bound. Addition of neutral donor bases to the gold silylene (eq 2) forms a base-stabilized silylene in which both Cp* groups are σ-bound. Prior to this, Malisch *et al.*[18] reported in a review article the formation of several ferriosilanes which contain an η^1-Cp* group attached to silicon (eqs 3 and 4). The η^1-

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[†] To whom correspondence should be addressed concerning X-ray structure determinations.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

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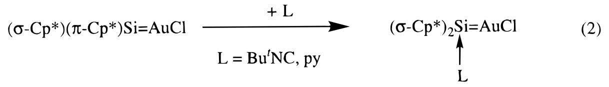
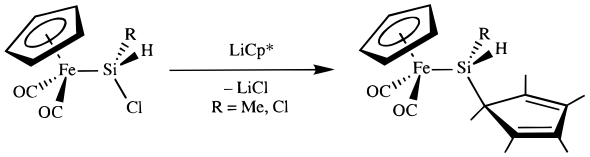
$$(\pi\text{-Cp*})_2Si + (CO)AuCl \xrightarrow[-CO]{} (\sigma\text{-Cp*})(\pi\text{-Cp*})Si{=}AuCl \quad (1)$$



$$(\sigma\text{-Cp*})(\pi\text{-Cp*})Si{=}AuCl \xrightarrow[L = Bu^tNC,\ py]{+L} (\sigma\text{-Cp*})_2Si{=}AuCl(\leftarrow L) \quad (2)$$



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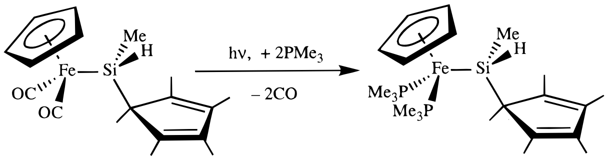
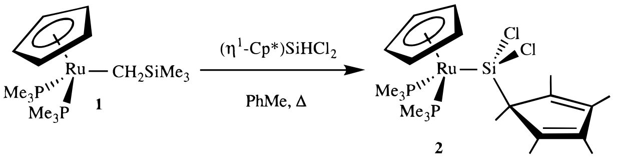


(4)

Cp* groups in these ferriosilanes are "mobile" and can readily be removed by CCl_4. Herein, we report the synthesis of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$, which contains a "static" η^1-Cp* group attached to silicon. This complex exhibits a rich reaction chemistry involving chloride substitution as well as Si−C and Ru−Si bond cleavages. The single-crystal X-ray structure of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$ is also reported.

Results and Discussion

Synthesis of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$. The title complex was prepared by reacting a ruthenium alkyl, $Cp(PMe_3)_2RuCH_2SiMe_3$ (**1**), with the corresponding hydrosilane, $(\eta^1\text{-Cp*})SiHCl_2$. The reaction of the chloride $Cp(PMe_3)_2RuCl$ with Me_3SiCH_2MgCl in refluxing Et_2O produces alkyl **1** as a yellow sublimable solid in high yields (ca. >85%).[19] Alkyl **1** reacts with $(\eta^1\text{-Cp*})SiHCl_2$ in refluxing toluene to form the $(\eta^1\text{-Cp*})$silyl complex $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$ (**2**; eq 5). Upon cooling of the reaction mixture to room temperature, silyl **2** precipitated as an analytically pure white solid in good yield (ca. 70%). Addition of hexanes to the mother liquor gave a second crop of white solid which was a mixture of **2** and the trichlorosilyl complex $Cp(PMe_3)_2RuSiCl_3$ (**3**). The exact origin of **3** is unknown, but is most likely due to a substituent redistribution reaction between **2** and excess $(\eta^1\text{-Cp*})SiHCl_2$. The room-temperature NMR data on **2** are consistent with the presence of a "static" η^1-Cp* group, in which the 1,2-migration of the silicon around the Cp* ring is very slow on the NMR time scale. Three sharp resonances (τ < 2.5 Hz) with integrated ratios of 1:2:2 are observed for the Cp* methyl protons in the ^1H NMR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum, resonances for the unique sp^3 and vinylic carbons of Cp* are observed. The η^1-Cp* configuration was also confirmed by a single-crystal X-ray diffraction study on **2** (*vide infra*).



