

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

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The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with HSiX_3 in benzene produced $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ ($\text{SiX}_3 = \text{SiCl}_3$ (**1**), SiMeCl_2 (**2**)) as white to light yellow solids in high yields (>80%). A mixture of $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})_2$ (**3**), $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})(\text{SiMeCl}_2)$ (**4**), and **2**, due to silicon substituent redistribution, was obtained from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with HSiMe_2Cl in benzene. $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiMe}_3)_2$ (**5**) was prepared by the methylation of **1**, **2**, or the **3/4** mixture with AlMe_3 . The related complexes $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiMeCl}_2)_2$ (arene = toluene (**6**), *o*-xylene (**7**), *m*-xylene (**8**), *p*-xylene (**9**), mesitylene (**10**), anisole (**11**)) were obtained from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ 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.

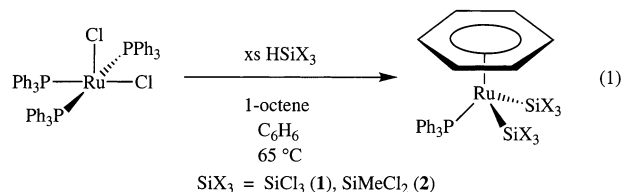
Introduction

Three-legged “piano-stool” ruthenium silyl complexes containing the cyclopentadienyl ligand, $\text{Cp}(\text{PR}_3)_2\text{RuSiX}_3^{1-6}$ and $\text{Cp}^*(\text{PR}_3)_2\text{RuSiX}_3$,^{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 $(\eta^6\text{-arene})\text{RuL}(\text{SiX}_3)_2$ complexes with the same three-legged “piano-stool” geometry. $(\eta^6\text{-C}_6\text{H}_{6-n}\text{R}_n)\text{Ru}(\text{CO})(\text{SiCl}_3)_2$ ($\text{R} = \text{Me}$, $n = 1\text{--}4$, 6; $\text{R} = \text{Bu}^t$, $n = 1$, 2; $\text{R} = \text{Cl}$, $n = 1$) were prepared by heating *cis*- or *trans*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ and the appropriate arene.¹² $(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\text{CO})(\text{xantsil})$ (xantsil = (9,9-dimethyl-xanthene-4,5-diyl)bis(dimethylsilyl)) was prepared from *cis*- $\text{Ru}(\text{CO})_4(\text{xantsil})$ in refluxing toluene; $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CO})(\text{xantsil})$ was obtained by dissolving $(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\text{CO})(\text{xantsil})$ 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 $(\eta^6\text{-arene})\text{RuL}(\text{SiX}_3)_2$ —an underrepresented class of three-legged “piano-stool” ruthenium(II) complexes. This paper describes the synthesis and characterization of $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiMeCl}_2)_2$ (arene = benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, anisole) complexes. The structural dependence of the benzene series, $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ ($\text{SiX}_3 = \text{SiCl}_3$, SiMeCl_2 , SiMe_3), on silyl substituents is described. Also reported is the substituent redistribution reaction of HSiMe_2Cl that was observed in the preparation of $(\eta^6\text{-benzene})\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})_2$.

Results and Discussion

Synthesis of $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$. The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with hydrosilanes (HSiCl_3 and HSiMeCl_2) and benzene in the presence of 1-octene at elevated temperatures provided a facile synthetic route to $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ ($\text{SiX}_3 = \text{SiCl}_3$ (**1**), SiMeCl_2 (**2**)) complexes (eq 1). Complexes **1** and **2** were isolated



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(1) Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183–11184.

(2) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980–3987.

(3) Lemke, F. R.; Simons, R. S.; Youngs, W. J. *Organometallics* **1996**, *15*, 216–221.

(4) Lemke, F. R.; Chaitheerapapkul, C. *Polyhedron* **1996**, *15*, 2559–2565.

(5) Lemke, F. R.; Galat, K. J.; Youngs, W. J. *Organometallics* **1999**, *18*, 1419–1429.

(6) Freeman, S. T. N.; Lofton, L. L.; Lemke, F. R. *Organometallics* **2002**, *21*, 4776–4784.

(7) Straus, D. A.; Zhang, C.; Quimbata, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673–2681.

(8) Straus, D. A.; Tilley, T. D.; Rheingold, A. J.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872–5873.

(9) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495–5496.

(10) Grumbine, S. K.; Straus, D. A.; Tilley, T. D. *Polyhedron* **1995**, *14*, 127–148.

(11) Grumbine, S. K.; Mitchell, G. P.; Straus, D. A.; Tilley, T. D. *Organometallics* **1998**, *17*, 5607–5619.

(12) Pomeroy, R. K.; Harrison, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 661–663.

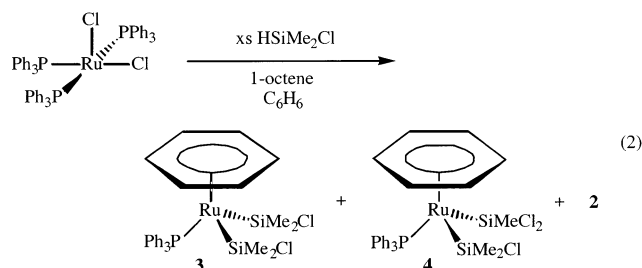
(13) Tobita, H.; Hasegawa, K.; Minglana, J. J. G.; Luh, L.-S.; Okazaki, M.; Ogino, H. *Organometallics* **1999**, *18*, 2058–2060.

