Notes

The Chloride Effect: Structural Dependence of Ruthenium Silyl Complexes on Phosphorus and Silicon Substituents

Samuel T. N. Freeman,† Jeffrey L. Petersen,‡ and Fredrick R. Lemke*,†

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, and Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

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Summary: The structures for a series of $Cp(PR_3)_2RuSiX_3$ {PR_3 = PMe_3, SiX_3 = $SiCl_3$, $SiMeCl_2$, $SiPhCl_2$; PR_3 = PMe_2Ph, SiX_3 = $SiCl_3$} complexes were determined and compared. The Ru−Si and Si−Cl distances in these complexes increased when Cl was replaced with Me or Ph groups and correlated with the observed spectroscopic properties of these complexes. The structural variations were explained by d(Ru)−σ(Si−Cl) π-back-bonding interactions.*

Introduction

Metal-silicon compounds have generated much interest in the past decade[1−4] owing to their intermediacy in reactions such as hydrosilylation[5,6] and dehydrogenative silylation.[7−9] Consequently, special attention has been given to the influence of transition metal fragments on the bonding and reactivity of silicon atoms. Previously, we had reported the effect of different silicon and phosphorus substituents on the spectroscopic properties for a series of ruthenium silyl compounds of the type $Cp(PR_3)_2RuSiX_3$.[10,11] Our studies indicated that the Ru−Si bond strengthened as the substituents on silicon became more electron-withdrawing (as evidenced by an increase in $^2J_{SiP}$, Figure 1 top) but was unaffected by changes in the phosphine ligand. Also, we observed that the ruthenium silyl groups were differentiated into three classes (a dichlorosilyl, a monochlorosilyl, and a non-chlorosilyl class; Figure 1 bottom); these classes were attributed to varying degrees of d(Ru)−σ*(Si−Cl) π-back-bonding.

