Ruthenium Silyl Complexes Containing the $Cp(PMe_3)_2Ru$ Moiety: Preparation, Substituent Effects, and Silylene Character in the Ru−Si Bond

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The preparation and characterization of new ruthenium(II) silyl complexes containing the $Cp(PM_3)_2Ru$ moiety are described. The ruthenium(II) hydride $Cp(PMe_3)_2RuH$ reacts with a variety of chlorosilanes to produce the ruthenium(II) silyl complexes $Cp(PMe_3)_2RuSiR_3$ [SiR_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), $SiMeCl_2$ (**4**), SiMeHCl (**5**), $SiMe_2Cl$ (**6**)] and the ruthenium(IV) dihydride $[Cp(PMe_3)_2RuH_2]Cl$. Silyl complexes **1**−**6** undergo chloride/hydride exchange with $LiAlH_4$ to give the corresponding ruthenium(II) hydrosilyl complexes $Cp(PMe_3)_2RuSiHR_2$ [$SiHR_2$ = SiH_3 (**7**), $SiMeH_2$ (**8**), $SiMe_2H$ (**9**)]. Methylation of **6** with $AlMe_3$ produces $Cp(PMe_3)_2RuSiMe_3$ (**10**). A method for recovering the $Cp(PMe_3)_2Ru$ moiety is described. The structure of **1** was determined by X-ray crystallography. Complexes **1**−**10** represent the first complete set of metal silicon compounds that contain every possible combination of H, Cl, and Me groups on silicon. The effects of the substituents on the spectroscopic properties of **1**−**10** were examined as a function of Tolman's electronic parameter (χ_i) for the substituents on silicon. The infrared stretching frequency, ν(Si−H), and the NMR coupling constants, $^2J_{SiP}$ and $^1J_{SiH}$, exhibit a linear relationship with $\sum\chi_i$, consistent with Bent's rule. However, when the NMR resonances SiR_3 $\delta(^{29}Si)$, SiH $\delta(^1H)$, and SiMe $\delta(^{13}C)$ were examined as a function of $\sum\chi_i$, the silyl groups differentiated into three classes: dichlorosilyl, monochlorosilyl, and "non-chlorosilyl"; within each class a linear but inverse relationship with $\sum\chi_i$ was observed. Silylene character in the Ru−Si bond resulting from d(Ru)−σ^*(Si−Cl) π-back-bonding interactions was used to explain the origin of the three silyl classes.

Introduction

The chemistry of transition metal silicon compounds continues to generate considerable attention and interest.[1−5] The diverse developments in this field indicate the extensive interest in the catalytic and stoichiometric chemistry of metal−silicon-bonded compounds. Metal silicon compounds play prominent roles in a variety of metal-catalyzed organosilicon transformations such as hydrosilylation,[6−8] dehydrogenative silylation,[9,10] dehydrogenative coupling of hydrosilanes,[11] and silane redistributions.[12] Investigations into the chemistry of functionalized metal silicon complexes, $L_nM\text{-}SiR_{3-m}X_m$ (m = 1−3; X = H, halogen, OTf, SAr; R = alkyl, aryl), have indicated a number of useful transformations involving the metal−silicon bond. Nucleophilic or radical-based substituent exchange reactions can generate new metal−silicon complexes.[13] Abstraction (and in some cases addition) of a group can generate complexes containing reactive silicon species (e.g., silylene, SiR_2; η^2-silenes, $R'_2C{=}SiR_2$; η^2-hydrosilanes, $H-SiR_3$)[14−18] as ligands; many of these species have been invoked as intermediates in catalytic and stoichiometric reactions of organosilanes.

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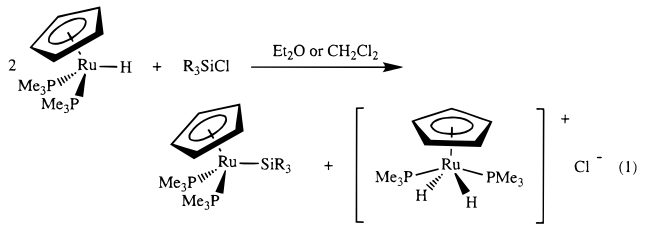
Functionalized transition metal silyl complexes have been conveniently prepared by the oxidative-addition of hydrosilanes to electron-rich metal centers which either possess a vacant coordination site or are accompanied by loss of a small molecule (H_2, alkane, etc.). The reaction of a variety of hydrosilanes ($HSiX_3$) with the metal(II) alkyl complexes $Cp'(PR_3)_2MR'$ ($Cp' = Cp$, Cp*; $PR_3 = PMe_3$, PPh_3; $M = Ru$, Os; $R' = Me$, CH_2SiMe_3) at elevated temperatures produced the metal(II) silyl $Cp'(PR_3)_2MSiX_3$ and/or metal(IV) bis(silyl) $Cp'(PR_3)MH(SiX_3)_2$ complexes with loss of alkane (R′H).[19−24] The product distribution of the metal−silicon complexes depended on reaction conditions and the strength of the metal−phosphorus bond. Alternatively, the alkali halide elimination method, in which a metal anion reacts with a halosilane or a metal halide reacts with a silyl anion, has also proved a convenient route to functionalized transition metal silyl complexes. Malisch and co-workers successfully prepared a wide variety of late transition metal silyl complexes of the type L_nMSiX_3 (ML_n = CpCr(CO)$_3$, CpMo(CO)$_3$, Cp*Mo(CO)$_3$, CpMo(CO)$_2$(PMe$_3$), Cp*Mo(CO)$_2$(PMe$_3$), CpW(CO)$_3$, Cp*W(CO)$_3$, CpW(CO)$_2$(PMe$_3$), Cp*W(CO)$_2$(PMe$_3$), CpFe(CO)$_2$, Cp*Fe(CO)$_2$, CpRu(CO)$_2$, Cp*Ru(CO)$_2$; SiX_3 = $SiHCl_2$, SiHMeCl, $SiHMe_2$, $SiPhHCl$, $SiPh_2H$, etc.) by reacting metal anions with the corresponding chlorosilane in hydrocarbon solvent.[25−30] Controlled exchange reactions at silicon afforded a variety of metallohydrosilanes,[27−30] -fluorosilanes,[31] -aminosilanes,[32,33] -silanols,[28,34−37] and -alkoxysilanes.[13]

Herein, we describe the formation of chlorosilyl ruthenium complexes $Cp(PMe_3)_2RuSiR_2Cl$ employing a little-used HCl elimination reaction between an electron-rich ruthenium hydride $Cp(PMe_3)_2RuH$ and the corresponding chlorosilanes; the formation of some of these chlorosilyl ruthenium complexes has been previously communicated.[18] Subsequent derivatization of these chlorosilyl ruthenium complexes produces the first complete series of metal silyl complexes that contain all possible combinations of H, Cl, and Me groups on silicon: $Cp(PMe_3)_2RuSiR_3$ (SiR_3 = $SiCl_3$, $SiHCl_2$, SiH_2Cl, $SiMeCl_2$, SiMeHCl, $SiMe_2Cl$, SiH_3, $SiMeH_2$, $SiMe_2H$, $SiMe_3$). Trends in the spectroscopic parameters (IR and multinuclear NMR) of this unique set of ruthenium silyl complexes are reported and analyzed in terms of electronic and structural features of the complexes. The probability of silylene character in the Ru−Si bond due to d(Ru)−σ*(Si−Cl) π-back-bonding is also discussed.

Results and Discussion

A. Synthesis of Ruthenium Silyl Complexes. The ruthenium silyl complexes used in this study were prepared by several different methods. One method involved the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes (R_3SiCl) to produce a nearly equimolar mixture of $Cp(PMe_3)_2RuSiR_3$ and $[Cp(PMe_3)_2RuH_2]Cl$ (eq 1).[38,39]



SiR_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), $SiMeCl_2$ (**4**), SiMeHCl (**5**), $SiMe_2Cl$ (**6**)

The chlorosilanes ($SiCl_4$, $SiHCl_3$, and SiH_2Cl_2) were much more reactive toward $Cp(PMe_3)_2RuH$ than the chloromethylsilanes ($SiMeCl_3$, $SiMeHCl_2$, $SiMe_2Cl_2$). Addition of $SiCl_4$, $SiHCl_3$, or SiH_2Cl_2 to a yellow solution of $Cp(PMe_3)_2RuH$ in Et_2O at −78 °C resulted in the immediate formation of $[Cp(PMe_3)_2RuH_2]Cl$ as a white precipitate and a light yellow solution of $Cp(PMe_3)_2RuSiR_3$ [SiR_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**)]. Under similar conditions, the chloromethylsilanes showed little or no reaction with $Cp(PMe_3)_2RuH$ in Et_2O, even after a day at room temperature. However, the chloromethylsilanes did readily react with $Cp(PMe_3)_2RuH$ in CH_2Cl_2 to give $Cp(PMe_3)_2RuSiR_3$ [SiR_3 = $SiMeCl_2$ (**4**), SiMeHCl (**5**), $SiMe_2Cl$ (**6**)] and $[Cp(PMe_3)_2RuH_2]Cl$ (eq 1). Regardless of the solvent used, the ruthenium silyl complexes **1**−**6** were obtained as light to dark yellow, air- and water-sensitive solids in good yields. The more substituted chloromethylsilanes $SiMe_2HCl$ and $SiMe_3Cl$ did not react with $Cp(PMe_3)_2RuH$ even in CH_2Cl_2.