1

2

(5)

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$ (2)

atom	x/a	y/b	z/c	U(eq)[a] (Å^2)
Ru	0.3159(1)	0.1672(1)	0.0966(1)	0.028(1)
Cl(1)	0.6304(1)	0.0644(1)	0.1126(1)	0.056(1)
Cl(2)	0.7212(1)	0.1522(1)	0.2967(1)	0.067(1)
P(1)	0.4782(1)	0.1915(1)	−0.0297(1)	0.037(1)
P(2)	0.1823(1)	0.1109(1)	−0.0399(1)	0.036(1)
Si	0.5089(1)	0.1141(1)	0.2090(1)	0.031(1)
C(1)	0.4888(4)	0.0717(1)	0.3486(3)	0.035(1)
C(2)	0.3542(4)	0.0363(1)	0.3013(3)	0.032(1)
C(3)	0.2289(4)	0.0469(1)	0.3507(3)	0.035(1)
C(4)	0.2718(5)	0.0868(1)	0.4380(3)	0.042(1)
C(5)	0.4229(5)	0.1008(1)	0.4418(3)	0.043(1)
C(6)	0.6478(5)	0.0459(2)	0.4086(4)	0.059(2)
C(7)	0.3690(5)	−0.0069(2)	0.2227(4)	0.057(2)
C(8)	0.0708(5)	0.0205(2)	0.3310(4)	0.061(2)
C(9)	0.1587(6)	0.1062(2)	0.5126(4)	0.077(2)
C(10)	0.5220(7)	0.1359(2)	0.5305(4)	0.083(2)
C(11)	0.3753(5)	0.2164(2)	−0.1790(4)	0.062(2)
C(12)	0.6260(6)	0.1553(2)	−0.0817(5)	0.085(2)
C(13)	0.6049(7)	0.2435(2)	0.0310(5)	0.098(3)
C(14)	0.0354(5)	0.1363(2)	−0.1705(4)	0.056(2)
C(15)	0.2798(5)	0.0687(2)	−0.1239(4)	0.071(2)
C(16)	0.0011(5)	0.0711(2)	0.0234(4)	0.071(2)
C(17)	0.1307(10)	0.1818(2)	0.2030(4)	0.104(4)
C(18)	0.0938(8)	0.2099(3)	0.0982(7)	0.109(4)
C(19)	0.2173(11)	0.2417(2)	0.1034(6)	0.093(3)
C(20)	0.3275(7)	0.2335(2)	0.2126(7)	0.083(3)
C(21)	0.2691(10)	0.1970(2)	0.2718(5)	0.088(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The formation of **2** requires temperatures of 100 °C or above and is consistent with PMe_3 loss from **1** as the rate-limiting step in the silane oxidative-addition/alkane reductive-elimination mechanism proposed by Tilley and co-workers.[20] Attempts to make derivatives of **2** by reacting **1** with other Cp*-containing silanes were unsuccessful. Sterically hindered silanes, such as $(\eta^1\text{-Cp*})_2SiHCl$ and $(\eta^1\text{-Cp*})_2SiH_2$, do not react with **1** in C_6D_6 at elevated temperatures (100 °C) over 7 days. This reaction is also strongly influenced by the electronics of the silane. The electron-rich silane $(\eta^1\text{-Cp*})SiH_3$ showed no reaction with **1** in C_6D_6 at 120 °C over 21 h. This suggests that a silane containing electron-withdrawing groups (*i.e* Cl) is required for the reaction in eq 5 to occur.[21] In support of this, a slow reaction (~80% conversion after 7 days) was observed between $(\eta^1\text{-Cp*})SiMeHCl$ and **1** in C_6D_6 at 120 °C to give what appears to be $Cp(PMe_3)_2RuSiMeCl(\eta^1\text{-Cp*})$.

Structure of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$ (2). The crystal structure of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-Cp*})$ (**2**) has been determined by X-ray diffraction at 291 K. Fractional atomic coordinates and equivalent isotropic displacement parameters for **2** are listed in Table 1, and pertinent interatomic distances and angles are presented in Table 2. The molecular structure of **2** is shown in Figure 1.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ (2)