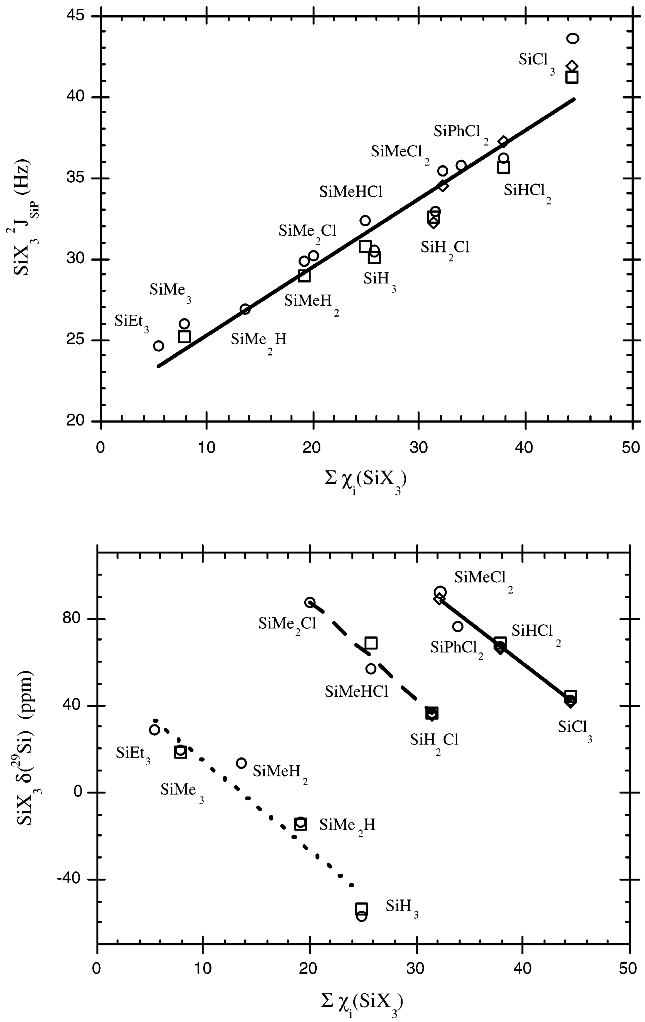

Figure 1. Top: $^2J_{SiP}$ (Hz) vs $\Sigma\chi_i(SiX_3)$ for ruthenium silyl complexes of the type $Cp(PR_3)_2RuSiX_3$ {PR_3 = PMe_3 (○), PMe_2Ph (□), $PMePh_2$ (◇)}. Bottom: ^{29}Si NMR chemical shift of the silyl groups vs $\Sigma\chi_i(SiX_3)$ for ruthenium silyl complexes of the type $Cp(PR_3)_2RuSiX_3$ {PR_3 = PMe_3 (○), PMe_2Ph (□), $PMePh_2$ (◇)} showing the three silyl classes: dichlorosilyl (solid line), monochlorosilyl (dashed line), and non-chlorosilyl (dotted line).

† Ohio University.
‡ West Virginia University, crystal structure determinations.

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $Cp(PR_3)_2RuSiX_3$

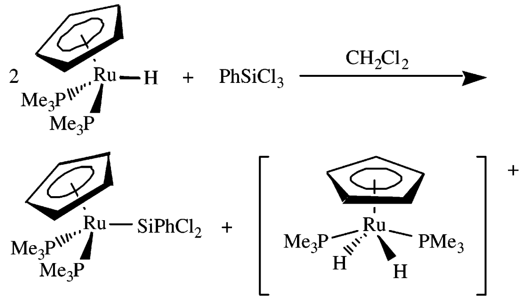
	2	1[a]	3	4
PR_3	PMe_2Ph	PMe_3	PMe_3	PMe_3
SiX_3	$SiCl_3$	$SiCl_3$	$SiMeCl_2$	$SiPhCl_2$
Ru−Si	2.2811(11)	2.265(2)	2.294(2)	2.31019(9)
Ru−P(1)	2.2912(10)	2.273(2)	2.276(2)	2.2712(9)
Ru−P(2)	2.2797(10)	2.280(2)	2.261(2)	2.2754(8)
Ru−Cnt[b]	1.903	1.887	1.917	1.910
Si−Cl(1)	2.124(2)	2.122(3)	2.145(3)	2.1545(12)
Si−Cl(2)	2.119(2)	2.114(3)	2.153(3)	2.1335(11)
Si−Z[c]	2.1130(14)	2.121(3)	1.905(7)	1.904(3)
P(1)−Ru−Si	91.09(4)	92.60(7)	93.22(7)	91.02(4)
P(2)−Ru−Si	92.67(4)	93.00(7)	94.42(8)	93.72(3)
Cnt−Ru−Si[b]	120.0	121.2	119.1	122.3
P(1)−Ru−P(2)	97.64(4)	95.80(7)	95.42(8)	95.27(3)
Cnt−Ru−P (av)[b]	123.6	123.2	123.6	123.1
Ru−Si−Cl(1)	117.53(5)	116.8(1)	114.92(10)	112.87(4)
Ru−Si−Cl(2)	114.89(6)	115.0(1)	122.22(10)	121.84(4)
Ru−Si−Z[c]	125.20(6)	125.6(1)	119.2(3)	120.35(9)
Cl(1)−Si−Cl(2)	98.93(6)	99.0(1)	97.96(13)	97.39(5)
Cl(2)−Si−Z[c]	98.21(7)	98.8(1)	99.0(3)	99.74(9)
Cl(1)−Si−Z[c]	97.30(6)	96.9(1)	99.1(3)	100.29(9)

[a] Data taken from ref 10. [b] Cnt = the centroid of the cyclopentadienyl ring. [c] Z represents either chlorine or a carbon bonded to silicon.

