4776 *Organometallics* **2002,** *21,* 4776−4784

Effect (or Lack Thereof) of Ancillary Groups on the Preparation and Spectroscopic Properties of Ruthenium Silyl Complexes Containing the $Cp(PR_3)_2Ru$ Moiety

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The preparation and characterization of $Cp(PR_3)_2RuSiX_3$ [$PR_3 = PPhMe_2$, $SiX_3 = SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), SiHMeCl (**4**), SiH_3 (**7**), $SiMeH_2$ (**8**), $SiMe_3$ (**9**); $PR_3 = PPh_2Me$, $SiX_3 = SiCl_3$ (**10**), $SiHCl_2$ (**5**), SiH_2Cl (**6**), $SiMeCl_2$ (**11**)] are described. Ruthenium silyl complexes **1**−**6** are prepared by the reaction of the ruthenium hydrides, $Cp(PR_3)_2RuH$, with the corresponding chlorosilane, $ClSiX_3$; the ruthenium dihydrides $[Cp(PR_3)_2RuH_2]Cl$ were obtained as coproducts. Increasing the steric demand of the phosphine decreased the reactivity of the corresponding ruthenium hydride toward chlorosilanes. Silyl complexes **1**−**4** undergo chloride/hydride exchange with $LiAlH_4$ to give the corresponding ruthenium hydrosilyl complexes $Cp(PPhMe_2)_2RuSiHX_2$ [$SiHX_2 = SiH_3$ (**7**), $SiMeH_2$ (**8**)]. Methylation of **1** with $AlMe_3$ produces $Cp(PPhMe_2)_2RuSiMe_3$ (**9**). Complexes **10** and **11** were prepared by the reaction of $Cp(PPh_2Me)_2RuMe$ with neat hydrosilanes $HSiX_3$ ($SiX_3 = SiCl_3$, $SiMeCl_2$) at 100 °C. The effects of the silicon substituents on the spectroscopic properties of **1**−**11** and the related $Cp(PMe_3)_2RuSiX_3$ complexes were examined as a function of Tolman's electronic parameter (χ_i) for the substituents on silicon. The NMR resonance PR_3 $\delta(^{31}P)$ and the NMR coupling constants, $^1J_{SiH}$ and $^2J_{SiP}$, exhibit a linear relationship with $\sum\chi_i(SiX_3)$. On the other hand, the silyl groups differentiated into three classes, dichlorosilyl, monochlorosilyl, and "non-chlorosilyl", when the NMR resonances SiX_3 $\delta(^{29}Si)$, SiH $\delta(^1H)$, and SiMe $\delta(^{13}C)$ were examined as a function of $\sum\chi_i(SiX_3)$. This "chloro effect" was attributed to Ru−Si silylene character from d(Ru)−σ*(Si−Cl) π-back-bonding interactions. Surprisingly, changing the phosphine attached to ruthenium had no effect on the spectroscopic properties of the silyl group.

Introduction

The bonding of silicon to a transition metal center is an area of considerable interest and attention.[1−4] Metal silicon complexes play key roles in important catalytic processes such as hydrosilylation[5−8] and dehydrogenative silylation.[9−11] Ancillary groups on silicon exhibit a substantial influence on the product distribution in these processes. $RuCl_2(PPh_3)_3$ efficiently catalyzed the hydrosilylation of phenylacetylene with $HSiMeCl_2$, but no hydrosilylation products were observed when the hydrosilane was changed to $HSiEt_3$.[12]

We have been studying the effects of silicon and ruthenium ancillary groups on the formation and properties of ruthenium silicon complexes. Ruthenium alkyl complexes $Cp(PR_3)_2RuR'$ (R = Ph, Me; R′ = Me, CH_2SiMe_3) react with various hydrosilanes ($HSiX_3$) to form ruthenium silyl ($Cp(PR_3)_2RuSiX_3$) and ruthenium hydridobis(silyl) ($Cp(PR_3)RuH(SiX_3)_2$) complexes.[13,14] The formation of ruthenium silyl complexes was favored by electron-deficient hydrosilanes; PMe_3 coordinated to ruthenium center also favored the formation of ruthenium silyl complexes. Silicon ancillary groups effected the relative reactivity of hydrosilanes toward $Cp(PMe_3)_2RuCH_2SiMe_3$, following the order $HSiCl_3 > HSiMeCl_2 > HSiMe_2Cl \gg HSiEt_3$. Ruthenium silyl complexes $Cp(PMe_3)_2RuSiX_3$ were also prepared from the reaction of the ruthenium hydride complex $Cp(PMe_3)_2RuH$ with a variety of chlorosilanes.[15,16] Electron-deficient chlorosi-

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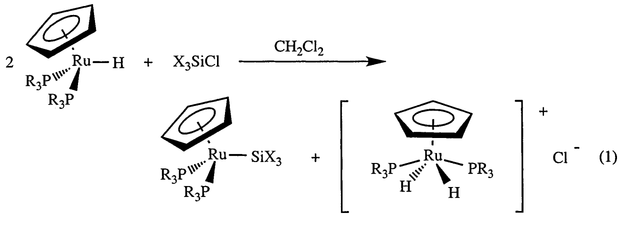
lanes ($SiCl_4$, $HSiCl_3$) were 6 orders of magnitude more reactive toward the ruthenium hydride than more electron-rich chlorosilanes (Me_2SiCl_2). Furthermore, significant silicon ancillary group effects were observed in the spectroscopic properties of these ruthenium silyl complexes.

Herein, we report our continued studies on ancillary group effects in ruthenium silyl complexes $Cp(PMe_3)_2RuSiX_3$. The effect of different phosphines (PMe_2Ph, $PMePh_2$, PPh_3) on the reaction of ruthenium hydrides with chlorosilanes and the properties of ruthenium silyl complexes is described. Surprisingly, the various phosphines exhibit no effect on the spectroscopic properties of the corresponding silyl complexes $Cp(PR_3)_2RuSiX_3$.

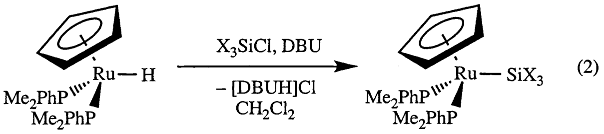
Results

Synthesis of Ruthenium Silyl Complexes. The ruthenium silyl complexes used in this study were prepared by several different methods. One method employed the direct reaction of $Cp(PR_3)_2RuH$ (PR_3 = PPh_2Me, $PPhMe_2$, PPh_3) with the corresponding chlorosilane X_3SiCl to produce a nearly equimolar mixture of $Cp(PR_3)_2RuSiX_3$ and $[Cp(PR_3)_2RuH_2]Cl$ (eq 1). The preparation of a series of ruthenium silyl complexes containing the $Cp(PMe_3)_2Ru$ moiety had been reported using a similar method.[15,16] $Cp(PPhMe_2)_2RuSiX_3$ [SiX_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), $SiHMeCl$ (**4**)] were obtained from the addition of $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and $SiHMeCl_2$ to a yellow solution of $Cp(PPhMe_2)_2RuH$ in CH_2Cl_2; $[Cp(PPhMe_2)_2RuH_2]Cl$ was obtained as a byproduct. No reaction was observed between $Cp(PPhMe_2)_2RuH$ and $SiMeCl_3$, $SiMe_2Cl_2$, or $SiPhCl_3$. Under similar conditions, $Cp(PPh_2Me)_2RuH$ was observed to react only with $SiHCl_3$ and SiH_2Cl_2 to produce $Cp(PPh_2Me)_2RuSiX_3$ [SiX_3 = $SiHCl_2$ (**5**), SiH_2Cl (**6**)] and $[Cp(PPh_2Me)_2RuH_2]Cl$. No reaction was observed between $Cp(PPh_3)_2RuH$ and any of the other chlorosilanes listed above.



