Facile Synthesis and Structures of η^6-Arene Bis(silyl) Complexes of Ruthenium(II): (η^6-arene)Ru(PPh$_3$)(SiX$_3$)$_2$

James Burgio,[†] Nicholas M. Yardy,[†] Jeffrey L. Petersen,[‡] and
Frederick R. Lemke*[,†]

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

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The reaction of RuCl$_2$(PPh$_3$)$_3$ with HSiX$_3$ in benzene produced (η^6-benzene)Ru(PPh$_3$)(SiX$_3$)$_2$ (SiX$_3$ = SiCl$_3$ (**1**), SiMeCl$_2$ (**2**)) as white to light yellow solids in high yields (>80%). A mixture of (η^6-benzene)Ru(PPh$_3$)(SiMe$_2$Cl)$_2$ (**3**), (η^6-benzene)Ru(PPh$_3$)(SiMe$_2$Cl)(SiMeCl$_2$) (**4**), and **2**, due to silicon substituent redistribution, was obtained from the reaction of RuCl$_2$(PPh$_3$)$_3$ with HSiMe$_2$Cl in benzene. (η^6-benzene)Ru(PPh$_3$)(SiMe$_3$)$_2$ (**5**) was prepared by the methylation of **1**, **2**, or the **3**/**4** mixture with AlMe$_3$. The related complexes (η^6-arene)Ru(PPh$_3$)(SiMeCl$_2$)$_2$ (arene = toluene (**6**), *o*-xylene (**7**), *m*-xylene (**8**), *p*-xylene (**9**), mesitylene (**10**), anisole (**11**)) were obtained from the reaction of RuCl$_2$(PPh$_3$)$_3$ with HSiMeCl$_2$ in the corresponding arene solvent at elevated temperature. Complexes **1**, **2**, and **5** were structurally characterized by single-crystal X-ray diffraction and exhibit a characteristic three-legged "piano-stool" geometry. The Ru−Si distances, in these complexes, ranged from 2.322 to 2.438 Å; the Ru−Si distance increased as the number of methyl groups on silicon increased.

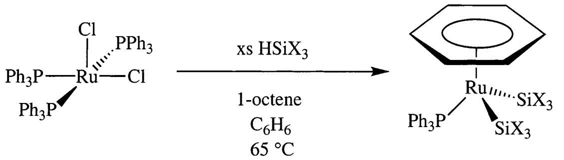
Introduction

Three-legged "piano-stool" ruthenium silyl complexes containing the cyclopentadienyl ligand, Cp(PR$_3$)$_2$RuSiX$_3$[1−6] and Cp*(PR$_3$)$_2$RuSiX$_3$,[7−11] have been used as model systems to explore the nature and reactivity of the ruthenium−silicon bond. However, there are only a few examples of (η^6-arene)RuL(SiX$_3$)$_2$ complexes with the same three-legged "piano-stool" geometry. (η^6-C$_6$H$_{6-n}$R$_n$)Ru(CO)(SiCl$_3$)$_2$ (R = Me, n = 1−4, 6; R = Bu^t, n = 1, 2; R = Cl, n = 1) were prepared by heating *cis*- or *trans*-Ru(CO)$_4$(SiCl$_3$)$_2$ and the appropriate arene.[12] (η^6-C$_6$H$_5$Me)Ru(CO)(xantsil) (xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethysilyl)) was prepared from *cis*-Ru(CO)$_4$(xantsil) in refluxing toluene; (η^6-C$_6$H$_6$)Ru(CO)(xantsil) was obtained by dissolving (η^6-C$_6$H$_5$Me)Ru(CO)(xantsil) in benzene.[13]

During our ongoing investigations into the chemistry of ruthenium(II) half-sandwich complexes,[1−6,14,15] we discovered a facile synthetic route for the formation of (η^6-arene)RuL(SiX$_3$)$_2$—an underrepresented class of three-legged "piano-stool" ruthenium(II) complexes. This paper describes the synthesis and characterization of (η^6-arene)Ru(PPh$_3$)(SiMeCl$_2$)$_2$ (arene = benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, anisole) complexes. The structural dependence of the benzene series, (η^6-benzene)Ru(PPh$_3$)(SiX$_3$)$_2$ (SiX$_3$ = SiCl$_3$, SiMeCl$_2$, SiMe$_3$), on silyl substituents is described. Also reported is the substituent redistribution reaction of HSiMe$_2$Cl that was observed in the preparation of (η^6-benzene)Ru(PPh$_3$)(SiMe$_2$Cl)$_2$.

Results and Discussion

Synthesis of (η^6-arene)Ru(PPh$_3$)(SiX$_3$)$_2$. The reaction of RuCl$_2$(PPh$_3$)$_3$ with hydrosilanes (HSiCl$_3$ and HSiMeCl$_2$) and benzene in the presence of 1-octene at elevated temperatures provided a facile synthetic route to (η^6-C$_6$H$_6$)Ru(PPh$_3$)(SiX$_3$)$_2$ (SiX$_3$ = SiCl$_3$ (**1**), SiMeCl$_2$ (**2**)) complexes (eq 1). Complexes **1** and **2** were isolated



(1)

SiX$_3$ = SiCl$_3$ (**1**), SiMeCl$_2$ (**2**)

[†] Ohio University.