Our spectroscopic studies indicated that the ruthenium silicon interaction was more dependent on the substituents on silicon than on the substituents on phosphorus. A major question concerning these $Cp(PR_3)_2$-$RuSiX_3$ complexes still remained. How were the spectroscopically observed substituent effects manifested in the structures of $Cp(PR_3)_2RuSiX_3$? To address this question, we have determined the structures of several $Cp(PR_3)_2RuSiX_3$ {SiX_3 = $SiCl_3$, PR_3 = PMe_3 (**1**), PMe_2Ph (**2**); PR_3 = PMe_3, SiX_3 = $SiMeCl_2$ (**3**), $SiPhCl_2$ (**4**)} complexes. A comparison between the structural and spectroscopic trends of **1**−**4** is reported herein. Prior to this study, only the structure of $Cp(PMe_3)_2RuSiCl_3$ (**1**) had been reported;[10] selected interatomic distances and angles for **1** are listed in Table 1.

Results and Discussion

Synthesis of Ruthenium Silyl Complexes. The complexes $Cp(PMe_2Ph)_2RuSiCl_3$ (**2**)[11] and $Cp(PMe_3)_2$-$RuSiMeCl_2$ (**3**)[10,12] were prepared by published methods. $Cp(PMe_3)_2RuSiPhCl_2$ (**4**) was prepared by the direct reaction of $Cp(PMe_3)_2RuH$ with $PhSiCl_3$ in CH_2Cl_2 (eq 1); the cationic dihydride $[Cp(PMe_3)_2RuH_2]Cl$ was a byproduct of this reaction. Complex **4** was obtained in good yields as a yellow solid and exhibited NMR resonances (^{1}H, ^{29}Si, and ^{31}P) characteristic of silyl complexes containing the $Cp(PR_3)_2Ru$ half-sandwich moiety.[10,11]



(1)

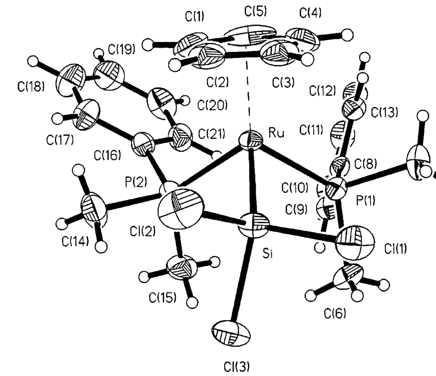


Figure 2. Perspective view of the molecular structure of $Cp(PMe_2Ph)_2RuSiCl_3$ (**2**) with atom labels provided for all unique non-hydrogen atoms.

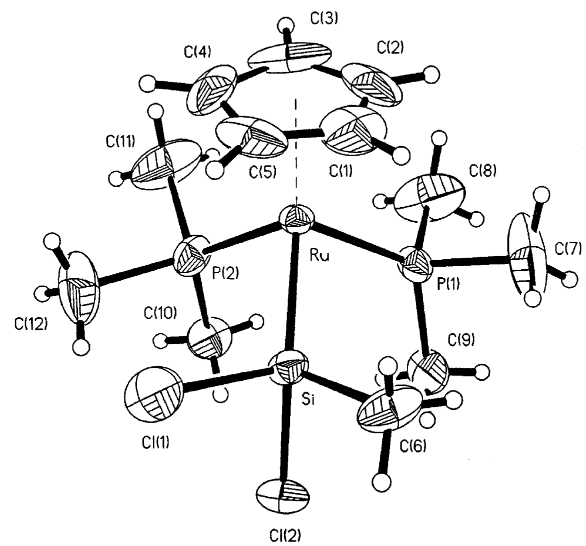


Figure 3. Perspective view of the molecular structure of $Cp(PMe_3)_2RuSiMeCl_2$ (**3**) with atom labels provided for all unique non-hydrogen atoms.