In the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes, the white, air-sensitive dihydride complex $[Cp(PMe_3)_2RuH_2]Cl$[38,39] was sometimes obtained in yields of >100%, based on the stoichiometry described in eq 1. These unusual yields of $[Cp(PMe_3)_2RuH_2]Cl$ can be rationalized by the sensitivity of chlorosilanes to trace amounts of water. Hydrolysis of the chlorosilane would have produced HCl, which readily protonated $Cp(PMe_3)_2RuH$ to give $[Cp(PMe_3)_2RuH_2]Cl$.[38] This hydrolysis problem was overcome by conducting the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes in the presences of an added base such as NEt_3 (eq 2). By this method, ruthenium

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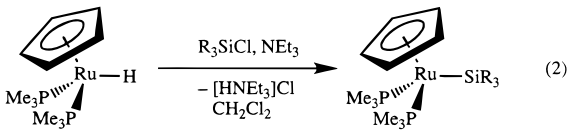


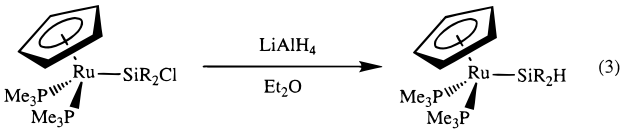
(2)

SiR_3 = $SiCl_3$ (**1**), $SiMeHCl$ (**5**), $SiMe_2Cl$ (**6**)

silyl complexes **1**, **5**, and **6** were obtained in high yields (>90%) with the added advantage that all of the ruthenium moiety ends up in the silyl complex (compared to eq 1).

The mechanism for the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes has been discussed in detail[18] and will therefore only be briefly described here. The chlorosilanes undergo a nucleophilic attack by $Cp(PMe_3)_2RuH$ with subsequent loss of HCl to give the ruthenium silyl complexes **1**−**6**. Concomitant protonation of a base, either $Cp(PMe_3)_2RuH$ or NEt_3, removes the liberated HCl from the system. HCl elimination reactions to form metal silyl complexes have been used only to a limited extent, and most of these involved a metal chloride reacting with a hydrosilane. Chatt and co-workers reported the reaction of triarylsilanes, Ar_3SiH (Ar = C_6H_4X, X = H, F, Cl, CF_3, Me, OMe, NMe_2), with $PtX_2(EMe_2Ph)_2$ (E = P, As) in the presence of Et_3N to form $PtX(SiAr_3)(EMe_2Ph)_2$ in 70−95% yields.[40] (η^7-C_7H_7)$Mo(CO)_2SiCl_3$ was prepared in 35% yield from (η^7-C_7H_7)$Mo(CO)_2Cl$ and $HSiCl_3$ in the presence of Et_3N.[41] The reactions described in eqs 1 and 2 represent an example of a metal hydride reacting with chlorosilanes to form metal silyl complexes by HCl elimination. The only other reported HCl elimination reaction involving a metal hydride with a chlorosilane was the intramolecular formation of the metallocycle $(CO)_4Mn(PMe_2CH_2CH_2SiCl_2)$ (30% yield) from $(CO)_4MnH(PMe_2CH_2CH_2SiCl_3)$ in the presence of Et_3N.[42]

The ruthenium hydrosilyl complexes $Cp(PMe_3)_2RuSiR_2H$ [SiR_2H = SiH_3 (**7**), $SiMeH_2$ (**8**), $SiMe_2H$ (**9**)] were prepared by a chloride/hydride exchange of the corresponding chlorosilyl complexes **1**−**6** with $LiAlH_4$ in Et_2O (eq 3). These hydrosilyl ruthenium complexes



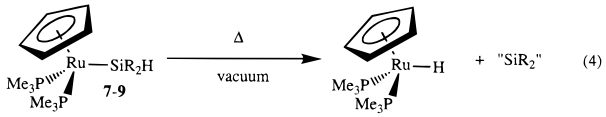
(3)

SiR_2Cl = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), $SiMeCl_2$ (**4**), $SiMeHCl$ (**5**), $SiMe_2Cl$ (**6**)

SiR_2H = SiH_3 (**7**), $SiMeH_2$ (**8**), $SiMe_2H$ (**9**)

7−**9** were isolated from solution in good yields (80−90%) as white or yellow, air-sensitive, waxy solids. No evidence for Ru−Si bond cleavage upon treatment of **1**−**9** with excess $LiAlH_4$ was observed (i.e., formation of $Cp(PMe_3)_2RuH$ and the corresponding hydrosilane).[43] Complexes **7**−**9** were soluble in common organic solvents but susceptible to hydride/chloride metathesis in chlorocarbon solvents ($CHCl_3$ at 50 °C, CH_2Cl_2 to a much lesser extent). Complexes **7**−**9** slowly decomposed in the solid state even when stored under an inert atmosphere.

Sublimation (80 °C, < 0.03 mmHg) can also be used to isolate complexes **7**−**9**, but this method of isolation is complicated by a fragmentation of the hydrosilyl group during the sublimation process. This fragmentation involves loss of silylene ($SiMe_2$, SiMeH, or SiH_2) with formation of the sublimable hydride $Cp(PMe_3)_2RuH$ (eq 4). The susceptibility of these hydrosilyl

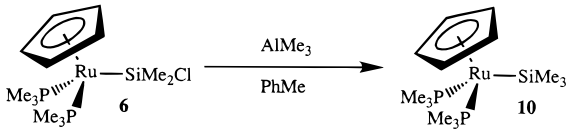


(4)

SiR_2 = SiH_2, SiMeH, $SiMe_2$

ruthenium complexes to silylene loss during sublimation increases as the number of methyl groups on silicon increases: $SiH_3 \leq SiMeH_2 < SiMe_2H$.[44]

Since $SiMe_3Cl$ does not react with $Cp(PMe_3)_2RuH$, an alternative route to $Cp(PMe_3)_2RuSiMe_3$ (**10**) was used which involved the reaction of **6** with $AlMe_3$ in toluene at room temperature (eq 5). Sublimation (80−100 °C,

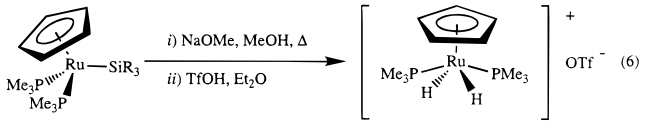


(5)

<0.03 mmHg) of the reaction residue gave **10** as a yellow-orange solid in good yields. Complex **10** can also be prepared by the reaction of **6** with LiMe in refluxing toluene; however, isolation of **10** from this reaction mixture was not as simple and clean as the reaction described in eq 5.

The ruthenium silyl complexes **1**−**10** prepared according to eqs 1−3 and 5 were characterized by multinuclear NMR and IR spectroscopies, mass spectrometry, and elemental analyses. The NMR and IR spectroscopic data are listed in Table 1, with the mass spectrometry and elemental analysis data listed in Table 2. The spectroscopic and analytical data are consistent with the $Cp(PMe_3)_2RuSiR_3$ formulation of these complexes.

The $Cp(PMe_3)_2Ru$ moiety was recovered through treatment of the ruthenium silyl complexes as described in eq 6. The first step involved the reaction of the



(6)

R = H, Me, Cl

ruthenium silyl complexes with methoxide in refluxing methanol. In this step, the chlorosilyl ruthenium com-

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(43) The W−Si bond in $Cp'(CO)_3WSiHCl_2$ (Cp′ = Cp, Cp*) was cleaved by $LiAlH_4$ into SiH_4 and $Li[Cp'W(CO)_3]$. On the other hand, a PMe_3 ligand in the tungsten coordination sphere stabilized the W−Si bond such that $Cp^*(CO)_2(PMe_3)WSiR_2Cl$ (SiR_2Cl = $SiHCl_2$, SiMeHCl) gave the corresponding hydrosilyl complexes $Cp^*(CO)_2(PMe_3)WSiR_2H$ (SiR_2H = SiH_3, $SiMeH_2$) upon treatment with $LiAlH_4$.[27]

(44) The susceptibility of the hydrosilanes $Cp(PMe_3)_2RuSiR_2H$ (SiR_2H = SiH_3, $SiMeH_2$, $SiMe_2H$) to silylene loss during sublimation parallels the preference for silylene loss observed in a mass spectral study of these hydrosilanes. Details of this mass spectral study will be reported in a later publication.