Bond Lengths[a]			
Ru(1)−Si(1)	2.335(1)	Si(1)−C(1)	1.976(4)
Ru(1)−P(1)	2.281(1)	Si(1)−Cl(1)	2.140(2)
Ru(1)−P(2)	2.277(1)	Si(1)−Cl(2)	2.168(2)
Ru(1)−Cnt	1.899	C(1)−C(2)	1.505(6)
C(2)−C(3)	1.341(6)	C(3)−C(4)	1.453(6)
C(4)−C(5)	1.334(7)	C(1)−C(5)	1.504(7)
Bond Angles[a]			
P(1)−Ru(1)−P(2)	94.5(1)	P(1)−Ru(1)−Si(1)	93.1(1)
P−Ru(1)−Cnt	121.6 (av)	P(2)−Ru(1)−Si(1)	96.6(1)
Cnt−Ru(1)−Si(1)	121.5	Ru(1)−Si(1)−Cl(1)	119.9(1)
Ru(1)−Si(1)−C(1)	127.4(1)	Ru(1)−Si(1)−Cl(2)	109.2(1)
Si(1)−C(1)−C(2)	107.4(3)	Cl(1)−Si(1)−Cl(2)	95.9(1)
Si(1)−C(1)−C(5)	109.4(3)	C(1)−Si(1)−Cl(1)	98.7(1)
Si(1)−C(1)−C(6)	112.3(3)	C(1)−Si(1)−Cl(2)	99.9(1)

[a] Cnt = the centroid of the cyclopentadienyl ring.

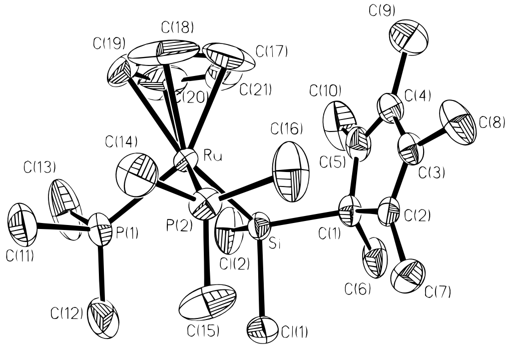
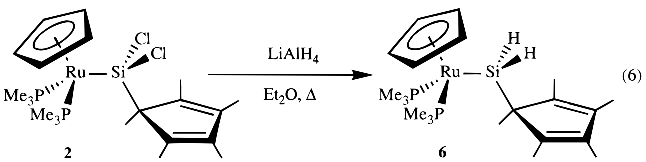


Figure 1. Labeling diagram for $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ (**2**). The thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms have been omitted for clarity.

Compound **2** adopts a "three-legged piano stool" geometry around ruthenium, with "legs" composed of one $SiCl_2(\eta^1\text{-}Cp^*)$ and two PMe_3 groups. The bond distances and angles in the $Cp(PMe_3)_2Ru$ fragment are normal when compared to the structures of related $Cp(PMe_3)_2RuX$ complexes.[22−24] Compound **2** has a staggered conformation about the Ru−Si bond with the Cp and Cl(1) groups in an *anti* relationship (Cp centroid−Ru−Si−Cl(1) dihedral angle = 178.8(5)°). The Ru−Si bond distance of 2.335(1) Å is consistent with a single bond and lies within the range (2.27−2.51 Å)[1,2,20,25] observed for other d^6 ruthenium silyl complexes. The silyl ligand has a distorted tetrahedral geometry with an average R−Si−R′ angle (R, R′ = C(1), Cl(1), or Cl(2)) of 98.2(1)° with a deviation of only 2.1°. The Ru−Si−C(1) angle of 127.4(1)° is quite large in comparison. The carbon ring (C(1)−C(5)) portion of the Cp* ligand is approximately planar with the largest deviation (0.029 Å) from planarity at C(1).

Several geometric trends are observed between the structure of **2** and the structures of the related (η^1-Cp*)silanes (η^1-Cp*)$SiCl_3$ (**4**)[15] and $(\eta^1\text{-}Cp^*)_2SiCl_2$ (**5**).[16] Replacing an electronegative Cl with an electron-rich Cp* or $Cp(PMe_3)_2Ru$ group results in an increase in both the Si−Cp* [**4** (1.867 Å) < **5** (1.885 Å) < **2** (1.976 Å)] and Si−Cl [**4** (2.036 Å) < **5** (2.073 Å) < **2** (2.154 Å)] bond distances. This trend is consistent with observations reported by Bent,[26] who noticed that Si−C and Si−halogen bond distances increased as the number of halogens attached to silicon decreased. Trends are also observed in the bond angles around silicon. An increase in the Cp*−Si−X angle is observed in the order **4** (X = Cl, 112.5°) < **5** (X = Cp*, 122.5°) < **2** (X = $Cp(PMe_3)_2Ru$, 127.4°), presumably due to steric repulsions between the two Cp* groups in **5** and the Cp ligand and the Cp* group in **2**. This increase in the Cp*−Si−X angle is accompanied by decreases in both the Cl−Si−Cl [**4** (104.4°) < **5** (101.1°) < **2** (95.9°)] and Cl−Si−Cp* [**4** (112.2°) < **5** (108.0°) < **2** (average 99.3°)] angles.