[‡] West Virginia University (crystal structure determinations).

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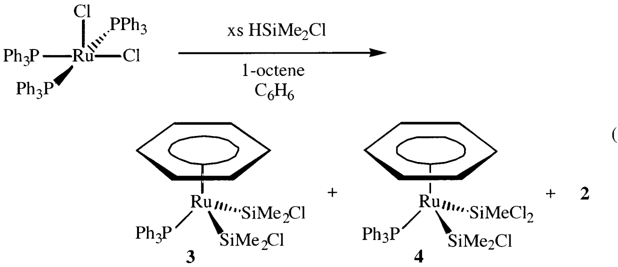
as orange and yellow solids, respectively, in high yields (>90%). 1-Octene was not required for the formation of **1** and **2**, although product yields and purity were increased when 1-octene was present. GC analysis of the mother liquor for the formation of **2** showed the presence of octane, indicating that 1-octene was acting as a hydrogen scavenger in this reaction. Also, no hydrosilylation products of 1-octene were observed, consistent with the reported observation that the $RuCl(PPh_3)_3/HSiMeCl_2$ system did not hydrosilylate styrene.[16] The reaction of $HSiEt_3$ with $RuCl_2(PPh_3)_3$ in benzene did not produce $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiEt_3)_2$ but instead formed $RuHCl(PPh_3)_3$; the formation of $RuHCl(PPh_3)_3$ from the reaction of $HSiEt_3$ with $RuCl_2(PPh_3)_3$ has been reported.[17−19]

The reaction of $RuCl_2(PPh_3)_3$ with $HSiMe_2Cl$ in the presence of benzene and 1-octene was more complicated (eq 2); redistribution of the substituents in $HSiMe_2Cl$ occurred, producing a mixture of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)_2$ (**3**), $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)(SiMeCl_2)$ (**4**), and **2**. Attempts to separate this mixture into its individual components by fractional recrystallization were unsuccessful, due to the similar solubility properties of complexes **2**−**4**. The composition of this mixture was dependent on reaction time and temperature. When the reaction described in eq 2 was carried out at room temperature for 3 days, the isolated solid was a mixture of **3** and **4** in a 3:1 ratio with only a trace of **2**. On the other hand, if the reaction temperature was increased to 65 °C, **4** was the major species in the isolated solid (a mixture of **4**, **3**, and **2** in a 12:7:1 ratio).



(2)

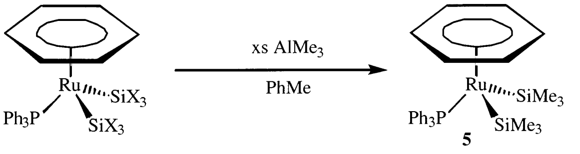
Table 1. Relative Concentrations of 2, 3, and 4 as a Function of Time in the Reaction of $RuCl_2(PPh_3)_3$ with $HSiMe_2Cl$[a]

time	2	3	4
2 h	trace	3.4	1
22 h	1	17	20
2 d	1	7	15
6 d	1	3	22

[a] Reaction conditions: $RuCl_2(PPh_3)_3$ (65 mg, 0.068 mmol), $HSiMe_2Cl$ (2 mL), 1-octene (1 mL), benzene (1.5 mL) heated to 65 °C.

The redistribution of substituents in organosilanes with the aid of transition metals has been investigated for some time.[20] The substituent redistribution of $HSiMe_2Cl$ observed in eq 2 poses an interesting set of questions. Does the redistribution of $HSiMe_2Cl$ precede the formation of the η^6-benzene bis(silyl) complexes, or does scrambling of the methyl groups occur after the η^6-benzene bis(silyl) complexes are formed? To address these questions, the reaction of $RuCl_2(PPh_3)_3$ with $HSiMe_2Cl$ at 65 °C was monitored as a function of time. The results of this study are reported in Table 1. The results indicated that methyl group scrambling occurred after the η^6-benzene bis(silyl) complexes were formed. Complex **3** was the initial species formed from the reaction of $RuCl_2(PPh_3)_3$ with $HSiMe_2Cl$ in benzene. The conversion of **3** to **4** was very facile; **4** became the major species in the reaction mixture in a matter of hours. On the other hand, the conversion of **4** to **2** was very slow; **2** was only a minor species even after **3** was converted to **4**. Also in this reaction, no evidence for the formation of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMeCl_2)(SiCl_3)$ or **1** was observed. The reaction of $RuCl_2(PPh_3)_3$ with $HSiMe_2Cl$ in benzene at room temperature, studied as a function of time, proceeded in manner similar to that for the 65 °C reaction, except that more time was required for the formation and conversion of **3** and **4**.