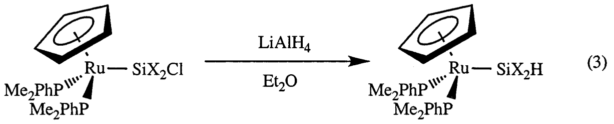
PR_3 = $PPhMe_2$; SiX_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**), $SiMeHCl$ (**4**)
PR_3 = PPh_2Me; SiX_3 = $SiHCl_2$ (**5**), SiH_2Cl (**6**)

In the reaction of $Cp(PR_3)_2RuH$ (PR_3 = $PPhMe_2$, PPh_2Me) with chlorosilanes, the ruthenium dihydrides $[Cp(PR_3)_2RuH_2]Cl$ were sometimes obtained in yields of >100% based on the stoichiometry described in eq 1. These unusual yields of $[Cp(PR_3)_2RuH_2]Cl$ were due to HCl, from the hydrolysis of the chlorosilanes with trace amounts of water, which readily protonated the ruthenium hydrides $Cp(PR_3)_2RuH$. Excessive ruthenium dihydride formation was also reported in the reaction of $Cp(PMe_3)_2RuH$ with chlorosilanes; this problem was overcome by the addition of NEt_3 to the reaction mixture.[16] The addition of NEt_3 to the reaction mixture of $Cp(PR_3)_2RuH$ (PR_3 = $PPhMe_2$, PPh_2Me) with chlorosilanes led to a mixture of ruthenium silyl and other unidentified ruthenium-containing species. When other bases were surveyed (pyridine, $LiN(SiMe_3)_2$, $NHPh_2$, piperidine, pyrazine, 1,8-bis(dimethylamino)naphthalene, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, imidazole, pyrazole, 3,5-dimethylpyrazole, 4-(dimethylamino)pyridine), either a mixture of ruthenium complexes was obtained or the base had no effect on the overall reaction. An exception was DBU (1,8-diazabicyclo[5,4,0]undec-7-ene). The reaction of $Cp(PPhMe_2)_2RuH$ with chlorosilanes in the presence of DBU led to the formation of ruthenium silyl complexes **1**, **2**, and **4** in high yields (>80%) with the added advantage that all of the ruthenium moiety ends up in the silyl complex (eq 2). Of the bases listed above, none were found to be effective and noninterfering in the reaction of $Cp(PPh_2Me)_2RuH$ with chlorosilanes.



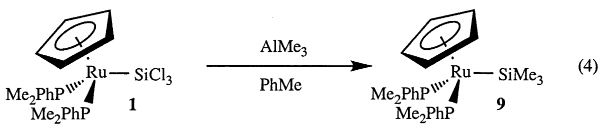
SiX_3 = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), $SiMeHCl$ (**4**)

Other $Cp(PPhMe_2)_2RuSiX_3$ complexes were prepared by derivatization of complexes **1**−**4**. The ruthenium hydrosilyl complexes $Cp(PPhMe_2)_2RuSiX_2H$ [SiX_2H = SiH_3 (**7**), $SiMeH_2$ (**8**)] were prepared by the chloride/hydride exchange between chlorosilyl complexes **1**−**4** and $LiAlH_4$ in Et_2O (eq 3). The trimethylsilyl derivative $Cp(PPhMe_2)_2RuSiMe_3$ (**9**) was obtained from the reaction of **1** with $AlMe_3$ in toluene at room temperature (eq 4). The reaction of complex **4** with $AlMe_3$ led to a complicated mixture of methylsilyl ruthenium complexes. By these methods, complexes **7**−**9** were obtained in good yields (75−85%) as yellow, air-sensitive solids.



SiX_2Cl = $SiCl_3$ (**1**), $SiHCl_2$ (**2**), SiH_2Cl (**3**)
$SiMeHCl$ (**4**)

SiX_2H = SiH_3 (**7**)
$SiMeH_2$ (**8**)



Due to difficulties in the isolation of $Cp(PPh_2Me)_2RuSiX_3$ complexes prepared according to eq 1 (vide infra), additional $Cp(PPh_2Me)_2RuSiX_3$ complexes were obtained by the reaction of a hydrosilane with a ruthenium alkyl complex.[14] $Cp(PPh_2Me)_2RuSiX_3$ [SiX_3 = $SiCl_3$ (**10**), $SiMeCl_2$ (**11**)] were obtained from the reaction of $Cp(PPh_2Me)_2RuMe$, prepared by reacting $Cp(PPh_2Me)_2RuCl$ with MeMgCl in THF, with the corresponding neat hydrosilane $HSiX_3$ at 100 °C (eq 5). The reaction of $Cp(PPh_2Me)_2RuMe$ with $HSiMe_2Cl$ produced a complex mixture of products, with $Cp(PPh_2Me)_2RuH$, $[Cp(PPh_2Me)_2RuH_2]^+$, and $Cp(PPh_2Me)_2RuCl$ being the most prevalent.

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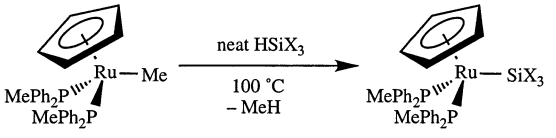
[16] Lemke, F. R.; Galat, K. J.; Youngs, W. J. *Organometallics* **1999**, *18*, 1419−1429.



(5)

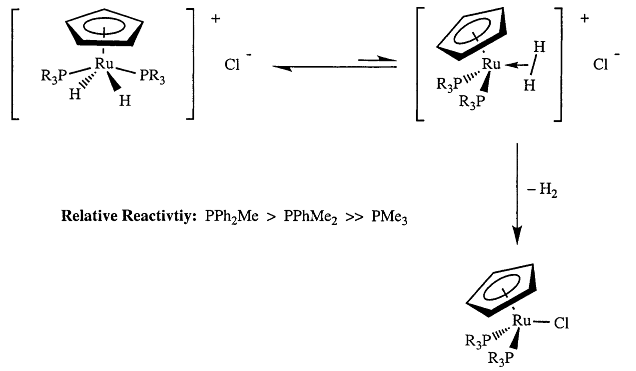
$SiX_3 = SiCl_3$ (**10**), $SiMeCl_2$ (**11**)

Ruthenium Dihydride to Ruthenium Chloride Conversion. The isolation and purification of the $Cp(PPh_2Me)_2RuSiX_3$ complexes prepared according to eq 1 proved to be difficult due to the facile conversion of $[Cp(PPh_2Me)_2RuH_2]Cl$ to $Cp(PPh_2Me)_2RuCl$. Silyl complexes **5** and **6** were always obtained contaminated with the ruthenium chloride $Cp(PPh_2Me)_2RuCl$. In a NMR tube, the reaction of $Cp(PPh_2Me)_2RuH$ with $HSiCl_3$ in CD_2Cl_2 formed a nearly equimolar mixture of silyl complex **5** and the ruthenium dihydride $[Cp(PPh_2Me)_2RuH_2]Cl$. However, as this reaction mixture was monitored by ^1H NMR, the Cp (5.12 ppm) and RuH (−8.43 ppm) resonances of $[Cp(PPh_2Me)_2RuH_2]Cl$ disappeared with the concomitant appearance of the Cp (4.31 ppm) resonance of $Cp(PPh_2Me)_2RuCl$. Also, during this experiment, the solution changed from ruthenium silyl yellow (the ruthenium dihydride is colorless in solution) to ruthenium chloride orange. Similar results were observed for the reaction of $Cp(PPh_2Me)_2RuH$ with H_2SiCl_2.