Reactivity of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ (2). Multiple reaction paths are exhibited by **2**: chloride substitution, cleavage of the Si−Cp* bond, cleavage of the Ru−Si bond, or a combination of chloride substitution and Si−Cp* bond cleavage. Complex **2** undergoes chloride substitution upon reaction with an excess of $LiAlH_4$ in Et_2O to give the dihydro derivative $Cp(PMe_3)_2RuSiH_2(\eta^1\text{-}Cp^*)$ (**6**; eq 6). Similar to **2**, **6** contains a "static" η^1-Cp* group. In the room-temperature ^1H NMR spectrum (C_6D_6) of **6**, three broad resonances (5 Hz < τ < 10 Hz) are observed for the Cp* methyl protons. The broadened Cp* methyl resonances of **6** suggest that the η^1-Cp* is more mobile in **6** than in **2**. The increased η^1-Cp* mobility of **6** is most pronounced when the solvent is changed from C_6D_6 to CD_2Cl_2. In the ^1H NMR spectrum (CD_2Cl_2) of **6**, the methyl protons of the η^1-Cp* group are observed as two very broad resonances (τ = 8 and 18 Hz, respectively) in a 3:2 ratio. In comparison, the ^1H NMR spectrum (CD_2Cl_2) of **2** shows three sharp resonances (1 Hz < τ < 2.5 Hz) for the η^1-Cp* methyl protons. According to Bent's rule[26] (*vide supra*), the Si−Cp* bond in **6** should be longer, and therefore weaker, than the Si−Cp* bond in **2**. This coupled with the replacement of the chlorides with sterically less demanding hydrides, can account for the increased mobility of the η^1-Cp* in **6** compared to **2**. A full investigation into the fluxional properties of the η^1-Cp* group in **2**, **6**, and related complexes is currently underway.



Cleavage of the Si−Cp* bond has been accomplished by two routes. Complex **2** slowly reacts with chlorocarbon solvents (*e.g.* CH_2Cl_2 and $CHCl_3$) to give the trichlorosilyl complex **3**.[27] Heating facilitates this cleavage reaction. For example, the conversion of **2** (~36 mM) to **3** in $CDCl_3$ is only ~5% complete after 4 days at room temperature. However, when this sample is heated to 50 °C, the conversion of **2** to **3** is 25% complete in 3 days and quantitative after 10 days (eq 7). The reaction of **2** with 1 equiv of HCl proves to be a more facile route to **3** (eq 7). Complex **2** reacts with pyridinium chloride, [pyH]Cl, in CD_2Cl_2 to generate **3** and pentamethylcyclopentadiene.

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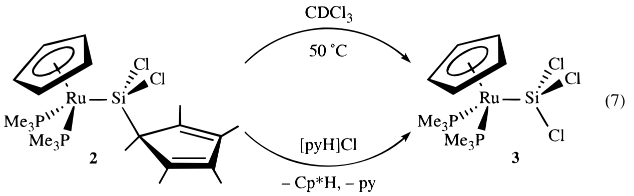
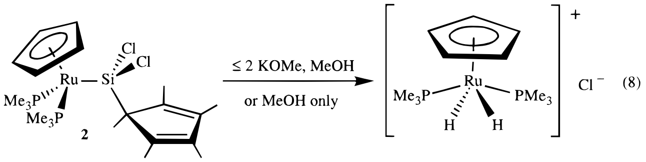
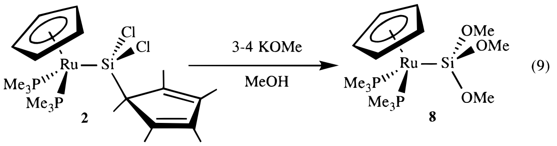


(7)