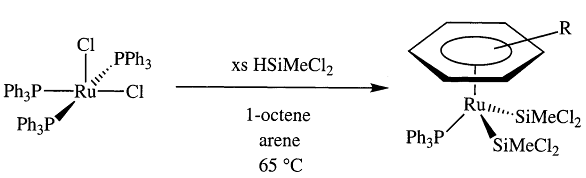
Recently, we have reported that Si−Cl bonds in ruthenium silyl complexes containing the $Cp(PR_3)_2Ru$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$) moiety could readily be methylated by $AlMe_3$.[5,6] Thus, in a similar manner, the trimethylsilyl derivative $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_3)_2$ (**5**) was prepared in good yield as a light yellow solid by the reaction of **1**, **2**, or the **2**/**3**/**4** mixture with $AlMe_3$ in toluene (eq 3).



(3)

$(SiX_3)_2 = (SiCl_3)_2$ (**1**), $(SiMeCl_2)_2$ (**2**), $(SiMe_2Cl)_2$ (**3**), $(SiMe_2Cl)(SiMeCl_2)$ (**4**)

The reaction in eq 1 was readily extended to other arene systems. $(\eta^6\text{-arene})Ru(PPh_3)(SiMeCl_2)_2$ (arene = toluene (**6**), *o*-xylene (**7**), *m*-xylene (**8**), *p*-xylene (**9**), mesitylene (**10**), anisole (**11**)) were obtained in good yields (65−85%) from the reaction of $RuCl_2(PPh_3)_3$ with $HSiMeCl_2$ in the corresponding arene (eq 4).



(4)

arene = toluene (**6**), *o*-xylene (**7**), *m*-xylene (**8**), *p*-xylene (**9**), mesitylene (**10**), anisole (**11**)

The simplicity and mild conditions employed in the preparation of complexes **1**−**11** are unusual compared to the methods used to prepare related $(\eta^6\text{-arene})RuL(SiX_3)_2$ complexes. The preparation of $(\eta^6\text{-}C_6H_5Me)Ru(CO)(xantsil)$ was a two-step process, employing temperatures up to 120 °C; $Ru_3(CO)_{12}$ was reacted with xantsilH_2 to form $Ru(CO)_4(xantsil)$, which was then reacted with toluene to form $(\eta^6\text{-}C_6H_5Me)Ru(CO)(xantsil)$.[13] $(\eta^6\text{-}C_6H_{6-n}R_n)Ru(CO)(SiCl_3)_2$ (R = Me, n = 1−4, 6; R = Bu^t, n = 1−2; R = Cl, n = 1) were prepared

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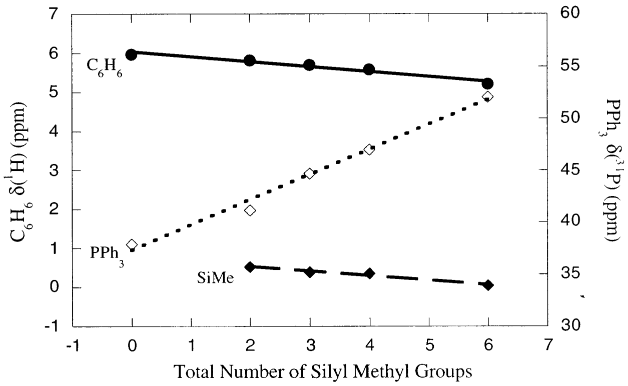

Figure 1. ^1H NMR chemical shifts of the C_6H_6 and SiMe groups and the ^{31}P NMR chemical shift of PPh_3 versus the total number of methyl groups in the ruthenium silyl complexes $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiX_3)_2$ (**1**–**5**). Average values were used for the SiMe ^1H NMR chemical shifts of **3** and **4**.

by heating *cis*- or *trans*-$Ru(CO)_4(SiCl_3)_2$ with the appropriate arene in excess of 120 °C.[12] The facile synthesis of $(\eta^6\text{-arene})Ru(PPh_3)(SiX_3)_2$ complexes reported herein will make this class of silyl complexes more readily available for further investigation.

NMR Spectra of $(\eta^6\text{-arene})Ru(PPh_3)(SiX_3)_2$. Multinuclear NMR characterizations of **1**–**11** were consistent with the formulation and molecular connectivity of these η^6-arene bis(silyl) ruthenium complexes. In ^1H NMR spectra, the η^6-arene CH and Me resonances were observed in the 5–6 ppm and 1.5–2.5 regions, respectively, while the SiMe resonances were observed as singlets in the 0–0.6 ppm region. The $SiMe_2Cl$ methyl groups in **3** and **4** were diastereotopic. Both the arene CH and SiMe resonances exhibited an inverse linear relationship with the total number of silyl methyl groups in complexes **1**–**5** (Figure 1). The silyl group silicons in **1**–**11** were observed as doublets (J_{SiP} = 25–32 Hz) around 72–79 ppm in the $^{29}Si\{^1H\}$ DEPT NMR spectra; the only exception was the $SiMe_3$ group of **5**, which was observed as a doublet (J_{SiP} = 26 Hz) at 10.46 ppm. The PPh_3 groups were observed in the $^{31}P\{^1H\}$ NMR spectra as singlets in the 35–55 ppm region and exhibited a linear relationship with the total number of silyl methyl groups in **1**–**5** (Figure 1).