Table 1. Multinuclear NMR and Infrared Spectroscopic Data and Electronic Factors for Ruthenium Silyl Complexes

complex	^{1}H NMR (ppm)[a]	^{13}C{^{1}H} NMR (ppm)[b]	^{29}Si DEPT NMR (ppm)[c]	^{31}P{^{1}H} NMR (ppm)[d]	ν(Si−H) (cm^{-1})[e]	$\sum\chi_i$[f]
$Cp(PMe_3)_2RuSiCl_3$ (**1**)	4.79 (s, 5H, Cp) 1.52 (fd, N = 9.0 Hz, 18H, PMe_3)	84.10 (t, J_{PC} = 1.6 Hz, Cp) 24.69 (vt, N = 32.0 Hz, PMe_3)	42.11 (t, J_{SiP} = 43.6 Hz)	9.33 (s, with ^{29}Si satellites J_{SiP} = 43.7 Hz)		44.4
$Cp(PMe_3)_2RuSiHCl_2$ (**2**)	6.41 (t, J_{PH} = 3.3 Hz, 1H, SiH) 4.75 (s, 5H, Cp) 1.46 (fd, N = 8.9 Hz, 18H, PMe_3)	83.66 (t, J_{PC} = 1.6 Hz, Cp) 24.54 (vt, N = 31.5 Hz, PMe_3)	66.79 (dt, J_{SiH} = 199.6 Hz, J_{SiP} = 36.2 Hz)	10.42 (s, with ^{29}Si satellites J_{SiP} = 36.0 Hz)	2073	37.9
$Cp(PMe_3)_2RuSiH_2Cl$ (**3**)	5.34 (t, J_{PH} = 3.7 Hz, 2H, SiH) 4.70 (s, 5H, Cp) 1.40 (fd, N = 8.6 Hz, 18H, PMe_3)	82.57 (t, J_{PC} = 1.7 Hz, Cp) 24.62 (vt, N = 31.0 Hz, PMe_3)	36.37 (tt, J_{SiH} = 171.1 Hz, J_{SiP} = 32.9 Hz)	11.50 (s, with ^{29}Si satellites J_{SiP} = 33.2 Hz)	2043	31.4
$Cp(PMe_3)_2RuSiMeCl_2$ (**4**)	4.72 (s, 5H, Cp) 1.48 (fd, N = 8.8 Hz, 18H, PMe_3) 0.97 (s, 3H, SiMe)	83.03 (t, J_{PC} = 1.6 Hz, Cp) 25.15 (vt, N = 31.1 Hz, PMe_3) 22.73 (s, SiMe)	92.16 (t, J_{SiP} = 35.4 Hz)	10.80 (s, with ^{29}Si satellites J_{SiP} = 36.1 Hz)		32.2
$Cp(PMe_3)_2RuSiMeHCl$ (**5**)	5.45 (tq, J_{PH} = 5.6 Hz, J_{HH} = 3.5 Hz, 1H, SiH) 4.68 (s, 5H, Cp) 1.45 (d, J_{PH} = 8.7 Hz, 9H, PMe_3) 1.37 (d, J_{PH} = 8.3 Hz, 9H, PMe_3) 0.73 (d, J_{HH} = 3.5 Hz, 3H, SiMe)	82.38 (t, J_{PC} = 1.7 Hz, Cp) 25.07 (dd, J_{PC} = 27.4, 3.2 Hz, PMe_3) 24.56 (dd, J_{PC} = 27.5, 3.3 Hz, PMe_3) 12.16 (s, SiMe)	57.17 (dt, J_{SiH} = 163.6 Hz, J_{SiP} = 30.5 Hz)	11.60 (AB, J_{PP} = 38.9 Hz, with ^{29}Si satellites J_{SiP} = 31.1 Hz)	2026	25.7
$Cp(PMe_3)_2RuSiMe_2Cl$ (**6**)	4.65 (s, 5H, Cp) 1.43 (fd, N = 8.8 Hz, 18H, PMe_3) 0.58 (s, 6H, SiMe)	82.28 (t, J_{PC} = 1.8 Hz, Cp) 25.81 (vt, N = 29.9 Hz, PMe_3) 16.66 (s, SiMe)	87.29 (t, J_{SiP} = 30.2 Hz)	11.83 (s, with ^{29}Si satellites J_{SiP} = 30.5 Hz)		20.0
$Cp(PMe_3)_2RuSiH_3$ (**7**)	4.59 (s, 5H, Cp) 3.09 (t, J_{PH} = 5.4 Hz, 3H, SiH) 1.36 (fd, N = 8.6 Hz, 18H, PMe_3)	81.08 (t, J_{PC} = 1.9 Hz, Cp) 24.68 (vt, N = 30.1 Hz, PMe_3)	−56.68 (qt, J_{SiH} = 149.5 Hz, J_{SiP} = 32.4 Hz)	12.02 (s, with ^{29}Si satellites J_{SiP} = 31.9 Hz)	2019	24.9
$Cp(PMe_3)_2RuSiMeH_2$ (**8**)	4.58 (s, 5H, Cp) 3.72 (tq, J_{PH} = 6.0 Hz, J_{HH} = 4.3 Hz, 2H, SiH) 1.35 (fd, N = 8.5 Hz, 18H, PMe_3) 0.26 (t, J_{HH} = 4.3 Hz, 3H, SiMe)	81.11 (t, J_{PC} = 1.9 Hz, Cp) 24.79 (vt, N = 29.6 Hz, PMe_3) 0.14 (t, J_{PC} = 1.9 Hz, SiMe)	−13.75 (tt, J_{SiH} = 146.6 Hz, J_{SiP} = 29.9 Hz)	12.41 (s, with ^{29}Si satellites J_{SiP} = 30.0 Hz)	1997	19.2
$Cp(PMe_3)_2RuSiMe_2H$ (**9**)	4.56 (s, 5H, Cp) 3.94 (nonet, $J_{HH} \sim J_{PH}$ = 3.6 Hz, 1H, SiH) 1.36 (fd, N = 8.4 Hz, 18H, PMe_3) 0.24 (d, J_{HH} = 3.8 Hz, 6H, SiMe)	81.04 (t, J_{PC} = 1.9 Hz, Cp) 25.24 (vt, N = 29.0 Hz, PMe_3) 6.31 (t, J_{PC} = 1.9 Hz, SiMe)	13.85 (dt, J_{SiH} = 144.1 Hz, J_{SiP} = 26.9 Hz)	12.29 (s, with ^{29}Si satellites J_{SiP} = 26.7 Hz)	1978	13.5
$Cp(PMe_3)_2RuSiMe_3$ (**10**)	4.57 (s, 5H, Cp) 1.36 (fd, N = 8.2 Hz, 18H, PMe_3) 0.10 (s, 9H, SiMe)	81.61 (t, J_{PC} = 2.0 Hz, Cp) 26.48 (vt, N = 27.7 Hz, PMe_3) 11.22 (t, J_{PC} = 1.4 Hz, SiMe)	19.56 (t, J_{SiP} = 26.0 Hz)	12.61 (s, with ^{29}Si satellites J_{SiP} = 25.8 Hz)		7.8

[a] At 250 MHz and ambient probe temperature in CD_2Cl_2 and referenced to residual proton peak (5.32 ppm). The PMe_3 resonances in these complexes appear as a $A_9XX'A_9$ pattern in the form of a "filled-in-doublet" (fd) with the separation of the outer lines $N = {}^2J_{PH} + {}^4J_{PH}$. [b] At 62.9 MHz and ambient probe temperature in CD_2Cl_2 and referenced to solvent (53.8 ppm). The PMe_3 resonances in these complexes appear as a "virtual triplet" (vt) with the separation of the outer lines $N = {}^1J_{PC} + {}^3J_{PC}$. [c] At 79.5 MHz and ambient probe temperature in CD_2Cl_2 and referenced to external $SiMe_4$ (0.00 ppm). [d] At 101 MHz and ambient probe temperature in CD_2Cl_2 and referenced to external H_3PO_4 (85%, 0.00 ppm). [e] In CH_2Cl_2. [f] Summation of the Tolman's electronic parameters for the three substituents on silicon: χ_i(Cl) = 14.8, χ_i(H) = 8.3, χ_i(Me) = 2.6.[56]

Table 2. Analytical Data for $Cp(PMe_3)_2RuSiR_3$ Complexes

SiR_3	MS[a]	formula	C found (calcd), %	H found (calcd), %
$SiCl_3$ (**1**)	454	$C_{11}H_{23}Cl_3P_2RuSi$	29.02 (29.18)	5.12 (5.12)
$SiHCl_2$ (**2**)	418	$C_{11}H_{24}Cl_2P_2RuSi$	31.49 (31.58)	5.71 (5.78)
SiH_2Cl (**3**)	384	$C_{11}H_{25}ClP_2RuSi$	34.28 (34.42)	6.54 (6.56)
$SiMeCl_2$ (**4**)	432	$C_{12}H_{26}Cl_2P_2RuSi$	33.32 (33.34)	5.65 (6.06)
SiMeHCl (**5**)	398	$C_{12}H_{27}ClP_2RuSi$	35.53 (36.22)	6.57 (6.84)
$SiMe_2Cl$ (**6**)	412	$C_{13}H_{29}ClP_2RuSi$	37.75 (37.91)	7.10 (7.10)
SiH_3 (**7**)	350	$C_{11}H_{26}P_2RuSi$	37.67 (37.81)	7.32 (7.50)
$SiMeH_2$ (**8**)	364	$C_{12}H_{28}P_2RuSi$	39.24 (39.66)	7.84 (7.76)
$SiMe_2H$ (**9**)	378	$C_{13}H_{30}P_2RuSi$	41.98 (41.36)	8.21 (8.01)
$SiMe_3$ (**10**)	392	$C_{14}H_{32}P_2RuSi$	42.55 (42.95)	8.10 (8.24)