As described in the previous section, removal of $[Cp(PPh_2Me)_2RuH_2]Cl$ by the addition of a base to the $Cp(PPh_2Me)_2RuH$/chlorosilane reaction mixture was not successful. Stabilization of the $[Cp(PPh_2Me)_2RuH_2]^+$ cation was attempted by metathesis of the chloride with a noncoordinating anion. A variety of sodium salts ($NaBF_4$, $NaBPh_4$, $NaBAr^f_4$ {Ar^f = 3,5-bis(trifluoromethyl)phenyl}) were added to the $Cp(PPh_2Me)_2RuH$/chlorosilane reaction mixture in an attempt to remove the chloride as NaCl. However, this approach was not successful. Finally, a low-yield (<10%) fractional crystallization method was developed (see Experimental Section) for ruthenium silyl **5**. Since the ruthenium silyl and ruthenium chloride complexes have very similar solubility properties, attempts to increase the yield of **5** resulted in significant contamination with ruthenium chloride. Unfortunately, this fractional crystallization method was not applicable for the isolation of **6**.

The conversion of $[Cp(PPhMe_2)_2RuH_2]Cl$ to $Cp(PPhMe_2)_2RuCl$ was also observed, but at a slower rate relative to $[Cp(PPh_2Me)_2RuH_2]Cl$. Over the course of an hour, a colorless solution of $[Cp(PPhMe_2)_2RuH_2]Cl$ (Cp 5.21 ppm, RuH −9.13 ppm) in CD_2Cl_2 converted to the dark orange of $Cp(PPhMe_2)_2RuCl$ (Cp 4.74 ppm), as determined by ^1H NMR spectroscopy. To verify that this conversion was not due to the chlorinated solvent, a similar experiment was run in THF-d_8. Over the course of ~24 h, a white slurry of $[Cp(PPhMe_2)_2RuH_2]Cl$ became a homogeneous, dark orange solution of $Cp(PPhMe_2)_2RuCl$, as determined by ^1H NMR spectroscopy. The isolation of ruthenium silyl complexes **1**−**4** from the reaction of $Cp(PPhMe_2)_2RuH$ with chlorosilanes (eq 1) was complicated by the formation of $Cp(PPhMe_2)_2RuCl$. Working quickly, $[Cp(PPhMe_2)_2RuH_2]Cl$ could be separated from the ruthenium silyl complexes **1**−**4**; however, $Cp(PPhMe_2)_2RuCl$ contamination was common. The addition of DBU (vide supra) to the reaction of $Cp(PPhMe_2)_2RuH$ with chlorosilanes (eq 2) avoided this ruthenium dihydride to ruthenium chloride conversion problem.

Scheme 1



The related $[Cp(PMe_3)_2RuH_2]Cl$ system exhibited little tendency to convert to the ruthenium chloride $Cp(PMe_3)_2RuCl$. In CD_2Cl_2, only a small amount (<5%) of $[Cp(PMe_3)_2RuH_2]Cl$ converted to $Cp(PMe_3)_2RuCl$ after a week at room temperature, as determined by ^1H NMR spectroscopy. However, at 100 °C overnight, a white slurry of $[Cp(PMe_3)_2RuH_2]Cl$ in C_6D_6 was converted to a homogeneous orange solution of $Cp(PMe_3)_2RuCl$ as determined by ^1H NMR spectroscopy.

A mechanism for the ruthenium dihydride to ruthenium chloride conversion is proposed in Scheme 1. The ruthenium dihydrogen complex, in tautomeric equilibrium with the ruthenium dihydride complex, undergoes chloride-assisted loss of dihydrogen to form the ruthenium chloride complex. Wilczewski reported a similar conversion of $[Cp(PPh_3)_2RuH_2]$[sulfonate] to $Cp(PPh_3)_2RuX$ (X = Br, Cl) when reacted with HX.[17] For the ruthenium dihydrides $[Cp(PR_3)_2RuH_2]Cl$ ($PR_3 = PPh_2Me$, $PPhMe_2$), this tautomeric equilibrium lies toward the left since no evidence for the ruthenium dihydrogen complexes is observed by ^1H NMR spectroscopy. However, enough of the ruthenium dihydrogen complex is present for the facile conversion of the ruthenium dihydrides to the ruthenium chlorides. In $[CpL_2RuH_2]^+$ systems, the dihydrogen tautomer was favored by π-acid ligands and less basic phosphines.[18−20] Our experimental results were consistent with this ligand dependence. Replacing methyl phosphines with phenyl phosphines favored the formation of the dihydrogen tautomer and was consistent with the relative reactivity described in Scheme 1.

Discussion

A. Effect of Ancillary Groups on the Preparation of Ruthenium Silyl Complexes. This study completes an investigation into the effect of ruthenium and silicon ancillary groups on the reaction of ruthenium hydrides with chlorosilanes (eq 6). A previous study observed that the relative reactivity of various chlorosilanes with $Cp(PMe_3)_2RuH$ covered *6 orders of magnitude*, with $HSiCl_3$ being the most reactive and Me_2SiCl_2 the least reactive.[15] This large substituent effect was attributed

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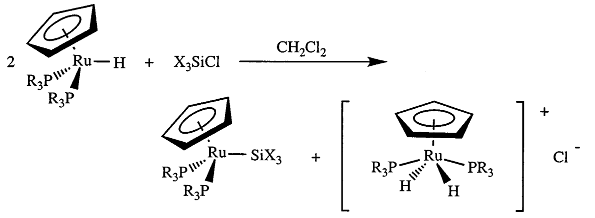
[17] Wilczewski, T. *J. Organomet. Chem.* **1989**, *361*, 219−229.

[18] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

[19] Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

[20] Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171.

to the electronic nature of the chlorosilane, with the electron-deficient chlorosilanes ($SiCl_4$, $HSiCl_3$) exhibiting the greatest reactivity toward $Cp(PMe_3)_2RuH$. Thus, the reaction of various chlorosilanes with a particular ruthenium hydride complex was dictated by the electronic nature of the substituents on silicon.



(6)

PR_3	SiX_3
PMe_3	$SiCl_3$, $SiHCl_2$, SiH_2Cl, $SiMeCl_2$, $SiMeHCl$, $SiMe_2Cl$
PMe_2Ph	$SiCl_3$, $SiHCl_2$, SiH_2Cl, $SiMeHCl$
$PMePh_2$	$SiHCl_2$, SiH_2Cl
PPh_3	N.R.

Changing the phosphines on ruthenium also had a pronounced effect on the reactivity of ruthenium hydrides with chlorosilanes (eq 6). A decrease in ruthenium hydride reactivity was observed as PMe_3 was replaced with phenyl-containing phosphines. The number of chlorosilanes that reacted with a ruthenium hydride decreased with increasing phenyl substitution on phosphorus, to the point that no reaction was observed between $Cp(PPh_3)_2RuH$ and any chlorosilane. This "phosphine effect" could be attributed to either electronics, PMe_3 being replaced with less basic phenyl phosphines, or sterics, small PMe_3 being replaced with bulkier phenyl phosphines. On the basis of the spectroscopic trends described in the next section, the "phosphine effect" can be attributed to the change in sterics around ruthenium and not a change in the electronics of the ruthenium hydride.

B. Spectroscopic Trends. The previously reported series of ruthenium silyl complexes $Cp(PMe_3)_2RuSiX_3$ ($SiX_3 = SiCl_3$, $SiHCl_2$, SiH_2Cl, SiH_3, $SiMeCl_2$, $SiMeHCl$, $SiMe_2Cl$, $SiMeH_2$, $SiMe_2H$, $SiMe_3$) were evaluated to determine the effect silicon substituents had on the spectroscopic properties of these complexes.[16] Complexes **1**−**11**, prepared in this study, offer an opportunity to evaluate how changing the phosphine ancillary groups on ruthenium influences the spectroscopic properties of $Cp(PR_3)_2RuSiX_3$ complexes.