Methanolysis of **2** (eq 8) results in cleavage of the Ru–Si bond and quantitative formation of the ruthenium dihydride $[Cp(PMe_3)_2RuH_2]Cl$ (**7**).[22] Even in the presence of 2 equiv of KOMe in MeOH, cleavage of the Ru–Si bond is the preferred reaction. Metal silyl complexes are known to be susceptible to M–Si bond cleavage when treated with alcohols.[1] For example, $(CO)_5MnSiMe_3$ reacts with MeOH to give $(CO)_5MnH$ and Me_3SiOMe.[28] In eq 8, methanolic cleavage of the Ru–Si bond would initially give $Cp(PMe_3)_2RuH$ and $(\eta^1\text{-}Cp^*)SiCl_2(OMe)$. Protonation of $Cp(PMe_3)_2RuH$ with HCl, from the methanolysis of the Si–Cl bonds in $(\eta^1\text{-}Cp^*)SiCl_2(OMe)$, would then generate dihydride **7**. On the other hand, in the presence of an excess of KOMe in MeOH, **2** undergoes chloride substitution and Si–Cp* bond cleavage instead of Ru–Si bond cleavage (eq 9). The trimethoxysilyl complex $Cp(PMe_3)_2RuSi(OMe)_3$ (**8**) was isolated as a yellow sublimable solid in high yields (ca. >90%). The reaction in eq 9 suggests that the nucleophilic substitution of the chloride and Cp* substituents on silicon by methoxide is faster than methanolic cleavage of the Ru–Si bond. Furthermore, the methoxide substituents in **8** stabilize the Ru–Si bond to the extent that it is no longer susceptible to methanolysis.



(8)



(9)

Conclusions

$Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ has been prepared and fully characterized by spectroscopic measurements and single-crystal X-ray diffraction. Although this complex contains a "static" η^1-Cp* group, the mobility of the η^1-Cp* group is found to increase when the chlorides on silicon are replaced with hydrides. The X-ray structure of $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ is the first structure of an $(\eta^1\text{-}Cp^*)$silyl complex and confirms the η^1-Cp* configuration. $Cp(PMe_3)_2RuSiCl_2(\eta^1\text{-}Cp^*)$ exhibits a rich reaction chemistry involving chloride substitution as well as Si–Cp* and Ru–Si bond cleavages.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive compounds were carried out either under an atmosphere of argon by using Schlenk or vacuum-line techniques or under a helium/argon atmosphere in a Vacuum Atmospheres drybox.[29] ^1H NMR (250 MHz) and $^{13}C\{^1H\}$ NMR (62.9 MHz) spectra were recorded on a Bruker AC-250 spectrometer. The PMe_3 resonances in these compounds do not appear as a simple first-order pattern in the ^1H NMR. The PMe_3 resonances appear as a $A_9XX'A'_9$ pattern; the appearance of which is a "filled-in-doublet" (fd) with the separation of the outer lines $N = {}^2J_{PH} + {}^4J_{PH}$.[30,31] Likewise, in the $^{13}C\{^1H\}$ NMR, the PMe_3 resonances appear as a virtual triplet (vt) with the separation of the outer lines $N = {}^1J_{PC} + {}^3J_{PC}$.[30,31] The ^1H chemical shifts were referenced to the residual proton peak of the solvent: C_6D_5H (7.15 ppm) and $CDHCl_2$ (5.32 ppm). The ^{13}C chemical shifts were referenced to the central peak of C_6D_6 (128.0 ppm). ^{29}Si DEPT NMR (79.5 MHz) spectra were referenced to the central peak of C_6D_6 (128.0 ppm). ^{29}Si DEPT NMR (79.5 MHz) spectra were recorded on a Varian VXR 400S spectrometer and referenced to external $SiMe_4$ (0.00 ppm). Widths-at-half-height (τ) in Hz were obtained using the Gaussian and Lorenzian curve fitting programs on the Bruker spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. Elemental analyses were carried out by Oneida Research Services or Galbraith Laboratories.