Structures of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiX_3)_2$. The crystal structures of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiX_3)_2$ ($SiX_3 = SiCl_3$ (**1**), $SiMeCl_2$ (**2**), $SiMe_3$ (**5**)) were determined by X-ray diffraction at 295 K. Pertinent interatomic distances and angles for **1**, **2**, and **5** are given in Table 2. The molecular structures of **1**, **2**, and **5** (Figures 2–4, respectively) confirm the formulation and connectivity of the (η^6-benzene)ruthenium bis(silyl) complexes described above. Complexes **1**, **2**, and **5** adopt a three-legged “piano-stool” geometry around ruthenium, with “legs” composed of one PPh_3 and two silyl groups. The Ru–Si distances of 2.32–2.44 Å are consistent with a single bond and fall within the range (2.27–2.51 Å) observed for d^6 ruthenium silyl complexes.[3,5,7,10,21,22] Also, in these complexes, the average Si–Cl distance (2.10 ± 0.01 Å) was slightly longer than the Si–Cl distances in $(\eta^6\text{-}p\text{-}Bu^t{}_2C_6H_4)Ru(CO)(SiCl_3)_2$ (2.07 ± 0.01 Å)[23] but shorter than the Si–Cl distances (2.11–2.17, 2.13 ± 0.01 Å average) observed in related d^6 $Cp(PR_3)_2Ru(SiX_3)$ complexes.[4,5,24]

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiX_3)_2$ ($SiX_3 = SiCl_3$ (1), $SiMeCl_2$ (2), $SiMe_3$ (5))

	$SiCl_3$	$SiMeCl_2$	$SiMe_3$
Ru–Si(1)	2.3273(8)	2.344(2)	2.4377(11)
Ru–Si(2)	2.3218(8)	2.354(2)	2.4352(10)
Ru–P	2.3486(7)	2.3413(13)	2.3048(10)
Ru–Ar(c)[a]	1.825	1.818	1.803
Si–Cl (av)[b]	2.086(12)	2.116(23)	
Si–C (av)[b]		1.905(21)	1.903(10)
P–C (av)[b]	1.843(6)	1.853(6)	1.853(5)
Ar(c)–Ru–Si(1)[a]	120.9	122.4	121.0
Ar(c)–Ru–Si(2)[a]	121.3	120.8	120.4
Ar(c)–Ru–P[a]	127.7	127.9	130.1
Ru–Si(1)–X[c]	124.48(4) (Cl(1))	129.2(2) (C(7))	124.03(13) (C(7))
	113.71(4) (Cl(2))	112.03(8) (Cl(1))	112.8(2) (C(8))
	114.59(5) (Cl(3))	110.66(8) (Cl(2))	113.45(14) (C(9))
Ru–Si(2)–X[c]	114.53(4) (Cl(4))	118.3(2) (C(8))	125.23(13) (C(10))
	112.26(4) (Cl(5))	122.33(8) (Cl(3))	112.8(2) (C(11))
	125.69(5) (Cl(6))	112.52(7) (Cl(4))	113.14(14) (C(12))
Cl–Si–Cl (av)[b]	100.1(11)	99.1(18)	
Cl–Si–C (av)[b]		100.5(12)	
C–Si–C (av)[b]			100.9(15)

[a] Ar(c) corresponds to the centroid of the benzene ring. [b] Numbers in parentheses represent the 95% confidence limit for average distances and angles. [c] X represents either a chlorine or carbon bonded to silicon.

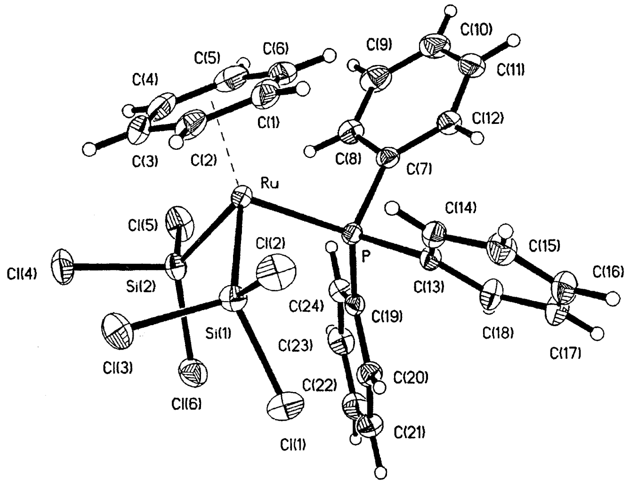

Figure 2. Perspective view of the molecular structure of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiCl_3)_2$ (**1**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

Complexes **1**, **2**, and **5** have a staggered conformation about the Ru–Si bond with the benzene and either a chloride or methyl group in an anti relationship (average benzene centroid–Ru–Si–X dihedral angle 166.3 ± 2.8°). The silyl group has a distorted-tetrahedral geometry with an average X–Si–X (X = Cl, C) angle of 100.3 ± 0.7° and an average Ru–Si–X angle of 117.3 ± 2.4°. The anti Ru–Si–X angles (125.2 ± 1.8° average) are significantly larger than the non-anti Ru–Si–X angles (113.4 ± 0.9°). In related three-legged “piano-stool” Cp ruthenium silyl complexes, the Ru–Si–X angle for substituents anti to a Cp group have also been observed to be ≥10° larger than Ru–Si–X angles