Structures of $Cp(PR_3)_2RuSiX_3$. The crystal structures of **2**−**4** were determined by X-ray diffraction at 295 K, and selected interatomic distances and angles are listed in Table 1. The molecular structures of **2**−**4** (Figures 2−4, respectively) adopted a three-legged "piano-stool" geometry around ruthenium with "legs" composed of one silyl group and two phosphine groups.[13] The Ru−Si distances of 2.28−2.31 Å were consistent with a single bond and fall on the low end of the range (2.27−2.51 Å) observed for related d^6 ruthenium silyl complexes.[1,2,10,14−16] The Si−Cl distances of 2.11−2.15 Å were considerably longer than the Si−Cl distance in

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(13) A preliminary structural analysis of $Cp(PMePh_2)_2RuSiCl_3$ showed that this compound crystallizes in a C-centered monoclinic crystal lattice with dimensions a = 15.168(1) Å, b = 12.121(1) Å, c = 17.369(1) Å, and β = 106.358(1)°. The X-ray diffraction data indicated either that the entire molecule was disordered about a crystallographic 2-fold axis or that the lattice dimensions were extended along one direction. Efforts to refine the molecular structure in the centrosymmetric space group $C2/c$ with four pairs of half-molecules with each pair symmetrically disposed about a different crystallographic 2-fold axis were sufficient to verify the atom connectivity. A perspective view of the molecular structure of $Cp(PMePh_2)_2RuSiCl_3$ showed that the Me substituent of each diphenylmethylphosphine ligand was directed away from the cyclopentadienyl ligand. The overall structure was consistent with that expected for a three-legged piano stool, with the three legs consisting of two $PMePh_2$ groups and one $SiCl_3$ group.

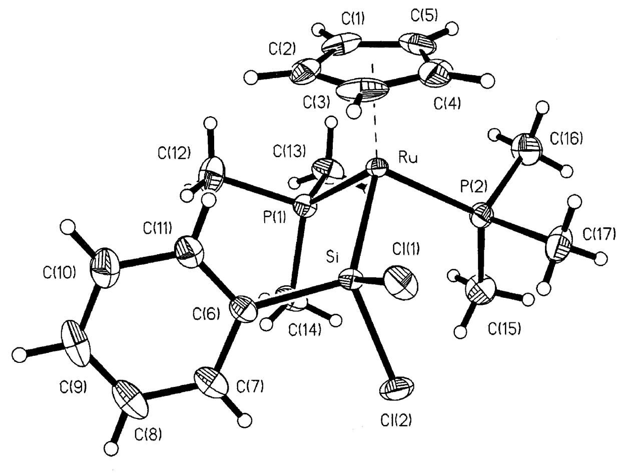

Figure 4. Perspective view of the molecular structure of $Cp(PMe_3)_2RuSiPhCl_2$ (**4**) with atom labels provided for all unique non-hydrogen atoms.

free polychlorosilanes (2.02 Å)[17] and other group 8 trichlorosilyl complexes (2.03−2.09 Å).[18−25]

Complexes **1**−**4** adopted a staggered conformation about the Ru−Si bond with the cyclopentadienyl and a chloride in an anti relationship (average cyclopentadienyl centroid−Ru−Si−Cl dihedral angle = 166.1 ± 9.1°). The silyl groups had a distorted tetrahedral geometry with an average Cl−Si−Z (Z = Cl, C) angle of 98.6 ± 0.6° and an average Ru−Si−Z angle of 118.9 ± 2.4°. The Ru−Si−Cl angles (123.7 ± 1.4° average) anti to the Cp group were significantly larger than the non-anti Ru−Si−Z angles (116.5 ± 1.7° average). In related three-legged piano-stool ruthenium silyl complexes, the Ru−Si−Z angle for substituents anti to a Cp or benzene group have also been observed to be larger (generally ≥ 10°) than the Ru−Si−Z angles of the other substituents on silicon: $Cp(PMe_3)_2RuSiCl_2Cp^*$ [Ru−Si−Cl(anti) 119.9° vs Ru−Si−Cl 109.2°],[14] $Cp^*(PMe_3)_2RuSiPh_2H$ [Ru−Si−H(anti) 112.9° vs Ru−Si−Ph 98.8° (av)],[26] $Cp^*(PMe_3)_2RuSiPh_2OTf$ [Ru−Si−OTf(anti) 118.2° vs Ru−Si−Ph 96.9° (av)],[16] $(C_6H_6)(PPh_3)Ru(SiX_3)_2$ (SiX_3 = $SiCl_3$, $SiMeCl_2$, $SiMe_3$) [Ru−Si−X(anti, X = Cl, C) 125.2° (av) vs Ru−Si−X 113.4° (av)].[27]