Materials. $Cp(PMe_3)_2RuCl$ was prepared by a modification of previously reported procedures.[32,33] Severe face rashes have been reported to result from exposure to $Cp(PMe_3)_2RuCl$, so adequate precautions should be taken.[34] $(\eta^1\text{-}Cp^*)SiHCl_2$,[15] $(\eta^1\text{-}Cp^*)SiHMeCl$,[16] $(\eta^1\text{-}Cp^*)SiH_3$,[16] $(\eta^1\text{-}Cp^*)_2SiHCl$,[16] and $(\eta^1\text{-}Cp^*)_2SiH_2$[16] were prepared by literature methods. Anhydrous diethyl ether was stored over $[Cp_2TiCl]_2ZnCl_2$[35] and vacuum transferred immediately prior to use. Dichloromethane was distilled from and stored over CaH_2 and vacuum transferred immediately prior to use. Methanol was dried over Mg and vacuum transferred immediately prior to use. Benzene-d_6 was dried over NaK and stored over $[Cp_2TiCl]_2ZnCl_2$. Dichloromethane-d_2 and chloroform-d_1 were dried over P_2O_5 and stored over CaH_2. KOMe was prepared by reacting solid K with excess MeOH in Et_2O, collecting the solid by filtration, and drying the solid under vacuum. Anhydrous HCl(g) was generated by slowly adding H_2SO_4(l) to NaCl(s) and stored over anhydrous $CaSO_4$(s) prior to use. Pyridinium chloride, [pyH]Cl, was prepared by reacting pyridine with anhydrous HCl(g) in Et_2O, collecting the white solid by filtration, and drying the solid under vacuum. PMe_3(Strem), C_5Me_5H (Strem), and Me_3SiCH_2MgCl (1.0 M in Et_2O; Aldrich) were used as received.

$Cp(PMe_3)_2RuCH_2SiMe_3$ (1). Diethyl ether (15 mL) was added by vacuum transfer to a flask charged with $Cp(PMe_3)_2RuCl$ (505 mg, 1.43 mmol) and cooled to −78 °C. Under an argon atmosphere, Me_3SiCH_2MgCl (2.1 mL, 2.1 mmol) was added by syringe. The reaction mixture was heated to reflux for 4 h, during which time the reaction changed from an orange to a yellow slurry. The volatiles were removed under vacuum. The residue was extracted with hexanes until the extracts were colorless. The hexane extracts were filtered through Celite and evaporated to dryness under vacuum. The yellow residue sublimed at 70 °C (>0.03 mmHg) to give **1** as a bright yellow solid (526 mg, 91% yield, >98% pure by ^1H NMR). ^1H NMR (C_6D_6): δ 4.47 (s, 5H, Cp), 1.05 (fd, N = 8.0 Hz, 18H, PMe_3), 0.82 (s, 9H, $SiMe_3$), −0.90 (t, $^3J_{PH}$ = 7.7 Hz, CH_2). ^{13}C-

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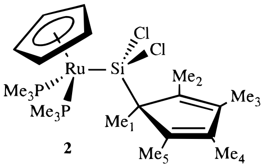
{^{1}H} NMR (C_6D_6): δ 78.99 (t, J_{PC} = 2.5 Hz, C_5H_5), 22.67 (vt, N = 26.2 Hz, P*Me*$_3$), 4.43 (s, Si*Me*$_3$), −25.70 (t, J_{PC} = 11.6 Hz, RuCH_2). ^{29}Si{^{1}H} DEPT NMR (C_6D_6): δ 7.44 (t, $^3J_{SiP}$ = 4.9 Hz). Anal. Calcd for $C_{15}H_{34}P_2RuSi$: C, 44.43; H, 8.45. Found: C, 44.07; H, 8.70.