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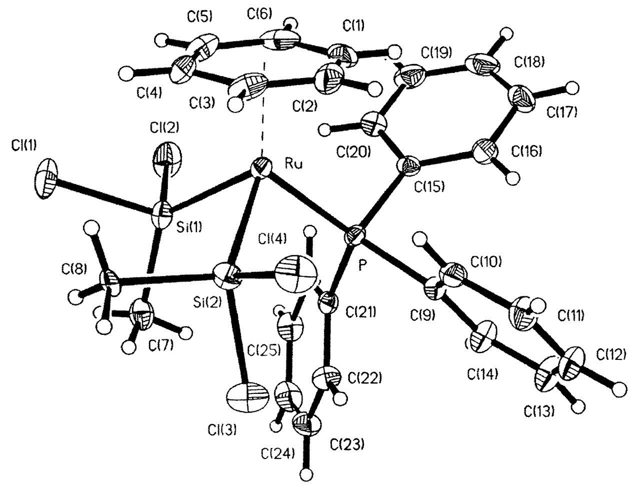

Figure 3. Perspective view of the molecular structure of (η^6-C_6H_6)Ru(PPh_3)($SiMeCl_2$)$_2$ (**2**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

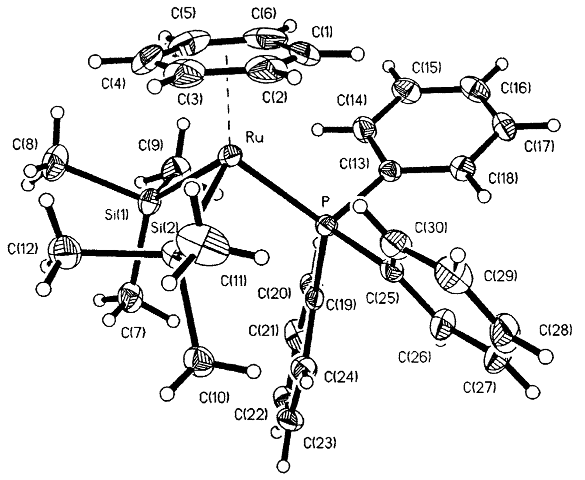

Figure 4. Perspective view of the molecular structure of (η^6-C_6H_6)Ru(PPh_3)($SiMe_3$)$_2$ (**5**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

for the other substituents on silicon: Cp(PMe_3)$_2$Ru$SiCl_3$ (Ru−Si−Cl(anti) = 125.6° vs Ru−Si−Cl = 115.9° (av)),[5] Cp(PMe_3)$_2$Ru$SiCl_2$Cp* (Ru−Si−Cl(anti) = 119.9° vs Ru−Si−Cl = 109.2°),[3] Cp*(PMe_3)$_2$Ru$SiPh_2$H (Ru−Si−H(anti) = 112.9° vs Ru−Si−Ph = 98.8° (av)),[7] and Cp*(PMe_3)$_2$Ru$SiPh_2$OTf (Ru−Si−OTf(anti) = 118.2° vs Ru−Si−Ph = 96.9° (av)).[10]

Within this series of η^6-benzene bis(silyl) ruthenium complexes, the Ru−Si distances increased from 2.325 Å (av, $SiCl_3$) to 2.436 Å (av, $SiMe_3$) as the electronegative chlorides were replaced with methyl groups. A similar trend was observed in the series Os(SiR_3)Cl(CO)(PPh_3)$_2$ (R = F, Cl, OH, Me), where the Os−Si distances increased from 2.273(6) Å (R = Cl) to 2.374(2) Å (R = Me).[25] These changes in Ru−Si and Os−Si distances can be attributed to a decrease in the π-acceptor ability of the silyl group as chlorides are replaced with methyl groups. On the basis of photoelectron studies of CpFe(CO)$_2SiR_3$ (SiR_3 = $SiCl_3$, $SiMe_3$), the π-acceptor ability of $SiCl_3$ was deduced to be about half the π-acceptor ability of CO, while the $SiMe_3$ group exhibited little to no π-acidity.[26] The increase in the Ru−Si distances of **1**, **2**, and **5** were accompanied by decreases in the Ru−P (2.349 Å ($SiCl_3$) to 2.305 Å ($SiMe_3$)) and Ru−Ar(c) (1.825 Å ($SiCl_3$) to 1.803 Å ($SiMe_3$)) distances. These interatomic distance changes were consistent with a decrease in the π-acidity of the silyl group being compensated by an increased π-interaction with PPh_3 and benzene.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using either standard vacuum line or glovebox techniques.[27] ^{1}H NMR (250, 400, and 500 MHz) were obtained using Bruker AC-250, Varian VXR 400S, and Varian Inova 500 spectrometers, respectively, and were referenced to the residual proton peak of the solvent. ^{31}P NMR (101.26 MHz) spectra were obtained using a Bruker AC-250 spectrometer and externally referenced to 85% H_3PO_4. ^{29}Si{^{1}H} DEPT (79.5 MHz) was recorded on a Varian VXR 400s spectrometer and externally referenced to $SiMe_4$.