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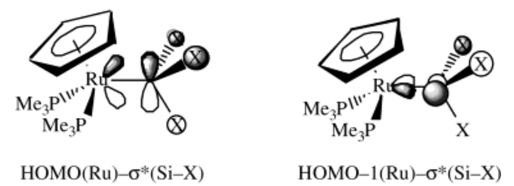

Figure 5. Interaction of the $Cp(PMe_3)_2Ru$ fragment HOMO and HOMO-1 with linear combinations of Si−X σ* orbitals.

Changing the phosphine from PMe_3 to PMe_2Ph had structurally very little effect. The bond distances and angles around ruthenium and silicon in **1** and **2** were essentially the same; the only exception was a slight lengthening of the Ru−Si distance from 2.27 Å in **1** to 2.28 Å in **2**. This similarity in structural parameters for **1** and **2** was consistent with the little to no phosphine dependence observed in the spectroscopic properties of these complexes (Figure 1).

On the other hand, changes in the substituents on silicon had more of an effect on the bond distances and angles around ruthenium and silicon. A lengthening of the Ru−Si distance was observed when an electronegative Cl (Ru−Si 2.265 Å in **1**) was replaced with less electronegative Me (Ru−Si 2.294 Å in **3**) and Ph (Ru−Si 2.310 Å in **4**) groups. This lengthening of the Ru−Si distances correlated with a decrease in $^2J_{SiP}$ for **1**, **3**, and **4** (Figure 1, top). The Ru−Si distance in **4** was longer than expected probably due to the larger steric demand of $SiPhCl_2$ compared to $SiMeCl_2$.

The long Si−Cl distances in **1**−**4** (range 2.11−2.15 Å) were attributable to d(Ru)−σ*(Si−X) π-back-bonding between the $Cp(PMe_3)_2Ru$ and SiX_3 groups. Linear combinations of the Si−X (X = Cl, Ph, Me) σ* orbitals of the silyl group gave rise to an a_1 and e set, assuming localized C_{3v} symmetry at silicon. The HOMO and HOMO-1 of the $Cp(PMe_3)_2Ru$ moiety[28−30] had the correct symmetry to interact with the doubly degenerate e set of Si−X σ* orbitals,[31,32] as shown in Figure 5. The magnitude of the d(Ru)−σ*(Si−X) π-back-bonding interaction depended on the silicon substituents and followed the order Cl ≫ Ph ≈ Me.[25] A ramification of this d(Ru)−σ*(Si−Cl) π-back-bonding interaction was a substantial lengthening of the Si−Cl distances compared to other group 8 trichlorosilyl complexes (range 2.04−2.09 Å).[18−25]

The Si−Cl distances also exhibited a significant dependence with respect to the other substituents on silicon. The average Si−Cl distance in **1** and **2** (2.119 ± 0.004 Å) was shorter than the average Si−Cl distance in **3** and **4** (2.147 ± 0.009 Å). This difference in Si−Cl distances can be attributed to more electron density in the σ*(Si−Cl) orbitals of **3** and **4** compared to the amount of electron density in the σ*(Si−Cl) orbitals of **1** and **2**. If the amount of electron density transferred from ruthenium to silicon by the d(Ru)−σ*(Si−X) π-back-bonding interaction was constant in **1**−**4**, then the

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Si−Cl distances will depend on the number of chlorines on the silicon. Thus, **1** and **2**, with three chlorines on silicon, will have on average less electron density in σ^*(Si−Cl) orbitals and subsequently shorter Si−Cl bonds than **3** and **4**, with only two chlorines on silicon.