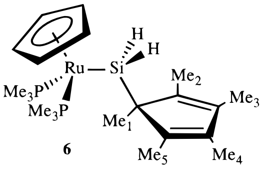
Cp(PMe$_3$)$_2$RuSiCl$_2$(η^1-Cp*) (2). A flask charged with **1** (511 mg, 1.26 mmol), (η^1-Cp*)SiHCl$_2$ (1.54 g, 6.5 mmol), and toluene (5 mL) was attached to a reflux condenser. The reaction mixture was heated to reflux for 2.5 h. The white precipitate, which formed as the reaction mixture cooled to room temperature, was isolated by filtration. Washing the solid with hexanes followed by vacuum drying gave **2** (491 mg, 71% yield, >99% pure by ^{1}H NMR) as a white solid. A second crop was obtained by concentrating the mother liquor and adding hexanes to initiate precipitation. A white solid (96 mg) was obtained which was a mixture of **2** (73%) and **3** (27%) as determined by ^{1}H NMR. ^{1}H NMR (C_6D_6): δ 4.39 (s, 5H, Cp), 2.30 (s, τ = 2.0 Hz, 6H, Me$_{3,4}$ or Me$_{2,5}$), 1.91 (s, τ = 1.0 Hz, 3H, Me$_1$), 1.81 (s, τ = 2.2 Hz, 6H, Me$_{3,4}$ or Me$_{2,5}$), 1.14 (fd, N = 8.8 Hz, 18H, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 141.70, 135.86, 67.09 (s, C_5Me$_5$), 81.44 (t, $^2J_{PC}$ = 1.7 Hz, C_5H_5), 24.92 (vt, N = 30.5 Hz, P*Me*$_3$), 18.70, 14.16, 12.06 (s, C$_5$*Me*$_5$). ^{29}Si{^{1}H} DEPT NMR (C_6D_6): δ 82.71 (t, $^2J_{SiP}$ = 33.0 Hz). Anal. Calcd for $C_{21}H_{38}Cl_2P_2RuSi$: C, 45.65; H, 6.93. Found: C, 45.30; H, 6.83.



2

Cp(PMe$_3$)$_2$RuSiCl$_3$ (3). CH_2Cl_2 (10 mL) was added by vacuum transfer to a flask charged with **2** (50 mg, 0.090 mmol) and [pyH]Cl (11 mg, 0.095 mmol). The reaction mixture was stirred under an argon atmosphere overnight. The volatiles were removed by vacuum to give **3** as a yellow solid (31 mg, 76%, >95% pure by ^{1}H NMR). NMR data are identical to reported values.[27]

Cp(PMe$_3$)$_2$RuSiH$_2$(η^1-Cp*) (6). A flask was charged with **2** (153 mg, 0.28 mmol), LiAlH$_4$ (60 mg, 1.6 mmol), and Et$_2$O (15 mL) and stirred under argon overnight. The reaction mixture was cooled in an ice/water bath, and EtOH (5 mL, 95%, degassed) was added slowly to quench the unreacted LiAlH$_4$. The volatiles were removed by vacuum. The residue was extracted with CH_2Cl_2 and filtered through Celite. The combined extract solution was evaporated to dryness and the residue sublimed at 100 °C (<0.03 mmHg). A light yellow solid (96 mg) was obtained which was a mixture of **6** (80%) and Cp(PMe$_3$)$_2$RuH (20%). Fractional sublimation of the solid at 60 °C (<0.03 mmHg) removed the Cp(PMe$_3$)$_2$RuH impurity and was followed by sublimation at 100 °C (<0.03 mmHg) which produced 58 mg (43%) of **6**. ^{1}H NMR (C_6D_6): δ 4.41 (s, 5H, Cp), 4.37 (fd, N = 16.8 Hz, 2H, SiH$_2$), 2.16 (br, τ = 10.1 Hz, 6H, Me$_{3,4}$ or Me$_{2,5}$), 1.96 (br, τ = 5.7 Hz, 6H, Me$_{3,4}$ or Me$_{2,5}$), 1.77 (br, τ = 9.7 Hz, 3H, Me$_1$), 1.09 (fd, N = 8.5 Hz, 18H, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 141.25, 131.52, 57.84 (br, C_5Me$_5$), 79.69 (t, $^2J_{PC}$ = 1.8 Hz, C_5H_5), 24.33 (vt, N = 29.6 Hz, P*Me*$_3$), 22.78, 12.44, 11.86 (br, C$_5$*Me*$_5$). ^{29}Si DEPT NMR (C_6D_6): δ 20.79 (tt, $^1J_{SiH}$ = 145.0 Hz, $^2J_{SiP}$ = 29.3 Hz). IR (CH_2Cl_2): ν(Si−H) 1989 (br) cm^{-1}. Anal. Calcd for $C_{21}H_{24}P_2RuSi$: C, 52.15; H, 8.34. Found: C, 52.07; H, 8.49.