Materials. $RuCl_2(PPh_3)_3$ was prepared by the published method[28] or used as received from Pressure Chemical (Lot #026588001). Hexanes, pentane, benzene, and toluene (Fisher) were deolefinated with concentrated H_2SO_4, distilled from potassium/benzophenone, and stored over $[Cp_2TiCl_2]_2ZnCl_2$.[29] Xylenes (*o*-, *m*-, and *p*-), mesitylene, and anisole were purified according to published procedures.[30] Benzene-d_6 (Cambridge Isotopes) and diethyl ether (Spectrum Chemical) were degassed and stored over $[Cp_2TiCl_2]_2ZnCl_2$.[29] Dichloromethane was distilled from and stored over CaH_2. Dichloromethane-d_2 (Cambridge Isotopes) was stored over CaH_2. Chlorohydrosilanes ($HSiCl_3$, $HSiMeCl_2$, $HSiMe_2Cl$; Gelest) were dried and stored over CaH_2. Triethylsilane (Gelest) was distilled under reduced pressure from molecular sieves and stored under argon. All solvents and volatile reagents were degassed prior to use by three standard freeze/pump/thaw degassing cycles.

Synthesis of (η^6-C_6H_6)Ru(PPh_3)(SiR_3)$_2$ (SiR_3 = $SiCl_3$ (1), $SiMeCl_2$ (2)). In a typical experiment, a 25 mL reaction vessel was charged with $RuCl_2(PPh_3)_3$ (250 mg, 2.6 mmol), benzene (5 mL), and 1-octene (4 mL) in the glovebox. $HSiCl_2Me$ (3 mL, ∼23.4 mmol) was added by vacuum transfer. The reaction vessel was sealed and placed in a 65 °C oil bath for 14 h. The reaction volume was reduced by 50%, and hexanes (2 mL) were added by vacuum transfer. The precipitate was collected, washed with hexanes, and dried in vacuo to afford **2** (150 mg, 86%) as a light yellow solid. GC analysis of the mother liquor shows the presence of 1-octene, octane, and triphenylphosphine. Complex **1** was obtained as an orange solid in good yields (75−85%). Qualitatively, $HSiMeCl_2$ was more reactive toward $RuCl_2(PPh_3)_3$ than $HSiCl_3$, possibly due to the decreased solubility of $SiCl_3$-containing species. **1**: ^{1}H NMR (CD_2Cl_2) δ 7.45, 7.64 (m, 15 H, PPh_3), 5.97 (s, 6H, C_6H_6); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 134.90, 131.20, 128.21 (s, Ph), 101.5 (d, J_{PC} = 32.1 Hz, C_6H_6); ^{29}Si{^{1}H} DEPT NMR (CD_2Cl_2) insufficient solubility of **1** to obtain spectrum; ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 37.87 (s). Anal. Calcd for $C_{24}H_{21}Cl_6PRuSi_2$: C, 40.58; H, 2.98. Found: C, 40.40; H, 3.21. **2**: ^{1}H NMR (CD_2Cl_2) δ 7.01, 7.22 (m, 15H PPh_3), 5.82 (s, 6H, C_6H_6), 0.52 (s, 6H, $SiCl_2Me$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 136.50, 134.96, 130.80, 128.05 (m, Ph), 100.30 (d, J_{PC} = 25.2 Hz, C_6H_6), 18.70 (s, $SiCl_2Me$); ^{29}Si{^{1}H}

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DEPT NMR (CD_2Cl_2) δ 77.26 (d, $J_{SiP} = 29.9$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 41.13 (s). Anal. Calcd for $C_{26}H_{27}Cl_4PRuSi_2$: C, 46.64; H, 4.06. Found: C, 46.49; H, 3.93.

Crystals of **1** suitable for X-ray diffraction were grown at room temperature by the slow vapor diffusion of THF into an acetonitrile solution of **1**, which was covered by a layer of hexanes. Crystals of **2** suitable for X-ray diffraction were grown at room temperature by the vapor diffusion of Et_2O into CH_2Cl_2 solutions of **2**. Details concerning the crystallographic analysis of **1** and **2** are given in the Supporting Information.