Experimental Section

General Considerations. All manipulations of the ruthenium-containing compounds were conducted under an inert atmosphere of argon. The compounds were stored in an M-Braun glovebox, and reactions were carried out using high-vacuum techniques.[33] ^{1}H NMR (250 MHz), ^{13}C{^{1}H} NMR (62.9 MHz), and ^{31}P{^{1}H} NMR (101.3 MHz) spectra were obtained using a Bruker 250 MHz spectrometer. ^{29}Si DEPT NMR (79.5 MHz) spectra were obtained using a Varian VXR 400S spectrometer. All NMR data were obtained in CD_2Cl_2. ^{1}H NMR data were referenced to the residual proton signal of the solvent at 5.32 ppm. ^{31}P NMR data were externally referenced (0.00 ppm) to a sealed capillary containing H_3PO_4 (85%) in a NMR tube containing CD_2Cl_2. ^{13}C NMR data were referenced to the carbon signal of the CD_2Cl_2 solvent at 53.8 ppm. ^{29}Si NMR data were externally referenced to a CD_2Cl_2 solution of TMS at 0.00 ppm. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

Materials. $Cp(PMe_3)_2RuH$,[34] $Cp(PMe_2Ph)_2RuSiCl_3$ (**2**),[11] $Cp(PMePh_2)_2RuSiCl_3$,[11] and $Cp(PMe_3)_2RuSiMeCl_2$ (**3**)[10] were prepared according to the literature procedure. $PhSiCl_3$ (Gelest) was degassed and stored in the glovebox. Hexanes was distilled from K/benzophenone and stored over $[Cp_2TiCl]_2ZnCl_2$.[35] CH_2Cl_2 and CD_2Cl_2 (Cambridge Isotope Labs) were dried over CaH_2. CH_2Cl_2, CD_2Cl_2, and hexanes were degassed and vacuum transferred prior to use.

Crystals of **2** and **4** suitable for X-ray diffraction were grown by liquid diffusion of hexanes into a CH_2Cl_2 solution of the corresponding ruthenium silyl complex at −30 °C.

Preparation of $Cp(PMe_3)_2RuSiPhCl_2$ (4). Compound **4** was prepared by an adaptation of the literature method.[10] In a typical reaction, $PhSiCl_3$ (0.75 equiv) was added via syringe to a solution of $Cp(PMe_3)_2RuH$ (100 mg, 0.313 mmol) in CH_2Cl_2 (∼15 mL). The reaction mixture was allowed to stir at ambient temperature for 1 h. The volume was reduced by one-half in vacuo. Hexanes were added to the flask to initiate precipitation of $[Cp(PMe_3)_2RuH_2]Cl$. The suspension was filtered, and the yellow filtrate was dried in vacuo to give **4** as a yellow residue (66 mg, 85%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.74 (m, 2H, SiPh), 7.33 (m, 3H, SiPh) 4.66 (s, 5H, Cp), 1.49 (fd, N = 8.7 Hz, 18H, PMe_3). ^{29}Si{^{1}H} NMR (79.5 MHz, CD_2Cl_2): δ 76.82 (t, J_{PSi} = 35.8 Hz). ^{31}P{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 10.20. Anal. Calcd for $C_{17}H_{28}P_2Cl_2RuSi$ (**4**): C, 41.30; H, 5.71. Found: C, 41.48; H, 5.54.

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Supporting Information Available: Tables of crystal data, data collection and refinement parameters, interatomic distances, and interatomic angles for **2**, **3**, and **4**. Full crystallographic data in CIF format for **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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