The spectroscopic properties of the various ruthenium silyl complexes were evaluated relative to the electronic nature (electron-withdrawing ability) of the silicon substituents. Tolman's electronic parameter, χ_i,[21] was used as a gauge of the electron-withdrawing ability of the substituents on silicon. The summation of Tolman's electronic parameters for the three substituents on silicon, $\sum\chi_i(SiX_3)$, represented the combined electron-withdrawing ability of the substituents on silicon. Larger $\sum\chi_i(SiX_3)$ values corresponded with more electron-withdrawing substituents on silicon.[22] $\sum\chi_i(SiX_3)$ values for the various silyl groups in complexes **1**−**11** are listed in Table 1.

B.1. NMR Chemical Shifts. The substituent effects on the chemical shifts of the NMR active nuclei in the various ruthenium silyl complexes, $Cp(PR_3)_2RuSiX_3$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$; X = Cl, H, Me), were grouped into three classes: silicon, nuclei attached to silicon, and nuclei two or more bonds from silicon. Plots of SiX_3 $\delta(^{29}Si)$, SiH $\delta(^1H)$, and SiMe $\delta(^{13}C)$ as a function of $\sum\chi_i(SiX_3)$ for the various $Cp(PR_3)_2RuSiX_3$ complexes are shown in Figures 1−3. One feature of these plots was that the ruthenium silyl complexes are grouped into three silyl classes: a dichlorosilyl, $SiXCl_2$ (X = Cl, H, Me), class; a monochlorosilyl, SiX_2Cl (X = H and/or Me), class; and a "non-chlorosilyl", SiX_3 (X = H and/or Me), class.[24] Several trends were observed from the plots in Figures 1−3. In Figure 1, the three silyl group classes exhibited an inverse linear relationship with respect to $\sum\chi_i(SiX_3)$ and were nearly parallel to each other. Within each silyl class, an upfield shift in $\delta(^{29}Si)$ was observed when a Me group was replaced with H (increasing $\sum\chi_i(SiX_3)$). In Figures 2 and 3, the SiH and SiMe chemical shifts were arranged in a triangular pattern; these chemical shifts also shifted upfield upon replacement of a Me group with H.

The most striking feature of the plots in Figures 1−3 was that SiX_3 $\delta(^{29}Si)$, SiH $\delta(^1H)$, and SiMe $\delta(^{13}C)$ for the various silyl groups were independent of the substituents on the phosphine. Replacing a Me group for a Ph group on phosphorus had no effect on the chemical shifts of silicon or the nuclei attached to silicon. This implied that the decrease in reactivity of the ruthenium hydrides $Cp(PR_3)_2RuH$ with chlorosilanes (eq 6) with increased Ph phosphine substitution was due to an increase in sterics around ruthenium and was not due to a change in the electronic environment at ruthenium.

The resonances of the PR_3 groups in the ^{31}P NMR spectra for the various $Cp(PR_3)_2RuSiX_3$ complexes did not exhibit a dependence on the number of chlorines present on silicon. A plot of PR_3 $\delta(^{31}P)$ as a function of $\sum\chi_i(SiX_3)$ for the ruthenium silyl complexes can be found in Figure 4. The ^{31}P NMR resonances for the various phosphines exhibited nearly linear but inverse relationships with $\sum\chi_i(SiX_3)$.

B.2. NMR Coupling Constants. Two sets of coupling constants were readily available from the NMR spectroscopic data: $^2J_{SiP}$ and $^1J_{SiH}$. The magnitude of $^2J_{SiP}$ and $^1J_{SiH}$ as a function of $\sum\chi_i(SiX_3)$ are plotted in Figures 5 and 6, respectively. Both coupling constants exhibited a nearly linear relationship with $\sum\chi_i(SiX_3)$. The magnitudes of the coupling constants increased as the electron-withdrawing ability of the substituents on silicon increased, consistent with Bent's rule.[25] The

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(21) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(22) Hammett σ_p or modified Taft $\sigma^*(Si)^{23}$ parameters can also be used as a gauge of 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 $\sigma^*(Si)$ parameters are the same as those observed using Tolman χ_i parameters.

(23) Attridge, C. J. *J. Organomet. Chem.* **1968**, *13*, 259−262.

(24) The ruthenium silyl complexes plotted in Figures 2 and 3 could also be classified using 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. Another set could be based on the number of methyl groups on silicon to give a trimethylsilyl class, a dimethylsilyl class, and a monomethylsilyl class. However, a classification criterion based on the number of chlorines on silicon was used throughout this paper for internal consistency.

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

SiX$_3$	^{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]	$\sum\chi_i$[e]
Cp(PPhMe$_2$)$_2$RuSiX$_3$ Complexes					
SiCl$_3$ (**1**)	7.33 (m, 10H, PPh) 4.60 (s, 5H, Cp) 1.81 (fd, $N = 9.2$ Hz, 6H, PMe$_2$) 1.72 (fd, $N = 8.8$ Hz, 6H, PMe$_2$)	85.01 (s, Cp) 24.28 (vt, $N = 33.5$ Hz, PMe) 19.58 (vt, $N = 33.4$ Hz, PMe)	44.11 (t, $J_{SiP} = 41.2$ Hz)	17.99 (s)	44.4
SiHCl$_2$ (**2**)	7.46 (m, 10H, PPh) 6.39 (t, $J_{PH} = 2.2$ Hz, 1H, SiH) 4.74 (s, 5H, Cp) 1.59 (fd, $N = 8.9$ Hz, 6H, PMe$_2$) 1.51 (fd, $N = 8.5$ Hz, 6H, PMe$_2$)	84.63 (s, Cp) 24.43 (vt, $N = 33.0$ Hz, PMe) 19.73 (vt, $N = 33.0$ Hz, PMe)	68.49 (dt, $J_{SiH} = 204.1$ Hz, $J_{SiP} = 35.6$ Hz)	21.79 (s)	37.9
SiH$_2$Cl (**3**)	7.30 (m, 10H, PPh) 5.43 (t, $J_{PH} = 3.1$ Hz, 2H, SiH) 4.64 (s, 5H, Cp) 1.55 (fd, $N = 9.1$ Hz, 6H, PMe$_2$) 1.51 (fd, $N = 8.8$ Hz, 6H, PMe$_2$)	83.74 (s, Cp) 24.51 (vt, $N = 32.5$ Hz, PMe) 19.88 (vt, $N = 32.5$ Hz, PMe)	36.79 (tt, $J_{SiH} = 174.7$, $J_{SiP} = 32.6$ Hz)	21.91 (s)	31.4
SiHMeCl (**4**)	7.29 (m, 10H, PPh) 5.52 (m, 1H, SiH) 4.67 (s, 5H, Cp) 1.65 (d, $J_{PH} = 4.2$ Hz, 6H, PMe$_2$) 1.62 (d, $J_{PH} = 5.1$ Hz, 6H, PMe$_2$) 0.69 (d, $J_{PH} = 3.9$ Hz, 3H, SiMe)	83.11 (s, Cp) 24.22 (vt, $N = 32.1$ Hz, PMe) 19.52 (vt, $N = 32.1$ Hz, PMe) 12.86 (s, SiMe)	68.4 (dt, $J_{SiH} = 165.1$, $J_{SiP} = 30.1$ Hz)	21.90 (AB quartet)[f]	25.7
SiH$_3$ (**7**)	7.3 (m, 10H, PPh) 4.49 (s, 5H, Cp) 3.28 (t, $J_{PH} = 4.9$ Hz, 3H, SiH$_3$) 1.44 (fd, $N = 8.3$ Hz, 6H, PMe$_2$) 1.39 (fd, $N = 7.8$ Hz, 6H, PMe$_2$)	82.48 (s, Cp) 24.59 (vt, $N = 31.5$ Hz, PMe) 19.95 (vt, $N = 31.6$ Hz, PMe)	−53.87 (qt, $J_{SiH} = 154.6$ Hz, $J_{SiP} = 30.8$ Hz)	22.3 (s)	24.9
SiMeH$_2$ (**8**)	7.31 (m, 10H, PPh) 4.53 (s, 5H, Cp) 3.88 (m, 2H, SiH$_2$) 1.54 (fd, $N = 8.4$ Hz, 6H, PMe$_2$) 1.47 (fd, $N = 8.2$ Hz, 6H, PMe$_2$) 0.29 (t, $J_{HH} = 4.4$ Hz, 3H, SiMe)	82.51 (s, Cp) 24.68 (vt, $N = 31.0$ Hz, PMe) 20.05 (vt, $N = 31.0$ Hz, PMe) 0.19 (s, SiMe)	−14.29 (tt, $J_{SiH} = 142.5$ Hz, $J_{SiP} = 28.9$ Hz)	22.5 (s)	19.2
SiMe$_3$ (**9**)	7.28 (m, 10H, PPh) 4.49 (s, 5H, Cp) 1.59 (fd, $N = 8.0$ Hz, 6H, PMe$_2$) 1.51 (fd, $N = 8.0$ Hz, 6H, PMe$_2$) 0.18 (s, 9H, SiMe$_3$)	83.02 (s, Cp) 26.15 (vt, $N = 29.1$ Hz, PMe) 21.56 (vt, $N = 29.0$ Hz, PMe) 10.98 (s, SiMe)	18.37 (t, $J_{SiP} = 25.2$ Hz)	24.30 (s)	7.8
Cp(PPh$_2$Me)$_2$RuSiX$_3$ Complexes					
SiHCl$_2$ (**5**)	7.25 (m, 20H, PPh$_2$) 6.59 (t, $J_{PH} = 1.8$ Hz, 1H, SiH) 4.71 (s, 5H, Cp) 1.70 (fd, $N = 8.2$ Hz, 6H, PMe)	86.33 (s, Cp) 17.64 (vt, $N = 31.8$ Hz, PMe)	65.80 (dt, $J_{SiH} = 206.3$ Hz, $J_{SiP} = 37.2$ Hz)	35.99 (s)	37.9
SiH$_2$Cl (**6**)	7.30 (m, 20H, PPh$_2$) 4.64 (s, 5H, Cp) 5.54 (t, $J_{PH} = 3.5$ Hz, 2H, SiH) 1.54 (fd, $N = 8.2$ Hz, 6H, PMe)	87.11 (s, Cp) 16.98 (vt, $N = 31.9$ Hz, PMe)	35.54 (tt, $J_{SiH} = 171.1$ Hz, $J_{SiP} = 32.2$ Hz)	38.46 (s)	31.4
SiCl$_3$ (**10**)	7.35 (m, 20H, PPh$_2$) 4.69 (s, 5H, Cp) 2.06 (fd, $N = 8.1$ Hz, 6H, PMe)	85.81 (s, Cp) 19.08 (vt, $N = 31.5$ Hz, PMe)	41.16 (t, $J_{SiP} = 41.9$ Hz)	33.36 (s)	44.4
SiMeCl$_2$ (**11**)	7.34 (m, 20H, PPh$_2$) 4.66 (s, 5H, Cp) 2.02 (fd, $N = 7.9$ Hz, 6H, PMe) 0.61 (s, 3H, SiMe)	84.97 (s, Cp) 21.24 (s, SiMe) 19.61 (vt, $N = 31.1$ Hz, PMe)	89.08 (t, $J_{SiP} = 34.5$ Hz)	35.97 (s)	32.2