6

[Cp(PMe$_3$)$_2$RuH$_2$]Cl (7). MeOH (5 mL) was added by vacuum transfer to a flask charged with **2** (49 mg, 0.089 mmol). After the solution became homogeneous, the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 (2 mL), and Et$_2$O was added to initiate precipitation of **7**. The white solid was isolated by filtration and dried *in vacuo* to give 31 mg (97%, >99% pure by ^{1}H NMR). NMR data are identical to reported values.[22]

Table 3. Crystal Data, Data Collection, and Refinement Parameters for Cp(PMe$_3$)$_2$RuSiCl$_2$(η^1-Cp*) (2)

empirical formula	$C_{21}H_{38}Cl_2P_2RuSi$
fw	552.5
cryst system	monoclinic
space group	$P2_1/n$
a (Å)	8.544(2)
b (Å)	27.483(5)
c (Å)	11.045(2)
β (deg)	103.19(3)
V (Å^3)	2525.1(9)
Z	4
d_{calcd} (Mg m^{-3})	1.453
radiation, λ (Å)	graphite monochromator Mo Kα, 0.710 73
μ, abs coeff (mm^{-1})	1.000
cryst dimens (mm)	0.4 × 0.3 × 0.3
temp (K)	291
F(000)	1144
2θ range (deg)	3.5−50.0
scan type	ω
scan range (deg)	1.60
scan speed (deg min^{-1} in ω)	4.19
index ranges	$-1 \le h \le 10$, $0 \le k \le 32$, $-13 \le l \le 13$
reflcns collcd	5387
indepdt reflcns	4429 (R_{int} = 0.0126)
obsd reflcns	3504 ($F > 4.0\sigma(F)$)
abs corr, T_{max}, T_{min}	semi-empirical via ψ scans, 0.6325, 0.5879
quantity minimized	$\sum w(F_o - F_c)^2$
weighting scheme	$w = 1/\sigma^2(F) + 0.0001F^2$
params refined	245
R, wR	0.0318, 0.0323
GOF	1.54
largest and mean Δ/σ	0.256, 0.050
data to param ratio	14.3 to 1
largest diff peak (eÅ^{-3})	0.34
largest diff hole (eÅ^{-3})	−0.29
H atoms	riding model, fixed isotropic U

Cp(PMe$_3$)$_2$RuSi(OMe)$_3$ (8). MeOH (10 mL) was added by vacuum transfer to a flask charged with **2** (49 mg, 0.089 mmol) and KOMe (30 mg, 0.43 mmol). The reaction mixture was stirred at room temperature for 3 h to give a yellow solution. The volatiles were removed under vacuum, and the residue was extracted with hexanes. The hexane extracts were filtered through Celite and evaporated to dryness under vacuum. The yellow residue sublimed at 80 °C (<0.03 mmHg) to give **8** as a light yellow waxy solid (36 mg, 92%, >99% pure by ^{1}H NMR). ^{1}H NMR (C_6D_6): δ 4.67 (s, 5H, Cp), 3.68 (s, 9H, OMe), 1.25 (fd, N = 8.7 Hz, 18H, PMe$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 80.50 (t, $^2J_{PC}$ = 1.7 Hz, C_5H_5), 49.55 (s, O*Me*), 26.01 (vt, N = 29.6 Hz, P*Me*$_3$). ^{29}Si{^{1}H} DEPT NMR (C_6D_6): δ 18.01 (t, $^2J_{SIP}$ = 37.8 Hz). Anal. Calcd for $C_{14}H_{32}O_3P_2RuSi$: C, 38.26; H, 7.34. Found: C, 37.96; H, 7.21.

Structure Determination of Cp(PMe$_3$)$_2$RuSiCl$_2$(η^1-Cp*) (2). Crystals of **2** suitable for X-ray diffraction analysis were grown in a sealed glass tube by slowly cooling a concentrated solution of **2** (183 mg) in toluene (2 mL) from 80 °C to room temperature. A clear parallelepiped crystal of **2** was flame sealed in a glass capillary under argon. Intensity data were collected on a Syntex P2$_1$ diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73) radiation. Refined lattice constants were determined from a least squares analysis of 25 reflections (2θ = 20−30°). Three standard reflections were measured every 97 reflections, and their intensities indicated no appreciable crystal decay. Intensity data were corrected for Lorentz and polarization factors. All calculations were performed with the SHELXTL PLUS program package. Crystallographic data and refinement parameters are listed in Table 3. The structure was solved by direct methods. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms were refined with isotropic thermal parameters in their calculated positions.

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Supporting Information Available: Tables of X-ray crystallographic data, hydrogen positional and *U* values, anisotropic displacement parameters, and interatomic distances and angles (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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