[a] Parent ion *m*/*z* in each case.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $Cp(PMe_3)_2RuSiCl_3$ (1)

Interatomic Distances[a]			
Ru(1)−Si(1)	2.265(2)	Si(1)−Cl(1)	2.122(3)
Ru(1)−P(1)	2.273(2)	Si(1)−Cl(2)	2.114(3)
Ru(1)−P(2)	2.280(2)	Si(1)−Cl(3)	2.121(3)
Ru(1)−Cnt	1.887		

Bond Angles[a]			
P(1)−Ru(1)−P(2)	95.80(7)	P(1)−Ru(1)−Si(1)	92.60(7)
P−Ru(1)−Cnt	123.2 (av)	P(2)−Ru(1)−Si(1)	93.00(7)
Cnt-Ru(1)−Si(1)	121.2	Ru(1)−Si(1)−Cl(1)	116.8(1)
Ru(1)−Si(1)−Cl(2)	115.0(1)	Ru(1)−Si(1)−Cl(3)	125.6(1)
Cl(1)−Si(1)−Cl(2)	99.0(1)	Cl(1)−Si(1)−Cl(3)	96.9(1)
Cl(2)−Si(1)−Cl(3)	98.8(1)		

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

plexes **1**−**6** were converted to the corresponding methoxysilyl complexes, while the nonchlorosilyl ruthenium complexes **7**−**10** were generally unaffected. Some $Cp(PMe_3)_2RuH$ was also formed in this step, presumably due to Ru−Si bond cleavage. The $Cp(PMe_3)_2Ru$-containing products were isolated by sublimation. The second step involved treatment of the sublimate with triflic acid (TfOH) in Et_2O. The triflic acid cleaved the Ru−Si bond to form $Cp(PMe_3)_2RuH$, which was readily protonated to afford the dihydride $[Cp(PMe_3)_2RuH_2]OTf$ with additional triflic acid. Conversion of the cationic dihydride $[Cp(PMe_3)_2RuH_2]^+$ to the neutral monohydride $Cp(PMe_3)_2RuH$ was readily accomplished with NaOMe in refluxing MeOH.[38] This provided a convenient method for the recovery of the $Cp(PMe_3)_2Ru$ moiety as the neutral monohydride $Cp(PMe_3)_2RuH$.

B. Structure of $Cp(PMe_3)_2RuSiCl_3$ (1). The crystal structure of $Cp(PMe_3)_2RuSiCl_3$ (**1**) has been determined by X-ray diffraction at 141 K. Pertinent interatomic distances and angles for **1** are presented in Table 3. The molecular structure of **1** (Figure 1) confirms the formulation and connectivity of the ruthenium silyl complexes described in section A. Complex **1** adopts a "three-legged piano stool" geometry around ruthenium, with "legs" composed of one $SiCl_3$ and two PMe_3 groups. The bond distances and angles in the $Cp(PMe_3)_2$ moiety are normal when compared to the structures of related $Cp(PMe_3)_2RuX$ complexes.[19,38,45−47] The Ru−Si bond distance of 2.265(2) Å is consistent with a single bond. This Ru−Si bond distance lies on the low end of the range

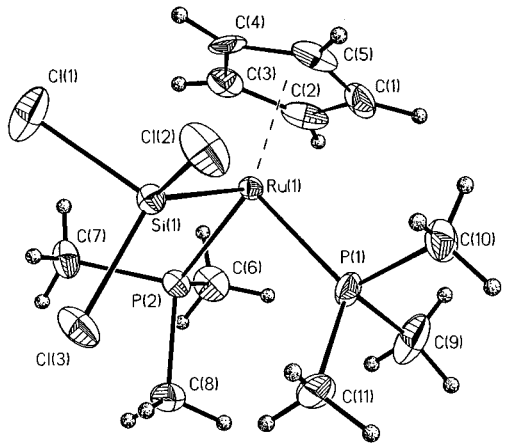

Figure 1. Perspective view of the molecular structure of $Cp(PMe_3)_2RuSiCl_3$ (**1**). The thermal ellipsoids are drawn at the 50% probability level.

(2.27−2.51 Å) observed for other d^6 ruthenium silyl complexes[1,2,19,22,23,48] but is in the middle of the range (2.20−2.34 Å) observed for other group 8 trichlorosilyl complexes, L_nMSiCl_3 (M = Fe,[49−54] Ru,[48] Os[55]). The Si−Cl bond distances in **1** [range 2.114−2.122 Å, 2.119 Å (av)] are significantly longer than the Si−Cl bond distances observed in the other group 8 trichlorosilyl complexes (range 2.026−2.090 Å). The short Ru−Si and long Si−Cl distances indicate a π-interaction between the ruthenium and the trichlorosilyl group (vide infra).

Complex **1** has a staggered conformation about the Ru−Si bond with the Cp and Cl(3) groups in an anti relationship (Cp centroid−Ru−Si−Cl(3) dihedral angle = 169.8°). The silyl group has a distorted tetrahedral geometry with an average Cl−Si−Cl angle of 98.2 ± 1.2°. By comparison, the average Ru−Si−Cl angle of 119.1 ± 5.7° is significantly larger but within the M−Si−Cl angle range (110−120°) observed for other group 8 trichlorosilyl complexes.[48,49,53,55] The Ru−Si−Cl(3) angle of 125.6(1)°, which is anti to the Cp group, lies noticeable outside the group 8 M−Si−Cl angle range. In other ruthenium silyl complexes, the Ru−Si−X angle for substituents anti to a Cp group have also been observed to be 10° or more larger than Ru−Si−X angles for the other substituents on silicon: $Cp(PMe_3)_2RuSiCl_2Cp^*$ [Ru−Si−Cl(anti) 119.9° vs Ru−Si−Cl 109.2°],[19] $Cp^*(PMe_3)_2RuSiPh_2H$ [Ru−Si−H(anti) 112.9° vs Ru−Si−Ph 98.8° (av)],[22] and $Cp^*(PMe_3)_2RuSiPh_2OTf$ [Ru−Si−OTf(anti) 118.2° vs Ru−Si−Ph 96.9° (av)].[23]

C. Spectroscopic Trends. The ruthenium silyl complexes **1**−**10** represent the first complete set of transition metal silicon complexes in which the substituents on silicon contain all possible combination of Cl,

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H, and Me groups. This series of 10 ruthenium silyl complexes offers a unique opportunity to evaluate how changing the substituents on silicon influences the spectroscopic properties of these complexes. Since the $Cp(PMe_3)_2Ru$ moiety is the same throughout this series, trends in the spectroscopic properties of complexes **1**−**10** should only arise from the steric and electronic effects of the Cl, H, and Me substituents on silicon. The cone angles for the silyl groups used in this study are relatively small, ranging from 122° for $SiCl_3$ to 118° for $SiMe_3$ to 87° SiH_3 (based on the assumption that the cone angles for the SiX_3 groups are similar to the cone angles of the corresponding phosphines, PX_3).[56,57] Therefore, the sterics of the silyl groups should not have a significant influence on the observed spectroscopic properties of the ruthenium silyl complexes and will not be considered any further. Only the effect of the electronic nature (electron-withdrawing ability) of the Cl, H, and Me groups on the spectroscopic properties of the ruthenium silyl complexes will be examined. Tolman's electronic parameter, χ_i, will be used as a gauge of the electron-withdrawing ability of the substituents on silicon [χ_i(Me) = 2.6, χ_i(H) = 8.3, χ_i(Cl) = 14.8].[56] The summation of Tolman's electronic parameters for the three substituents on silicon, $\sum\chi_i$, represents the combined electron-withdrawing ability of the substituents on silicon.[58] The larger the $\sum\chi_i$ value, the more electron-withdrawing the substituents on silicon. The $\sum\chi_i$ values for the various silyl groups used in this study are listed in Table 1.