[a] At 250 MHz and ambient probe temperature in CD$_2$Cl$_2$ and referenced to residual proton peak (5.32 ppm). The PMe and PMe$_2$ resonances in these complexes appear as a A$_3$XX′A′$_3$ and A$_6$XX′A′$_6$ pattern, respectively, 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$_2$Cl$_2$ and referenced to solvent (53.8 ppm). The PMe and PMe$_2$ resonances 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$_2$Cl$_2$ and referenced to external SiMe$_4$ (0.00 ppm). [d] At 101 MHz and ambient probe temperature in CD$_2$Cl$_2$ and referenced to external H$_3$PO$_4$ (85%, 0.00 ppm). [e] Summation of the Tolman's electronic parameters for the three substituents on silicon: $\chi_i(\mathrm{Cl}) = 14.8$, $\chi_i(\mathrm{H}) = 8.3$, $\chi_i(\mathrm{Me}) = 2.6$. [f] $J_{PP} = 36.6$ Hz.

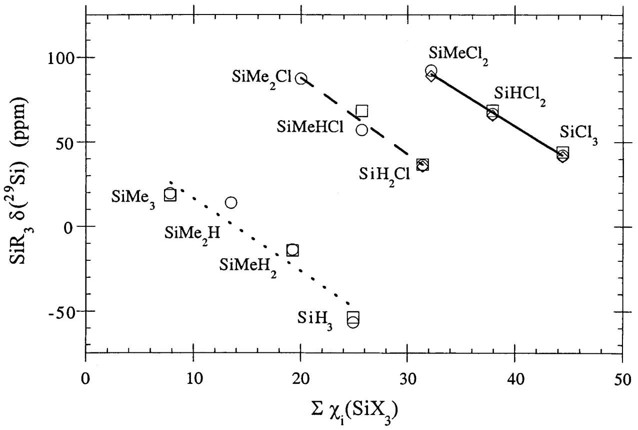

Figure 1. ^{29}Si NMR chemical shift of the silyl groups vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the various ruthenium silyl complexes $\mathrm{Cp(PR_3)_2RuSiX_3}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)} showing the three silyl classes: dichlorosilyl (solid line, slope = −3.93 ppm per χ_i unit, R = 0.997), monochlorosilyl (long dashed line, slope = −4.51 ppm per χ_i unit, R = 0.986), and non-chlorosilyl (short dashed line, slope = −4.29 ppm per χ_i unit, R = 0.957).

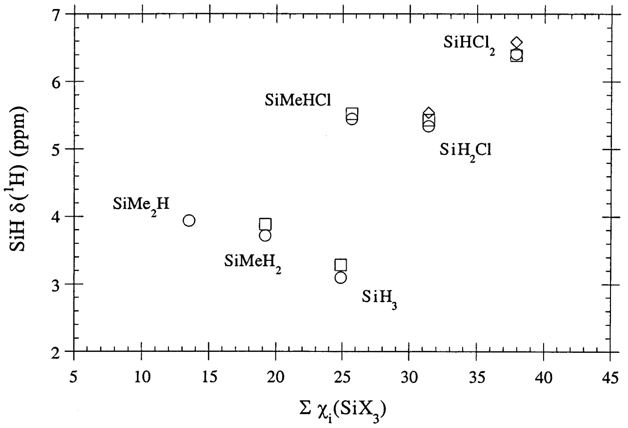

Figure 2. ^{1}H NMR chemical shift of the SiH group vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the ruthenium hydrosilyl complexes $\mathrm{Cp(PR_3)_2}$-$\mathrm{RuSiHX_2}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)}.

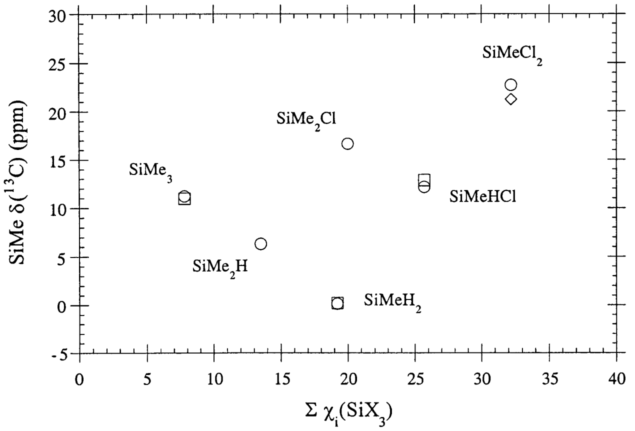

Figure 3. ^{13}C NMR chemical shifts of the SiMe group vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the ruthenium methylsilyl complexes $\mathrm{Cp(PR_3)_2RuSiMeX_2}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)}.