Synthesis of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)_2$ (3) and $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_2Cl)(SiMeCl_2)$ (4). A mixture of complexes **3**, **4**, and **2** was obtained from the reaction of $RuCl_2(PPh_3)_3$ with $HSiCl_2Me$ in benzene. The composition of this mixture was dependent on the reaction temperature. In a typical experiment, a 25 mL reaction vessel was charged with $Ru(PPh_3)_3Cl_2$ (250 mg, 2.6 mmol), benzene (5 mL), and 1-octene (4 mL) in the glovebox. $HSiCl_2Me$ (3 mL, ~23.4 mmol) was added by vacuum transfer. If this reaction mixture was stirred at room temperature for 3 days, a yellow solution with an off-white precipitate was obtained. Workup of this sample, as described for **1** and **2**, afforded 132 mg of an off-white solid, which was determined by ^1H NMR spectroscopy to be a mixture of **3** and **4** in a 3:1 ratio with a trace of **2**. On the other hand, heating the $RuCl_2(PPh_3)_3/HSiMe_2Cl$ reaction mixture to 65 °C for 14 h followed by the usual workup afforded an off-white solid in similar yields. The composition of this solid was determined to be a mixture of **4**, **3**, and **2** in a 12:7:1 ratio. **3**: ^1H NMR (CD_2Cl_2) δ 7.39, 7.67 (m, 15H, PPh_3), 5.57 (s, 6H, C_6H_6), 0.53 (s, 6H, $SiMe_2Cl$), 0.17 (s, 6H, $SiMe_2Cl$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 72.31 (d, $J_{SiP} = 23.2$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 46.99 (s). **4**: ^1H NMR (CD_2Cl_2) δ 7.39, 7.67 (m, 15H, PPh_3), 5.70 (s, 6H, C_6H_6), 0.70 (s, 3H, SiMe), 0.32 (s, 3H, SiMe), 0.15 (s, 3H, SiMe); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 79.31 (d, $J_{SiP} = 33.0$ Hz), 73.27 (d, $J_{SiP} = 26.9$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 44.67 (s).

Synthesis of $(\eta^6\text{-}C_6H_6)Ru(PPh_3)(SiMe_3)_2$ (5). Complex **5** was prepared by the reaction of $AlMe_3$ with **1**, **2**, or the **2**/**3**/**4** mixture. In a typical experiment, a 25 mL Schlenk flask was charged with **1** (50 mg, 0.07 mmol) and toluene (10 mL) to form a yellow slurry. $AlMe_3$ (0.25 mL, 0.5 mmol, 2.0 M in toluene or hexanes) was added by syringe, and the reaction mixture was stirred for 1 h at room temperature. The resulting clear yellow solution was filtered through Celite and the filtrate evaporated to dryness. The residue was slurried with hexanes, filtered, and dried under vacuum to yield **5** (14 mg, 33%) as a yellow solid. Similar yields of **5** were obtained upon the methylation of either **2** or the **2**/**3**/**4** mixture. ^1H NMR (CD_2Cl_2): δ 7.2, 7.4 (m, 15H, PPh_3), 5.21 (s, 6H, C_6H_6), 0.037 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 134.40, 129.36, 127.51 (m, Ph), 92.18 (d, $J_{PC} = 2.3$ Hz, C_6H_6), 11.04 (s, $SiMe_3$). $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2): δ 10.46 (d, $J_{SiP} = 25.7$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.04 (s).

Crystals of **5** suitable for X-ray diffraction were grown at room temperature by the vapor diffusion of Et_2O into CH_2Cl_2 solutions of **5**. Details concerning the crystallographic analysis of **5** are given in the Supporting Information.