1. Infrared Spectra. The Si−H stretching frequencies for the ruthenium hydrosilyl complexes, $Cp(PMe_3)_2RuSiHR_2$, were observed in the 1975−2075 cm^{-1} region. In comparison with nonmetalated silanes, the ν(Si−H) for these ruthenium hydrosilyl complexes are shifted to lower wavenumbers by 140−190 cm^{-1} compared to the corresponding methylhydro- ($MeSiHR_2$), dihydro- (H_2SiR_2), and chlorohydrosilanes ($ClSiHR_2$,).[59] These relatively low ν(Si−H) values suggest significant hydride character for the SiH hydrogen, which is consistent with the hydride/chloride metathesis reactions in chlorocarbon solvents described in part A.[26,27,31]

A plot of ν(Si−H) as a function of $\sum\chi_i$ for the ruthenium hydrosilyl complexes can be found in Figure 2. A linear relationship between ν(Si−H) and $\sum\chi_i$ is observed and is consistent with Bent's rule.[60] According to Bent's rule and in the context of this study, a more electron-withdrawing substituent (i.e., Cl) requires more p character at the silicon atom for bonding, leaving more s character for the other atoms or groups bound to silicon (i.e., H, Me, and Ru). Thus, the Si−H bond strength and ν(Si−H) should increase with increasing

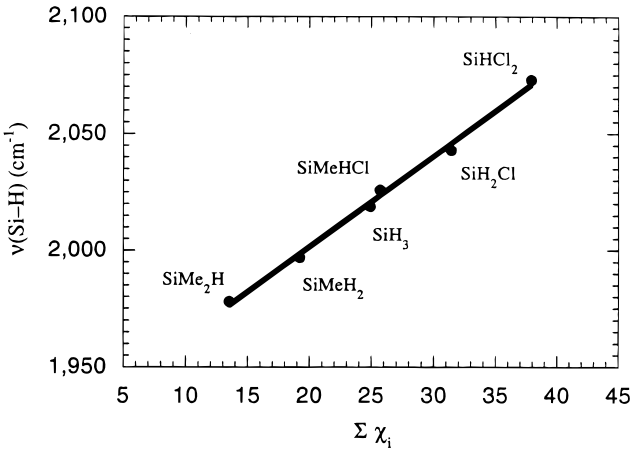

Figure 2. ν(Si−H) versus $\sum\chi_i$ for the ruthenium hydrosilyl complexes $Cp(PMe_3)_2RuSiHR_2$: slope = 3.88 cm^{-1} per χ_i unit, R = 0.998.

$\sum\chi_i$ values. Complex **1**, which has the largest $\sum\chi_i$ value also has the strongest Si−H bond (largest ν(Si−H) value at 2073 cm^{-1}), while complex **9**, with the smallest $\sum\chi_i$ value, has the weakest Si−H bond (ν(Si−H) = 1978 cm^{-1}).

A similar linear relationship between ν(Si−H) and the electron-withdrawing ability of the other substituents on silicon has been observed for a variety of nonmetalated hydrosilanes, $HSiR_3$ (R = H, alkyl, Cl, F, Ph, OMe, NMe_2).[59] A general increase in ν(Si−H) was also observed in some iron, molybdenum, and tungsten hydrosilyl systems when a H or Me group was replaced with a Cl;[25,27] more detailed analyses of ν(Si−H) were hampered by a lack of metalated hydrosilyl complexes. The entirety of the ruthenium hydrosilyl series (**2**, **3**, **5**, and **7**−**9**) allows, for the first time, a thorough examination of how ν(Si−H) is effected by the other substituents on silicon in metalated hydrosilanes.

2. NMR Chemical Shifts. The substituent effects on the chemical shifts of the NMR active nuclei in complexes **1**−**10** can be grouped into three classes: silicon, nuclei attached to silicon, and nuclei two or more bonds from silicon. The resonances for the silyl group in the ^{29}Si NMR spectra of complexes **1**−**10** were observed over a 160 ppm range (Table 1). A plot of $\delta(^{29}Si)$ as a function of $\sum\chi_i$ for complexes **1**−**10** is shown in Figure 3. The most striking feature of this plot is that the ruthenium silyl complexes are arranged into three silyl classes: a dichlorosilyl, $SiRCl_2$ (R = Cl, H, Me), class; a monochlorosilyl, SiR_2Cl (R = H and/or Me), class; and a "non-chlorosilyl", SiR_3 (R = H and/or Me), class. A couple of trends are observed from the plot in Figure 3. First, the silyl complexes within a class exhibit a linear relationship with respect to $\sum\chi_i$. Second, the silyl classes are nearly parallel with respect to each other. Third, within a silyl class, $\delta(^{29}Si)$ moves upfield with increasing $\sum\chi_i$ (i.e., replacing a Me group with a H). Fourth, a general downfield shift in $\delta(^{29}Si)$ is observed upon going from one silyl class to another (i.e., replacement of a Me group or a H with Cl). Table 4 lists the effect of substituent changes on $\delta(^{29}Si)$. Large standard deviation values (±27 ppm) are observed for the average $\Delta\delta(^{29}Si)$ of the H/Cl and Me/Cl exchanges. This is due to the fact that the magnitude of $\Delta\delta(^{29}Si)$ for the conversion between "non-chlorosilyl" and monochlorosilyl classes [$\Delta\delta(^{29}Si)$

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(57) Tolman's PX_3 cone angles may actually overestimate the SiX_3 cone angles. On the basis of the method described by Tolman,[56] the $SiCl_3$ cone angle in **1** was calculated to be 115° (compared to 122° for PCl_3) using an average Ru−Si−Cl angle (119°), an average Si−Cl distance (2.12 Å), and the van der Waals radii of Cl (1.80 Å).

(58) Hammett σ_p or modified Taft σ^*(Si)[59] parameters can also be used as a gauge of the electron-withdrawing ability of the substituents on silicon. Plots of the various spectroscopic properties as a function of $\sum\sigma_p$ or $\sum\sigma^*$(Si) for the substituents on silicon are very similar to the plots of these spectroscopic properties as a function of $\sum\chi_i$. The observed trends and relationships based on Hammett σ_p or modified Taft σ^*(Si) parameters are the same as those observed using Tolman χ_i parameters.

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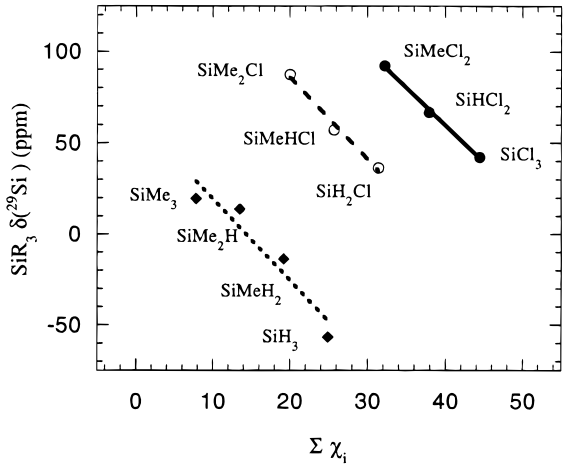


Figure 3. ^{29}Si NMR chemical shift of the silyl group versus $\sum\chi_i$ for the ruthenium silyl complexes $Cp(PMe_3)_2RuSiR_3$ (**1**−**10**) showing the three silyl classes: dichlorosilyl (●, slope = −4.10 ppm per χ_i unit, R = 0.999), monochlorosilyl (○, slope = −4.47 ppm per χ_i unit, R = 0.994), and "non-chlorosilyl" (◆, slope = −4.50 ppm per χ_i unit, R = 0.950).

Table 4. Substituent Effects on the NMR Chemical Shifts and Coupling Constants of $Cp(PMe_3)_2RuSiR_3$ Complexes 1−10

R group replace	R group with	SiR_3 $\Delta\delta(^{29}Si)$ (av, ppm)[a]	SiH $\Delta\delta(^1H)$ (av, ppm)[a]	SiMe $\Delta\delta(^{13}C)$ (av, ppm)[a]	Δ^1J_{SiH} (av, Hz)[b]
Me	H	−25.4 ± 12.2	−0.32 ± 0.27	−5.19 ± 0.87	4.3 ± 2.8
H	Cl	60.6 ± 26.9[c]	1.68 ± 0.59	10.98 ± 0.91	22.4 ± 5.8
Me	Cl	35.1 ± 27.0[d]	1.36 ± 0.35	5.79 ± 0.32	26.7 ± 8.5

[a] $\Delta\delta = \delta$ final complex − δ initial complex. [b] $\Delta^1J_{SiH} = {}^1J_{SiH}$ final complex − ${}^1J_{SiH}$ initial complex. [c] The $SiHCl_2/SiCl_3$ conversion ($\Delta\delta$ = −24.7 ppm) was excluded from the average calculation. [d] The $SiMeCl_2/SiCl_3$ conversion ($\Delta\delta$ = −50.1 ppm) was excluded from the average calculation.

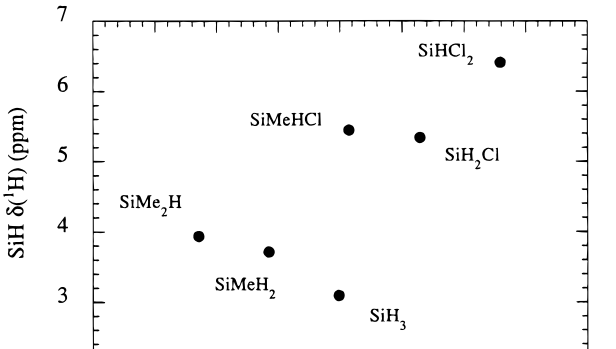


Figure 4. ^{1}H NMR chemical shift of the SiH group versus $\sum\chi_i$ for the ruthenium hydrosilyl complexes $Cp(PMe_3)_2RuSiHR_2$.

= 79.1 ± 12.1 ppm for H/Cl and 53.7 ± 12.6 ppm for Me/Cl exchanges] is much larger than the magnitude of $\Delta\delta(^{29}Si)$ for the conversion between monochlorosilyl and dichlorosilyl classes [$\Delta\delta(^{29}Si)$ = 32.7 ± 3.2 ppm for H/Cl and 7.3 ± 3.4 ppm for Me/Cl exchanges].