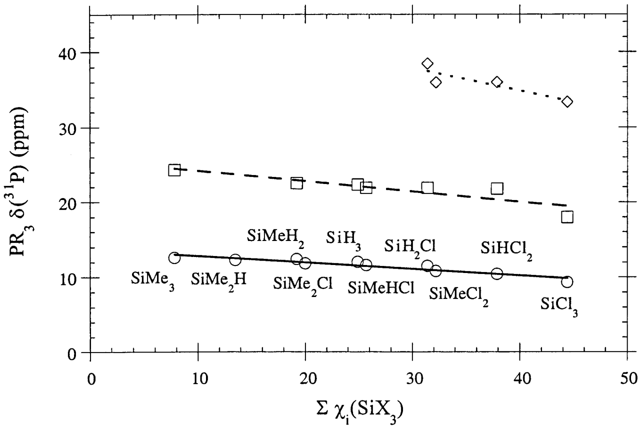

Figure 4. ^{31}P NMR chemical shift of the $\mathrm{PR_3}$ group vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the ruthenium silyl complexes $\mathrm{Cp(PR_3)_2RuSiX_3}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)}.

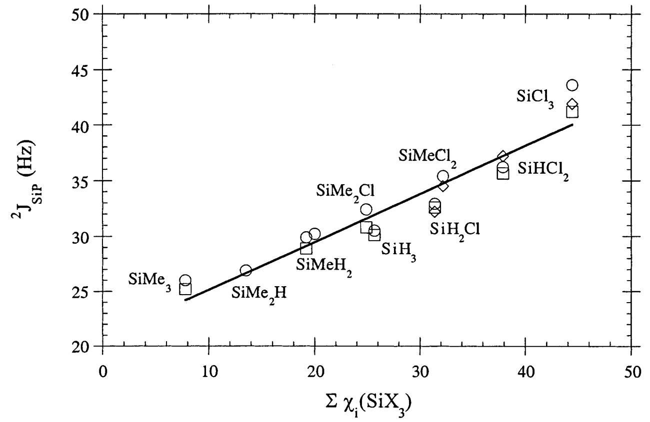

Figure 5. $^2J_{\mathrm{SiP}}$ (Hz) vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the ruthenium silyl complexes $\mathrm{Cp(PR_3)_2RuSiX_3}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)}: slope = 0.43 Hz per χ_i unit, R = 0.955.

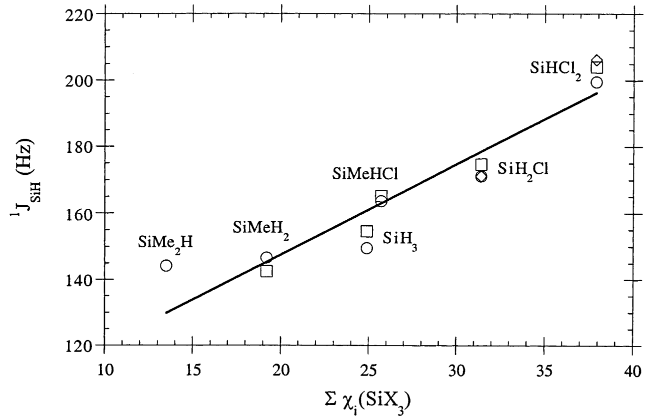

Figure 6. $^1J_{\mathrm{SiH}}$ (Hz) vs $\Sigma\chi_i(\mathrm{SiX_3})$ for the ruthenium hydrosilyl complexes $\mathrm{Cp(PR_3)_2RuSiHX_2}$ {$\mathrm{PR_3}$ = $\mathrm{PMe_3}$ (○),[16] $\mathrm{PMe_2Ph}$ (□), $\mathrm{PMePh_2}$ (◇)}: slope = 2.73 Hz per χ_i unit, R = 0.942.

electronegative chlorides required more p-character in their bonding with silicon, leaving more s-character in the bonding of silicon with the electropositive ruthenium and hydrogen. An increase in s-character in the Ru−Si and Si−H bonds (with increasing $\Sigma\chi_i(\mathrm{SiX_3})$) resulted in these bonds becoming stronger, which in turn increased the communication (coupling) between silicon and phosphorus or hydrogen.

Another interesting feature of the plots in Figures 5 and 6 was that the nature of the phosphine did not effect the magnitude of $^2J_{\mathrm{SiP}}$ or $^1J_{\mathrm{SiH}}$. For example, $^2J_{\mathrm{SiP}}$ and

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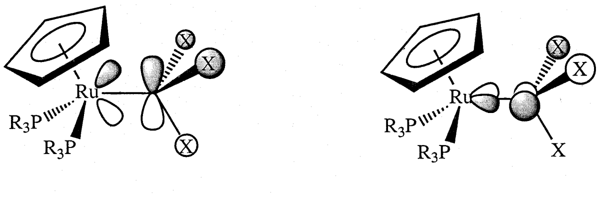
[25] Bent, H. A. *Chem. Rev.* **1961**, *61*, 276−311.



HOMO(Ru)–σ*(Si–X) SHOMO(Ru)–σ*(Si–X)

Figure 7. Interaction of the $Cp(PR_3)_2Ru$ fragment HOMO and SHOMO with linear combinations of Si−X σ^* orbitals which give rise to the ruthenium silyl group classifications.

$^1J_{SiH}$ values for the SiH_2Cl group were essentially the same regardless of which phosphine was coordinated to ruthenium, $Cp(PR_3)_2RuSiH_2Cl$: $^2J_{SiP} = 32.9$ Hz (PMe_3), 32.6 Hz (PMe_2Ph), 32.2 Hz ($PMePh_2$) and $^1J_{SiH} = 171.1$ Hz (PMe_3), 174.7 Hz (PMe_2Ph), 171.1 Hz ($PMePh_2$). Replacing PMe_3 with either PMe_2Ph or $PMePh_2$ did not effect the electronegativity of the ruthenium fragment enough to influence the interaction between ruthenium and silicon.

B.3. Silyl Group Classifications. The grouping of the ruthenium silyl complexes into different classes (dichlorosilyl, monochlorosilyl, and "non-chlorosilyl"), as illustrated in Figures 1−3, was dependent on the number of chlorides on silicon. Tolman's χ_i parameters were not sufficient to account for the effect of chloride substitution on the spectroscopic parameters of the ruthenium silyl complexes. This "chloride effect" was attributed to d(Ru)−σ^*(Si−X) π-back-bonding between the $Cp(PR_3)_2Ru$ and SiX_3 groups. The "chloride effect" in $Cp(PMe_3)_2RuSiX_3$ complexes has been discussed in detail[16] and will be described briefly here. Linear combinations of the Si−X (X = Cl, H, Me) σ^* orbitals of the silyl group gave rise to an a_1 and e set, assuming C_{3v} localized symmetry. The HOMO and SHOMO (second highest occupied molecular orbital) of the $Cp(PR_3)_2Ru$ moiety[26−28] had the correct symmetry to interact with the doubly degenerate e set of Si−X σ^* orbitals,[29] as shown in Figure 7. The magnitude of the d(Ru)−σ^*(Si−X) π-back-bonding interaction depended on the silicon substituents and followed the order Cl $\gg$ H $\approx$ Me. A ramification of this d(Ru)−σ^*(Si−Cl) π-back-bonding interaction was a change of hybridization at silicon, which manifested itself as a downfield chemical shift when a H or Me group was replaced with Cl, as observed in Figures 1−3. Surprisingly, replacing PMe_3 with the more π-acidic phosphines PMe_2Ph and $PMePh_2$ did not cause a noticeable change in the d(Ru)−σ^*(Si−Cl) π-back-bonding interaction.