Synthesis of $(\eta^6\text{-arene})Ru(PPh_3)(SiMeCl_2)_2$ (arene = Toluene (6), *o*-Xylene (7), *m*-Xylene (8), *p*-Xylene (9), Mesitylene (10), Anisole (11)). In a typical experiment, a 25 mL reaction vessel was charged with $RuCl_2(PPh_3)_3$ (115 mg, 1.2 mmol), toluene (3 mL), and 1-octene (4 mL) in the glovebox. $HSiCl_2Me$ (1 mL, ~7.8 mmol) was added by vacuum transfer. The reaction vessel was sealed and placed in a 65 °C oil bath for 14−24 h. The reaction volume was reduced by 50%, and hexanes (2 mL) were added by vacuum transfer. The precipitate was collected, washed with hexanes, and dried in vacuo to afford **6** (58 mg, 71%) as a light yellow solid. Complexes **7**−**11** were also obtained as light yellow to orange solids in good yields (65−85%). **6**: ^1H NMR (CD_2Cl_2) δ 7.43, 7.75 (m, 15H, PPh_3), 5.97 (m, 3H, CH), 5.43 (d, $J_{HH} = 5.9$ Hz, 2H, CH), 1.90 (s, 3H, Me), 0.48 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 136.24 (d, $J_{PC} = 45.0$ Hz, PPh_3 *ipso*-C), 135.32 (d, $J_{PC} = 10.7$ Hz, PPh_3 *o*-C), 130.82 (s, PPh_3 *p*-C), 128.04 (d, $J_{PC} = 10.0$ Hz, PPh_3 *m*-C), 118.93 (s, *C*Me), 101.99, 99.87, 97.66 (s, toluene CH), 19.49 (s, C*Me*), 18.90 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 77.86 (d, $J_{SiP} = 29.9$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 44.27 (s). Anal. Calcd for $C_{29}H_{27}Cl_4PRuSi_2$: C, 47.44; H, 4.28. Found: C, 46.17; H, 4.27. **7**: ^1H NMR (CD_2Cl_2) δ 7.42, 7.70 (m, 15H, PPh_3), 5.97 (m, 2H, CH), 5.75 (m, 2H, CH), 1.73 (s, 6H, Me), 0.45 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135.52 (d, $J_{PC} = 10.7$ Hz, PPh_3 *o*-C), 130.74 (d, $J_{PC} = 1.5$ Hz, PPh_3 *p*-C), 127.93 (d, $J_{PC} = 9.8$ Hz, PPh_3 *m*-C), 117.30 (s, *C*Me), 103.21 (s, xylene CH), 97.60 (s, xylene CH), 18.96 (s, C*Me*), 17.90 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 78.82 (d, $J_{SiP} = 29.3$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 45.66 (s). Anal. Calcd for $C_{28}H_{31}Cl_4PRuSi_2$: C, 48.21; H, 4.48. Found: C, 47.93; H, 4.68. **8**: ^1H NMR (CD_2Cl_2) δ 7.43, 7.79 (m, 15H, PPh_3), 6.07 (t, $J_{HH} = 6.1$ Hz, 1H, CH), 5.76 (d, $J_{HH} = 6.1$ Hz, 2H, CH), 4.94 (s, 1H, CH), 2.06 (s, 6H, Me), 0.44 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135.67 (d, $J_{PC} = 10.8$ Hz, PPh_3 *o*-C), 130.83 (d, $J_{PC} = 2.3$ Hz, PPh_3 *p*-C), 127.97 (d, $J_{PC} = 9.9$ Hz, PPh_3 *m*-C), 117.64 (s, *C*Me), 106.90 (s, xylene CH), 99.65 (d, $J_{PC} = 2.3$ Hz, xylene CH), 97.52 (d, $J_{PC} = 2.3$ Hz, xylene CH), 19.68 (s, C*Me*), 19.08 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 77.87 (d, $J_{SiP} = 30.0$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 46.37 (s). Anal. Calcd for $C_{28}H_{31}Cl_4PRuSi_2$: C, 48.21; H, 4.48. Found: C, 48.13; H, 4.37. **9**: ^1H NMR (CD_2Cl_2) δ 7.41, 7.74 (m, 15H, PPh_3), 5.37 (s, 4H, CH), 2.37 (s, 6H, Me), 0.52 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 137.01 (d, $J_{PC} = 45.8$ Hz, PPh_3 *ipso*-C), 135.42 (d, $J_{PC} = 10.7$ Hz, PPh_3 *o*-C), 130.65 (d, $J_{PC} = 2.3$ Hz, PPh_3 *p*-C), 127.92 (d, $J_{PC} = 9.8$ Hz, PPh_3 *m*-C), 117.34 (s, *C*Me), 100.49 (d, $J_{PC} = 3.0$ Hz, xylene CH), 19.80 (s, C*Me*), 19.76 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 78.67 (d, $J_{SiP} = 29.3$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 44.61 (s). Anal. Calcd for $C_{28}H_{31}Cl_4PRuSi_2$: C, 48.21; H, 4.48. Found: C, 48.31; H, 4.52. **10**: ^1H NMR (CD_2Cl_2) δ 7.43, 7.84 (m, 15H, PPh_3), 5.35 (s, 3H, CH), 2.23 (s, 9H, Me), 0.43 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135.82 (d, $J_{PC} = 9.7$ Hz, PPh_3 *o*-C), 130.82 (s, PPh_3 *p*-C), 127.84 (d, $J_{PC} = 9.9$ Hz, PPh_3 *m*-C), 112.88 (s, *C*Me), 105.72 (d, $J_{PC} = 1.5$ Hz, mesitylene CH), 19.84 (s, C*Me*), 19.13 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 77.46 (d, $J_{SiP} = 31.2$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 46.49 (s). Anal. Calcd for $C_{29}H_{33}Cl_4PRuSi_2$: C, 48.95; H, 4.67. Found: C, 48.84; H, 4.80. **11**: ^1H NMR (CD_2Cl_2) δ 7.73, 7.43 (m, 15H, PPh_3), 6.31 (t, $J_{HH} = 6.1$ Hz, 2H, CH), 5.37 (m, 3H, CH), 3.33 (s, 3H, OMe), 0.50 (s, 6H, $SiCl_2Me$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 135.38 (d, $J_{PC} = 10.8$ Hz, PPh_3 *o*-C), 130.78 (d, $J_{PC} = 2.2$ Hz, PPh_3 *p*-C), 127.92 (d, $J_{PC} = 9.8$ Hz, PPh_3 *m*-C), 114.22 (s, *C*Me), 103.41 (d, $J_{PC} = 2.2$ Hz, anisole CH), 89.10 (d, $J_{PC} = 3.1$ Hz, anisole CH), 84.78 (s, anisole CH), 56.59 (s, OMe), 18.67 (s, $SiCl_2Me$); $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2) δ 78.91 (d, $J_{SiP} = 28.7$ Hz). Anal. Calcd for $C_{27}H_{29}Cl_4OPRuSi_2$: C, 46.36; H, 4.18. Found: C, 46.27; H, 4.17.

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Supporting Information Available: Text describing the collection of X-ray data and tables of crystal data, data collection and refinement parameters, interatomic distances, and interatomic angles for **1**, **2** and **5**. Full crystallographic data as CIF files are also available for **1**, **2**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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