The resonances for nuclei attached to silicon are also influenced by the other substituents on silicon. Figure 4 shows a plot of the SiH $\delta(^1H)$ as a function of $\sum\chi_i$ for the ruthenium silyl complexes. In this plot, the ruthenium hydrosilyl complexes are arranged in a triangular

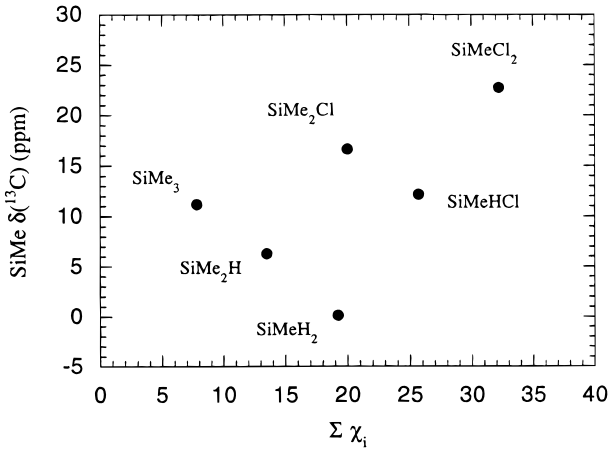


Figure 5. ^{13}C NMR chemical shift of the SiMe group versus $\sum\chi_i$ for the ruthenium methylsilyl complexes $Cp(PMe_3)_2RuSiMeR_2$.

formation which, as observed in Figure 3, can be grouped into the three silyl classes: dichlorosilyl, monochlorosilyl, and "non-chlorosilyl".[61] Similarly, a plot of the SiMe $\delta(^{13}C)$ as a function of $\sum\chi_i$ for the ruthenium methylsilyl complexes, Figure 5, exhibits the same three classes of silyl complexes in a triangular formation. Changes in the SiH $\delta(^1H)$ or SiMe $\delta(^{13}C)$ which resulted from the conversion of one silyl group to another were well behaved and did not depend on if the conversion was within a class or between classes (Table 4).[61] In general, replacing a Me group for a H shifted the SiH $\delta(^1H)$ and the SiMe $\delta(^{13}C)$ upfield, while replacing a Me group or a H with Cl shifted the SiH $\delta(^1H)$ and the SiMe $\delta(^{13}C)$ downfield, similar to the substituent trends observed for the $\delta(^{29}Si)$ of the silyl group.

The resonances of the PMe_3 group in the ^{31}P NMR spectra of complexes **1**−**10** did not exhibit a dependence on the number of chlorines present on silicon. A plot of PMe_3 $\delta(^{31}P)$ as a function of $\sum\chi_i$ for the ruthenium silyl complexes can be found in Figure 6. The ^{31}P NMR resonances were observed in the 8−13 ppm range and exhibit a nearly linear but inverse relationship with $\sum\chi_i$.

3. NMR Coupling Constants. Two sets of coupling constants were readily accessible from the NMR spectroscopic data: $^2J_{SiP}$ and $^1J_{SiH}$. The $^2J_{SiP}$ values for the ruthenium silyl complexes were in the range 25−45 Hz, and a plot of $^2J_{SiP}$ as a function of $\sum\chi_i$ can be found in Figure 7. This plot shows a nearly linear relationship with $\sum\chi_i$. The magnitude of the coupling constant $^2J_{SiP}$ increases as the electron-withdrawing ability of the substituents on silicon increases, consistent with Bent's rule.[60] An increase in the s character in the Ru−Si bond (with increasing $\sum\chi_i$) results in this bond becoming stronger, which in turn increases the communication (coupling) between silicon and phosphorus. Thus, the

(61) The ruthenium silyl complexes plotted in Figure 4 could also be classified using two other sets of criteria. One set could be based on the number of hydrogens on silicon to give a trihydrosilyl class, a dihydrosilyl class, and a monohydrosilyl class. The other set could be based on the number of methyl groups on silicon to give a dimethylsilyl class, a monomethylsilyl class, and a "non-methylsilyl" class. The ability to use different criteria to classify the silyl groups probably explains why ^{1}H and ^{13}C chemical shift changes are so well behaved compared to ^{29}Si chemical shift changes upon H/Cl, H/Me, and Cl/Me exchanges (see text). All substituent exchanges can be viewed as conversions within a silyl class just by changing the classification criteria. A classification criterion based on the number of chlorines on silicon is used throughout this paper for internal consistency.

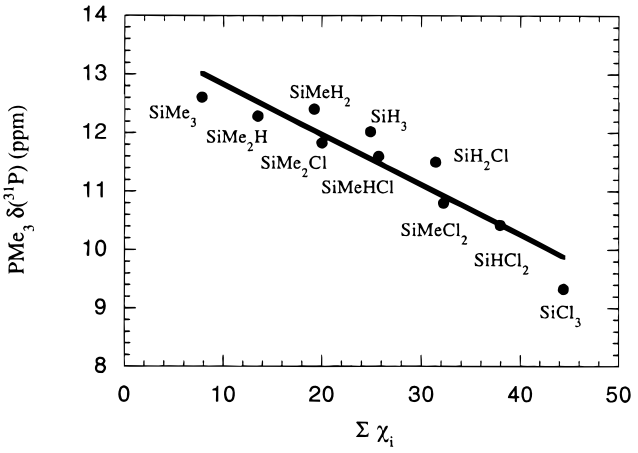


Figure 6. ^{31}P NMR chemical shift of the PMe_3 groups versus $\sum\chi_i$ for the ruthenium silyl complexes $Cp(PMe_3)_2RuSiR_3$ (**1**−**10**): slope = −0.086 ppm per χ_i unit, $R = 0.935$.

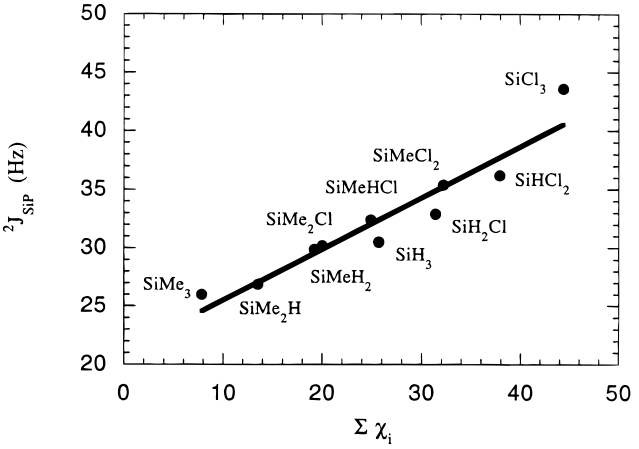


Figure 7. $^2J_{SiP}$ (Hz) versus $\sum\chi_i$ for the ruthenium silyl complexes $Cp(PMe_3)_2RuSiR_3$ (**1**−**10**): slope = 0.44 Hz per χ_i unit, $R = 0.953$.

$SiCl_3$ complex has the largest $^2J_{SiP}$ value, while the $SiMe_3$ complex has the smallest $^2J_{SiP}$ value.

Assuming Bent's rule holds for the other substituents on silicon, a similar trend should be observed for the other coupling constant $^1J_{SiH}$. The $^1J_{SiH}$ values for the ruthenium hydrosilyl complexes were in the range 140−200 Hz, and a plot of $^1J_{SiH}$ as a function of $\sum\chi_i$ can be found in Figure 8. A rough linear relationship is observed between $^1J_{SiH}$ and $\sum\chi_i$, consistent with Bent's rule. The effects on $^1J_{SiH}$ of replacing one substituent with another are listed in Table 4. In all of the exchange cases, replacing an electropositive group (Me) or atom (H) with a more electronegative atom (H or Cl) results in an increase in $^1J_{SiH}$.

D. Silyl Group Classifications. From the plots in Figures 3−5, it is apparent that the grouping of ruthenium silyl complexes **1**−**10** into different classes (dichlorosilyl, monochlorosilyl, and "non-chlorosilyl") is dependent on the number of chlorides on silicon. The chloride substituents influence the spectroscopic properties of these ruthenium silyl complexes beyond the electronic contributions which can be accounted for using Tolman's χ_i parameter. This "chloride effect" has limited range and is most predominate in the NMR resonances of silicon and nuclei attached to silicon (H, C). Very little, if any, contribution from the "chloride effect" is observed in the NMR resonances of phosphorus, two bonds from silicon, and the SiH and SiP coupling constants.