Summary

The effect of silicon and phosphorus ancillary groups on the reaction of ruthenium hydride complexes $Cp(PR_3)_2RuH$ (R = Me, Ph), with a variety of chlorosilanes, $ClSiX_3$ (X = H, Cl, Me), to yield ruthenium silyl complexes $Cp(PR_3)_2RuSiX_3$ was investigated. This reaction was favored by electron-withdrawing groups on silicon and hindered by bulky groups on phosphorus. The nature of the substituents on silicon also effected the spectroscopic properties of $Cp(PR_3)_2RuSiX_3$. NMR coupling constants, $^2J_{SiP}$ and $^1J_{SiH}$, increased in magnitude as the electron-withdrawing ability of the substituents on silicon increased. The $^{29}Si(SiX_3)$, $^1H(SiH)$, and $^{13}C(SiMe)$ chemical shift data indicated the silyl groups were differentiated into three different classes: a dichlorosilyl class ($SiCl_2X$), a monochlorosilyl class ($SiClX_2$), and a "non-chlorosilyl" class (SiX_3). This silyl group classification was due to π-back-bonding between the filled HOMO and SHOMO orbitals of the ruthenium fragment and the empty σ^* orbitals of the silicon−chlorine bonds. The most surprising result of this study was that the substituents on phosphorus had no effect on the spectroscopic properties of the silyl group. Thus, for a particular silyl group, the NMR coupling constants, $^2J_{SiP}$ and $^1J_{SiH}$, and chemical shifts, $^{29}Si(SiX_3)$, $^1H(SiH)$, $^{13}C(SiMe)$, were essentially the same regardless of the phosphine (PMe_3, PMe_2Ph, $PMePh_2$) attached to ruthenium.

Experimental Section

General Considerations. All manipulations of the ruthenium-containing compounds were conducted under an inert atmosphere of argon. These compounds were stored in an MBraun glovebox, and reactions were carried out using high-vacuum techniques. ^1H (250 MHz), $^{13}C\{^1H\}$ (62.9 MHz), and $^{31}P\{^1H\}$ (101.3 MHz) NMR spectra were obtained using a Bruker 250 MHz spectrometer. ^{29}Si DEPT (79.5 MHz) NMR spectra were obtained using a Varian VXR 400S spectrometer. The PMe and PMe_2 resonances in these compounds did not appear as a simple first-order pattern in the ^1H NMR spectrum;[16] instead, they appeared as an $A_3XX'A'_3$ and $A_6XX'A'_6$ pattern, respectively. The appearance of these patterns were described as 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 spectrum, the PMe and PMe_2 resonances appeared as a virtual triplet (vt) with the separation of the outer lines $N = {}^1J_{PC} + {}^3J_{PC}$.[30,31] All NMR data were obtained in CD_2Cl_2. ^1H 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 capillary containing H_3PO_4 (85%) sealed in a NMR tube containing CD_2Cl_2. ^{13}C NMR data were referenced to the carbon signal of the solvent at 53.8 ppm. ^{29}Si NMR data were externally referenced to a CD_2Cl_2 solution of $SiMe_4$ at 0.00 ppm. The multinuclear NMR data were summarized in Table 1. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY) and Desert Analytics (Tucson, AZ).

Materials. The chloro ruthenium complexes $Cp(PR_3)_2RuCl$ (PR_3 = PPh_2Me, $PPhMe_2$)[32] and the ruthenium hydrides $Cp(PR_3)_2RuH$ (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$)[33] were prepared by the literature methods. The chlorosilanes and CH_2Cl_2 were stored over CaH_2, degassed, and vacuum transferred immediately prior to use. $AlMe_3$ (2 M in toluene, Aldrich) and MeMgCl (3 M in THF, Aldrich) were used as received. $LiAlH_4$ (Aldrich) was degassed in vacuo and stored in the glovebox. DBU was degassed prior to use. Hexanes, toluene, and THF were dried and distilled from potassium/benzophenone. Hexanes, toluene, THF, and anhydrous diethyl ether were stored

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over $[Cp_2TiCl]_2ZnCl_2$.[34] CD_2Cl_2 was stored over CaH_2. C_6D_6 was dried using NaK and stored over $[Cp_2TiCl]_2ZnCl_2$.[34] All solvents were transferred under vacuum.

$Cp(PPhMe_2)_2RuSiX_3$ [SiX_3 = $SiCl_3$ (1), $SiHCl_2$ (2), SiHMeCl (4)]. These ruthenium silyl complexes were prepared by the reaction of $Cp(PPhMe_2)_2RuH$ with X_3SiCl in CH_2Cl_2 in the absence or presence of excess DBU. **Without DBU.** In a typical reaction, CH_2Cl_2 (15 mL) was added by vacuum transfer to a flask charged with $Cp(PPhMe_2)_2RuH$ (50 mg, 0.113 mmol). Using calibrated gas-bulb techniques, $SiCl_4$ (0.75 equiv) was transferred to the frozen $Cp(PPhMe_2)_2RuH/CH_2Cl_2$ solution. The reaction mixture was allowed to slowly warm to room temperature and stirred for ~15 min. The solution volume was reduced to ~1/4 and then doubled with hexanes to precipitate $[Cp(PPhMe_2)_2RuH_2]Cl$. $[Cp(PPhMe_2)_2RuH_2]Cl$ was isolated by filtration. The yellow filtrate solution was evaporated to dryness to afford a mixture of **1** and $Cp(PPhMe_2)_2RuCl$. **With DBU.** In a typical reaction, a flask was charged with $Cp(PPhMe_2)_2RuH$ (50 mg, 0.113 mmol), DBU (25.3 μL, 0.169 mmol), and CH_2Cl_2 (15 mL) in the glovebox. Using calibrated gas-bulb techniques, excess $SiCl_4$ (1.5 equiv) was transferred to the frozen $Cp(PPhMe_2)_2RuH/DBU/CH_2Cl_2$ solution. The frozen yellow mixture was warmed to room temperature and allowed to stir for 1.5 h. The volatiles were removed under vacuum to give a yellow-orange paste. This paste was extracted with diethyl ether and filtered through Celite. The extracts were reduced to 1/2 volume and tripled with hexanes. The mixture was then reduced to 1/4 volume. The precipitate was isolated by filtration and dried under vacuum to afford **1** as a pale yellow solid (57.5 mg, 88.2%). Typical yields for **1**, **2**, and **4** were in the range of 80−90%. Anal. Calcd for $C_{21}H_{27}Cl_3P_2RuSi$ (**1**): C, 43.72; H, 4.72. Found: C, 43.28; H, 4.66. Anal. Calcd for $C_{21}H_{28}Cl_2P_2RuSi$ (**2**): C, 46.50; H, 5.20. Found: C, 46.39; H, 4.97. Anal. Calcd for $C_{22}H_{31}ClP_2RuSi$ (**4**): C, 50.62; H, 5.99. Found C, 49.65; H, 5.43. $[Cp(PhMe_2)_2RuH_2]Cl$: ^1H NMR (CD_2Cl_2) δ 7.44 (m, 10H, PPh), 5.21 (s, 5H, Cp), 1.78 (fd, $N = 9.6$ Hz, 12H, PMe_2), −9.13 (t, $^2J_{PH} = 27.7$ Hz, 2H, RuH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 25.12 (s).

$Cp(PR_3)_2RuSiH_2Cl$ [PR_3 = $PPhMe_2$ (3), PPh_2Me (6)]. These ruthenium silyl complexes were prepared by the reaction of $Cp(PR_3)_2RuH$ with SiH_2Cl_2 in CH_2Cl_2. However, this reaction was complicated by formation of $Cp(PR_3)_2RuCl$, and due to the similar solubilities of **3** or **6** and the corresponding $Cp(PR_3)_2RuCl$, analytically pure samples of **3** or **6** were not obtained. In a typical reaction, CH_2Cl_2 (15 mL) was added by vacuum transfer to a flask charged with $Cp(PPh_2Me)_2RuH$ (50 mg, 0.088 mmol). Using calibrated gas-bulb techniques, SiH_2Cl_2 (0.75 equiv) was transferred to the frozen $Cp(PPh_2Me)_2RuH/CH_2Cl_2$ solution. The reaction mixture was allowed to slowly warm and stirred at room temperature for ~15 min. The solution volume was reduced to ~1/4 and then doubled with hexanes. The resulting solid was isolated by filtration to give 40 mg of a light orange solid, which was determined (by ^1H NMR) to be a mixture of **6**, $Cp(PPh_2Me)_2RuCl$, and $[Cp(PPh_2Me)_2RuH_2]Cl$. Similarly, **3** was obtained contaminated with $Cp(PPhMe_2)_2RuCl$, even with the addition of DBU as described above.

$Cp(PPhMe_2)_2RuSiH_2X$ [SiH_2X = SiH_3 (7), SiH_2Me (8)]. These ruthenium hydrosilyl derivatives were prepared by the reaction of $LiAlH_4$ with the respective chlorosilyl complex. In a typical reaction, a 25 mL Kjeldahl flask was charged with **4** (100 mg, 0.192 mmol) and $LiAlH_4$ (25 mg, 0.659 mmol). Et_2O (15 mL) was added to the mixture by vacuum transfer. The yellow solution was allowed to stir for 1.5 h at room temperature. The solvent was removed under vacuum to give a light gray residue. The residue was extracted with hexanes (15 mL) and filtered through Celite. The yellow extracts were evaporated to dryness to afford **8** as a yellow solid (75 mg, 80%). The reaction of **1**, **2**, or **3** with $LiAlH_4$ in Et_2O was used to prepare **7**. Typical yields of **7** and **8** were between 75 and 85%. Anal. Calcd for $C_{21}H_{30}P_2RuSi$ (**7**): C, 53.26; H, 6.39. Found: C, 52.84; H, 6.02. Anal. Calcd for $C_{22}H_{32}P_2RuSi$ (**8**): C, 54.19; H, 6.61. Found: C, 53.56; H, 6.13.

$Cp(PPhMe_2)_2RuSiMe_3$ (9). $AlMe_3$ (0.27 mL, 0.554 mmol) was added by syringe to a cold suspension of **1** (100 mg, 0.173 mmol) in toluene (25 mL) under an argon atmosphere. Upon addition of the $AlMe_3$, complex **1** dissolved to give a bright yellow solution, which was allowed to stir at room temperature for 1 h. The reaction volatiles were removed under vacuum to give a yellow paste. This paste was extracted with hexanes (10 × 2 mL) and filtered through Celite. The yellow extracts were evaporated to dryness to afford a yellow residue. This residue was extracted again with hexanes and filtered through Celite. The final yellow extract solution was evaporated to dryness to afford **9** as a yellow solid (66.7 mg, 76%). Anal. Calcd for $C_{24}H_{36}P_2RuSi$ (**9**): C, 55.90; H, 7.04. Found: C, 55.32; H, 6.52.

$Cp(PPh_2Me)_2RuSiHCl_2$ (5). This ruthenium silyl complex was prepared by the direct reaction of $Cp(PPh_2Me)_2RuH$ with $HSiCl_3$ in CH_2Cl_2. Typically, CH_2Cl_2 (15 mL) was added by vacuum transfer to a 25 mL O-ring, Kjeldahl flask charged with $Cp(PPh_2Me)_2RuH$ (200 mg, 0.352 mmol). $HSiCl_3$ (1.5 equiv) was transferred using calibrated gas-bulb techniques to the liquid nitrogen cooled flask. The reaction mixture was slowly allowed to warm to room temperature and stirred for 1 h. The reaction volatiles were removed under vacuum to give a dark yellow-orange residue. The residue was taken up in CH_2Cl_2 (~0.5 mL) and pipetted into a 10 × 75 mm test tube, hexanes (~1.5 mL) were carefully layered on top of the CH_2Cl_2 solution, and the entire setup was cooled to −30 °C in the glovebox. Complex **5** was obtained as a crystalline yellow solid (10 mg, 8.5%). Anal. Calcd for $C_{31}H_{32}P_2Cl_2RuSi$ (**5**): C, 55.86; H, 4.84. Found: C, 54.84; H, 4.03. $[Cp(PPh_2Me)_2RuH_2]Cl$: ^1H NMR (CD_2Cl_2) δ 7.45(m, 20H, PPh), 5.11 (s, 5H, Cp), 1.85 (fd, $N = 9.2$ Hz, 6H, PMe), −8.43 (t, $^2J_{PH} = 25.4$ Hz, 2H, RuH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 41.10 (s).

$Cp(PPh_2Me)_2RuMe$. This ruthenium alkyl was prepared by an adaptation of the literature method.[35] A 25 mL, sidearm Schlenk flask, equipped with a condenser and magnetic stirbar, was charged with $Cp(PPh_2Me)_2RuCl$ (100 mg, 0.166 mmol). THF (~15 mL) was transferred to the flask via vacuum. Under a heavy flow of argon, MeMgCl (2 equiv) was added by syringe to the cool, stirring reaction mixture. The orange reaction mixture was heated to reflux for 16 h. The reaction volatiles were removed under vacuum to give a brown-yellow residue. The residue was extracted with hexanes (~25 × 1.5 mL) and filtered through Celite. The bright yellow solution was evaporated to dryness to afford $Cp(PPh_2Me)_2RuMe$ as a bright yellow solid (85 mg, 88%). ^1H NMR (CD_2Cl_2): δ 7.23 (m, 20H, PPh_2), 4.35 (s, 5H, Cp), 1.32 (fd, $N = 7.85$ Hz, 6H, PMe), 0.13 (t, $^3J_{PH} = 5.9$ Hz, 3H, RuMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.53 (s). $^{13}C\{^1H\}$ (CD_2Cl_2): δ 145.36, (vt, $N =$ 38.44, Hz, *ipso*-PPh), 141.25 (vt, $N = 39.37$ Hz, *ipso*-P′Ph), 133.29 (vt, $N = 10.98$ Hz, *ortho*-PPh), 131.09 (vt, $N = 10.07$ Hz, *ortho*-P′Ph), 128.82 (s, *para*-PPh), 128.02 (s, *para*-P′Ph), 127.80 (vt, $N = 9.15$ Hz, *meta*-PPh) 127.60 (vt, $N = 8.24$, *meta*-PPh), 82.85 (t, $^2J_{PC} = 2.29$ Hz, Cp), 15.72 (vt, $N = 25.64$ Hz, PMe), −26.78 (t, $^2J_{PC} = 14.19$ Hz, RuMe).

$Cp(PPh_2Me)_2RuSiX_3$ [SiX_3 = $SiCl_3$ (10), $SiMeCl_2$ (11)]. In a typical reaction, a 50 mL round-bottom reaction vessel, equipped with a Teflon plug and stir bar, was charged with $Cp(PPh_2Me)_2RuMe$ (50 mg, 0.086 mmol) and $HSiCl_3$ (~25 mL). While frozen with liquid nitrogen, the headspace above this mixture was evacuated. The reaction mixture was allowed to

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warm to room temperature. The sealed flask was heated to 100 °C with stirring for ∼16 h. The reaction mixture was allowed to cool to room temperature, and the volatiles were removed to give a pale yellow residue. The residue was dissolved in CH_2Cl_2 (∼1.5 mL) and filtered through a plug of glass wool. The solution volume was doubled with hexanes, then reduced to 1/2 in vacuo to initiate precipitation. The light precipitate was isolated by filtration and dried to afford **10** as a yellow solid (55 mg, 92%). Anal. Calcd for $C_{31}H_{31}P_2Cl_3RuSi$ (**10**): C, 53.11; H, 4.46. Found: C, 52.54; H, 4.46. Anal. Calcd for $C_{32}H_{34}P_2Cl_2RuSi$ (**11**): C, 56.47; H, 5.04. Found: C, 55.29; H, 5.25.

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