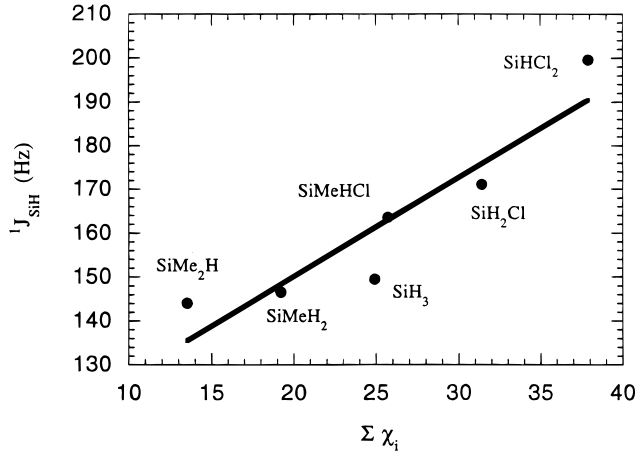
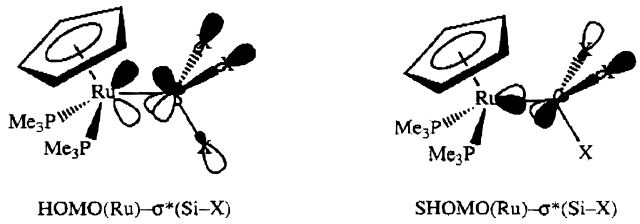


Figure 8. $^1J_{SiH}$ (Hz) versus $\sum\chi_i$ for the ruthenium hydrosilyl complexes $Cp(PMe_3)_2RuSiHR_2$: slope = 2.25 Hz per χ_i unit, $R = 0.925$.

Scheme 1



The differentiation of ruthenium silyl complexes **1**−**10** into the three silyl classes by the "chloride effect" can be rationalized by π-back-bonding from the d^6 ruthenium center to the silyl group. In a main group element like silicon, the d orbitals are too diffuse and high in energy to play a significant role in π-back-bonding with a metal center.[62−64] On the other hand, the Si−X (X = H, Me, Cl) σ^* orbitals of the silyl group would have the appropriate symmetry for π-back-bonding with the ruthenium center. Linear combinations of the Si−X σ^* orbitals of SiX_3 give an a_1 and an e set, assuming C_{3v} localized symmetry. The doubly degenerate e set has the correct symmetry to interact with the HOMO and the SHOMO (second highest occupied molecular orbital) of the $Cp(PM_3)_2Ru$ moiety,[65] as shown in Scheme 1. The short Ru−Si and long Si−Cl distances observed in the solid-state structure of **1** (Figure 1) offer good supporting evidence for the d(Ru)−σ^*(Si−X) π-back-bonding described in Scheme 1.

The presence of d(Ru)−σ^*(Si−X) π-back-bonding explains the differentiation of the ruthenium silyl complexes into the three classes. Recently, ab initio calculations and natural bond order (NBO) analyses on a series of osmium silyl complexes, $Os(SiX_3)Cl(CO)(PPh_3)_2$, revealed an increasing importance in d(Os)−σ^*(Si−X) π-bonding in the order $SiMe_3$ < $Si(OH)_3$ <

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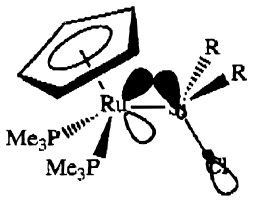
(65) Kostíc, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974−982.

Scheme 2



HOMO(Ru)–σ*(Si–Cl)
R = H and/or Me

$SiCl_3$ < SiF_3.[55] Thus, in the present study, d(Ru)−σ*(Si−X) π-back-bonding should be least prevalent with Me and H substituents on silicon and most prevalent with Cl substituents on silicon. Therefore, very little d(Ru)−σ*(Si−X) π-back-bonding is expected in the "non-chlorosilyl" class. The d(Ru)−σ*(Si−X) π-back-bonding in the monochlorosilyl class would be dominated by the d(Ru)−σ*(Si−Cl) interaction (Scheme 2) which would be most favorable with the HOMO of the ruthenium moiety. In the dichlorosilyl class, the d(Ru)−σ*(Si−X) π-back-bonding would be dominated by the interaction of the ruthenium moiety HOMO and SHOMO with linear combinations of σ*(Si−Cl) (similar to those described in Scheme 1).

The presence of d(Ru)−σ*(Si−Cl) π-back-bonding would introduce some silylene character into the Ru−Si bond. In the ^{29}Si NMR spectrum, the resonances for the silicon center of base-free metal silylene complexes have been observed around 300 ppm.[66,67] Thus, even a small amount of silylene character due to d(Ru)−σ*(Si−Cl) π-back-bonding should dramatically shift downfield the observed δ(^{29}Si) for monochlorosilyl and dichlorosilyl groups compared to the δ(^{29}Si) of the "non-chlorosilyl" groups. This is nicely illustrated in Figure 3, where, in general, δ(^{29}Si) for the dichlorosilyl class is more downfield than the δ(^{29}Si) for the monochlorosilyl class, which is more downfield than the δ(^{29}Si) for the "non-chlorosilyl" class. The most dramatic evidence for the presence of d(Ru)−σ*(Si−Cl) π-back-bonding in the ruthenium silicon bond comes from examining the δ(^{29}Si) for complexes with nearly the same $\sum\chi_i$ value. The "non-chlorosilyl"/monochlorosilyl pairs **7** (SiH_3, $\sum\chi_i$ = 24.9)/**5** (SiMeHCl, $\sum\chi_i$ = 25.7) and **8** ($SiMeH_2$, $\sum\chi_i$ = 19.2)/**6** ($SiMe_2Cl$, $\sum\chi_i$ = 20.0) are separated, $\Delta\delta$(^{29}Si), by 114 and 101 ppm, respectively, and suggest the presence of significant silylene character at silicon. The silylene character at silicon increases even more when a second chloride is added, as is evident in the monochlorosilyl/dichlorosilyl pair **3** (SiH_2Cl, $\sum\chi_i$ = 31.4)/**4** ($SiMeCl_2$, $\sum\chi_i$ = 32.2) with $\Delta\delta$(^{29}Si) = 56 ppm. It is interesting to note the smaller $\Delta\delta$(^{29}Si) due to the second chloride on silicon and that a third chloride on silicon does not generate a new silyl class.

Summary

The first series of transition metal silyl complexes, $Cp(PMe_3)_2RuSiR_3$, which contain all possible combinations of H, Cl, or Me groups on silicon has been prepared. The nature of the subsitiuents on silicon greatly effect the spectroscopic properties of these silyl complexes. NMR coupling constants, $^2J_{SiP}$ and $^1J_{SiH}$, and Si−H stretching frequencies increase in magnitude as the electron-withdrawing ability of the substituents on silicon increases, consistent with Bent's rule. However, examination of ^{29}Si, ^{1}H(SiH), and ^{13}C(SiMe) chemical shifts indicates that the silyl groups are differentiated into three different classes: a dichlorosilyl class ($SiCl_2R$), a monochlorosilyl class ($SiClR_2$), and a "non-chlorosilyl" class (SiR_3). This silyl group classification is due to π-back-bonding between the filled HOMO and SHOMO orbitals of the ruthenium moiety and the empty σ* orbitals of the silicon−chlorine bonds.

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 glovebox.[68] ^{1}H NMR (250 MHz), ^{13}C{^{1}H} NMR (62.9 MHz), and ^{31}P{^{1}H} NMR (101.3 MHz) spectra were recorded on a Brüker AC-250 spectrometer. ^{29}Si DEPT NMR (79.5 MHz) spectra were recorded on a Varian VXR 400S spectrometer. The PMe_3 resonances in these compounds did not appear as a simple first-order pattern in the ^{1}H NMR, but as a $A_9XX'A'_9$ pattern, the appearance of which was a "filled-in-doublet" (fd) with the separation of the outer lines $N = {}^2J_{PH} + {}^4J_{PH}$.[69,70] Likewise, in the ^{13}C{^{1}H} NMR, the PMe_3 resonances appeared as a virtual triplet (vt) with the separation of the outer lines $N = {}^1J_{PC} + {}^3J_{PC}$.[69,70] The ^{1}H chemical shifts were referenced to the residual proton peak of the solvent $CDHCl_2$ (5.32 ppm). The ^{13}C chemical shifts were referenced to the central peak of CD_2Cl_2 (53.8 ppm). The ^{29}Si chemical shifts were referenced to external $SiMe_4$ (0.00 ppm). The ^{31}P chemical shifts were referenced to external H_3PO_4 (85%, 0.00 ppm). IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. The multinuclear NMR and IR data are summarized in Table 1. Electron-impact mass spectra were obtained with a Hewlett-Packard 5988A GC−MS instrument. Elemental analyses were carried out by Oneida Research Services (Whitesboro, NY). Mass spectrum and elemental analysis data are summarized in Table 2.

Materials. $Cp(PMe_3)_2RuH$[38] was prepared by the literature method. $AlMe_3$ (2 M in toluene, Aldrich) was used as received. Chlorosilanes were stored over CaH_2 and vacuum transferred immediately prior to use. Anhydrous diethyl ether and hexanes were stored over $[Cp_2TiCl]_2ZnCl_2$[71] and vacuum transferred immediately prior to use. Dichloromethane was distilled from and stored over CaH_2 and vacuum transferred immediately prior to use. Dichloromethane-d_2 was dried over P_2O_5 and stored over CaH_2.

$Cp(PMe_3)_2RuSiR_2Cl$ [SiR_2Cl = $SiCl_3$ (1), $SiHCl_2$ (2), SiH_2Cl (3)]. These ruthenium silyl complexes were prepared by the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes in Et_2O. In a typical reaction, excess H_2SiCl_2 (0.53 mmol) was added by vacuum transfer to a cold (−78 °C) solution of $Cp(PMe_3)_2$-RuH (225 mg, 0.70 mmol) in Et_2O. The precipitate that formed was isolated by filtration, washed with hexanes, and dried under vacuum to afford $[Cp(PMe_3)_2RuH_2]Cl$ as a white solid in 104% yield (130 mg). The filtrate was evaporated to dryness

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(71) Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2192−2199.

to give **3** as a yellow solid in 81% yield (110 mg). Isolated yields for ruthenium silyl complexes **1**−**3** were in the 80−90% range.

$Cp(PMe_3)_2RuSiRMeCl$ [SiRMeCl = $SiMeCl_2$ (4), $SiMeHCl$ (5), $SiMe_2Cl$ (6)]. These ruthenium silyl complexes were prepared by the reaction of $Cp(PMe_3)_2RuH$ with chloromethylsilanes in CH_2Cl_2, since the reactions of $Cp(PMe_3)_2RuH$ with these chloromethylsilanes in Et_2O were slow and incomplete. Excess chloromethylsilane (∼1 equiv) was added by vacuum transfer to a solution of $Cp(PMe_3)_2RuH$ in CH_2Cl_2 cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction volatiles were removed under vacuum. The reaction residue was extracted with hexane and the hexane solution filtered through a glass frit. Extraction was continued until the hexane extracts were colorless. The white solid that remained was vacuum-dried to give $[Cp(PMe_3)_2RuH_2]Cl$ in >90% yields. The hexane extracts were combined and evaporated to dryness to give the corresponding silyl complexes **4**−**6** as yellow air- and water-sensitive solids in 60−85% yields.

$Cp(PMe_3)_2RuSiR_2H$ and Chlorosilanes with NEt_3. Ruthenium silyl complexes **1**, **5**, and **6** were prepared by the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes in CH_2Cl_2 in the presence of excess NEt_3. In a typical reaction, excess $MeSiHCl_2$ (1.4 equiv) was added by vacuum transfer to a solution of $Cp(PMe_3)_2RuH$ (340 mg, 1.07 mmol) and NEt_3 (0.75 mL, ∼5 equv) in CH_2Cl_2 (25 mL). The reaction mixture was stirred at room temperature for 1−2 h. The reaction volatiles were removed under vacuum. The reaction residue was extracted with Et_2O/hexane (1:1), and the extract solution was filtered through a Celite plug to remove the insoluble $[HNEt_3]Cl$. The filtrate solution was evaporated to dryness to give silyl complex **5** as light yellow air- and water-sensitive solid (402 mg, 95%). Similar yields were obtained for silyl complexes **1** and **6**.

$Cp(PMe_3)_2RuSiR_2H$ [SiR_2H = SiH_3 (7), $SiMeH_2$ (8), $SiMe_2H$ (9)]. These hydrosilyl ruthenium complexes were prepared from the reaction of $LiAlH_4$ with the corresponding chlorosilyl ruthenium complexes. In a typical reaction, Et_2O (15 mL) was added by vacuum transfer to a flask charged with **6** (585 mg, 1.42 mmol) and $LiAlH_4$ (60 mg, 1.58 mmol). The reaction mixture was stirred overnight at room temperature under an Ar atmosphere. Removal of the volatiles under vacuum gave a gray residue, which was extracted with hexanes (2 × 15 mL). The hexane extracts were filtered through Celite and evaporated to dryness to give **9** as a yellow solid (478 mg, 89%). Complex **8** was prepared in a similar manner from the reaction of either **4** or **5** with $LiAlH_4$ in Et_2O. The reaction of **1**, **2**, or **3** with $LiAlH_4$ in Et_2O was used to prepare **7**. Typical yields of hydrosilylruthenium complexes **7**−**9** were in the 80−90% range.

$Cp(PMe_3)_2RuSiMe_3$ (10). $AlMe_3$ (0.6 mL, 1.2 mmol) was added by syringe to a cold (−78 °C) slurry of **6** (505 mg, 1.2 mmol) in toluene (25 mL) under argon. Upon addition of the $AlMe_3$, complex **6** dissolved to give a light green solution, which turned yellow as the solution warmed to room temperature. After 30 min, the volatiles were removed under vacuum to give a yellow residue, which was extracted with hexanes (2 × 10 mL). The hexane extracts were filtered through Celite and evaporated to dryness. The residue was sublimed at 100 °C (<0.03 mmHg) to afford **10** as a tan solid in 86% yield (414 mg). Resublimation (80 °C, <0.03 mmHg) of the tan solid gave **10** as an analytically pure, yellow-orange solid (378 mg, 79%).

Structure Determination of $Cp(PMe_3)_2RuSiCl_3$ (1). Crystals of **1** suitable for X-ray diffraction analysis were grown in a sealed glass tube by slowly cooling a saturated toluene/hexanes solution of **1** from 80 °C to room temperature. Intensity data were collected on a Syntex $P2_1$ diffractometer using Mo Kα (λ = 0.710 73 Å) radiation. The structure was solved using a combination of direct methods and difference Fourier syntheses (SHELXTL Plus)[72] and was refined on $|F_o^2|$ using full-matrix least-squares. All hydrogen atoms were placed in calculated positions and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Refinement of 163 parameters against all 4255 unique data (R_{int} = 3.32%) with one restraint yielded an R index, wR2, of 11.19% (R1 = 4.76% for $I > 2\sigma(I)$) with a goodness of fit of 1.193. Crystallographic data and refinement parameters are listed in Table 5.

Table 5. Crystal Data, Data Collection, and Refinement Parameters for $Cp(PMe_3)_2RuSiCl_3$ (1)

empirical formula	$C_{11}H_{23}Cl_3P_2RuSi$
fw	452.74
cryst syst	monoclinic
space group	$P2_1$
a (Å)	8.455(3)
b (Å)	8.820(3)
c (Å)	12.436(4)
β (deg)	90.35(3)
V (Å^3)	927.4(6)
Z	2
d_{calcd} (Mg m^{-3})	1.621
radiation, λ (Å)	graphite monochromator Mo Kα, 0.710 73
μ, abs coeff (mm^{-1})	1.498
cryst dimens (mm)	0.20 × 0.20 × 0.20
temp (K)	141(2)
$F(000)$	456
2Θ range for data collection (deg)	4.82−55.00
index ranges	$-1 \le h \le 10$, $-11 \le k \le 11$, $-16 \le l \le 16$
no. of reflns collected	5104
no. of ind reflns	4255 (R_{int} = 0.0332)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4255/1/163
goodness-of-fit on F^2 [a]	1.193
final R indices [$I > 2\sigma(I)$][b,c]	R1 = 0.0476, wR2 = 0.1094
R indices (all data)[b,c]	R1 = 0.0536, wR2 = 0.1119
absolute struct param	0.01(6)
largest diff peak and hole (e Å^{-3})	0.929 and −1.292

[a] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$. The goodness of fit is based on F^2 where n = number of data and p = number of parameters refined. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. Conventional R factors are calculated using the observed criterion. This criterion is irrelevant to the choice of reflections used in the refinement. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. Weighted R-factors are based on F^2 and are statistically about twice as large as those based on F.

Recovery of the $Cp(PMe_3)_2Ru$ Moiety. The $Cp(PMe_3)_2Ru$ moiety can be recovered from ruthenium silyl complexes **1**−**10** or other waste materials (failed reactions, decomposed samples, NMR samples, etc.) by the following method. MeOH was added by vacuum transfer to a flask charged with $Cp(PMe_3)_2Ru$ containing material and equipped with a reflux condenser. A large excess of Na metal was added to the MeOH solution. The mixture was heated to reflux for 3 h, and the reaction 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. Sublimation (80 °C, <0.03 mmHg) of the resulting mixture afforded a yellow-orange waxy solid, which was a mixture of $Cp(PMe_3)_2RuH$, $Cp(PMe_3)_2RuSi(OMe)_3$, and/or $Cp(PMe_3)_2RuSiRR'R''$ (R, R′, R″ = H, Me, and/or OMe); the distribution of ruthenium-containing species depended on the initial composition of the original $Cp(PMe_3)_2Ru$ waste material. The sublimate was dissolved in Et_2O, and triflic acid (TfOH) was added dropwise until no more white precipitate formed upon addition of TfOH. The precipitate was isolated by filtration, washed with Et_2O, and dried under vacuum to give the ruthenium dihydride $[Cp(PMe_3)_2RuH_2]OTf$[38] as a white solid. $[Cp(PMe_3)_2RuH_2]OTf$ was then reacted with NaOMe (8 equiv) in refluxing MeOH for 2 h. The volatiles were removed

(72) *SHELXTL PLUS Software Package for the Determination of Crystal Structures, Version 5.0*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.

under vacuum, and the residue was extracted with hexanes until the extracts were colorless. The hexane extracts were filtered through Celite and evaporated to dryness. Sublimation of the residue (60 °C, <0.03 mmHg) afforded $Cp(PMe_3)_2RuH$[38] as a yellow, air-sensitive solid in >80% yield (based on $[Cp(PMe_3)_2RuH_2]OTf$).

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Supporting Information Available: Tables of crystal data, collection, and refinement parameters, positional and anisotropic displacement parameters, and interatomic distances and angles for $Cp(PMe_3)_2RuSiCl_3$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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