(14) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721–1727.

(15) Freeman, S. T. N.; Lemke, F. R.; Haar, C. M.; Nolan, S. P.; Petersen, J. L. *Organometallics* **2000**, *19*, 4828–4833.

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 $\text{RuCl}(\text{PPh}_3)_3/\text{HSiMe}_2\text{Cl}$ system did not hydrosilylate styrene.¹⁶ The reaction of HSiEt_3 with $\text{RuCl}_2(\text{PPh}_3)_3$ in benzene did not produce $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiEt}_3)_2$ but instead formed $\text{RuHCl}(\text{PPh}_3)_3$; the formation of $\text{RuHCl}(\text{PPh}_3)_3$ from the reaction of HSiEt_3 with $\text{RuCl}_2(\text{PPh}_3)_3$ has been reported.^{17–19}

The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ 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 $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})_2$ (**3**), $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})(\text{SiMeCl})_2$ (**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).

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 $\text{RuCl}_2(\text{PPh}_3)_3$ 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

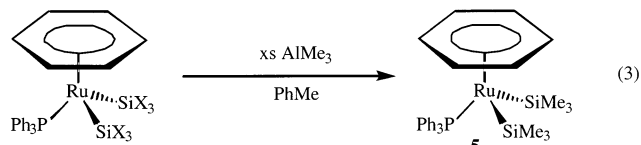
Table 1. Relative Concentrations of **2, **3**, and **4** as a Function of Time in the Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with HSiMe_2Cl ^a**

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: $\text{RuCl}_2(\text{PPh}_3)_3$ (65 mg, 0.068 mmol), HSiMe_2Cl (2 mL), 1-octene (1 mL), benzene (1.5 mL) heated to 65 °C.

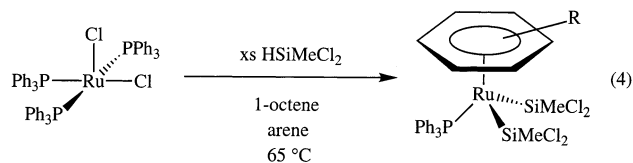
reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with HSiMe_2Cl in benzene. The conversion of **3** to **4** was very facile; **4** became the major species in the reaction mixture in a matter of hours. On the other hand, the conversion of **4** to **2** was very slow; **2** was only a minor species even after **3** was converted to **4**. Also in this reaction, no evidence for the formation of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})(\text{SiCl}_3)$ or **1** was observed. The reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ 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 $\text{Cp}(\text{PR}_3)_2\text{Ru}$ ($\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$) moiety could readily be methylated by AlMe_3 .^{5,6} Thus, in a similar manner, the trimethylsilyl derivative $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_3)_2$ (**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).



($\text{SiX}_3)_2 = (\text{SiCl}_3)_2$ (**1**), $(\text{SiMeCl}_2)_2$ (**2**), $(\text{SiMe}_2\text{Cl})_2$ (**3**), $(\text{SiMe}_2\text{Cl})(\text{SiMeCl}_2)$ (**4**)

The reaction in eq 1 was readily extended to other arene systems. $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})_2$ (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 $\text{RuCl}_2(\text{PPh}_3)_3$ with HSiMe_2Cl in the corresponding arene (eq 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 $(\eta^6\text{-arene})\text{RuL}(\text{SiX}_3)_2$ complexes. The preparation of $(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\text{CO})(\text{xantsil})$ was a two-step process, employing temperatures up to 120 °C; $\text{Ru}_3(\text{CO})_{12}$ was reacted with xantsilH_2 to form $\text{Ru}(\text{CO})_4(\text{xantsil})$, which was then reacted with toluene to form $(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\text{CO})(\text{xantsil})$.¹³ $(\eta^6\text{-C}_6\text{H}_6\text{-}n\text{R}_n)\text{Ru}(\text{CO})(\text{SiCl}_3)_2$ ($\text{R} = \text{Me}$, $n = 1\text{--}4$, 6; $\text{R} = \text{Bu}^t$, $n = 1\text{--}2$; $\text{R} = \text{Cl}$, $n = 1$) were prepared

(16) Yardy, N. M.; Lemke, F. R. *Main Group Chem.* **2000**, 3, 143–147.

(17) Kono, H.; Wakao, N.; Ito, K.; Nagai, Y. *J. Organomet. Chem.* **1977**, 132, 53–67.

(18) Svoboda, P.; Rericha, R.; Hettflejs, J. *Collect. Czech. Chem. Commun.* **1974**, 39, 1324–1329.

(19) Haszeldine, R. N.; Malkin, L. S.; Parish, R. V. *J. Organomet. Chem.* **1979**, 182, 323–332.

(20) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, 19, 213–255.

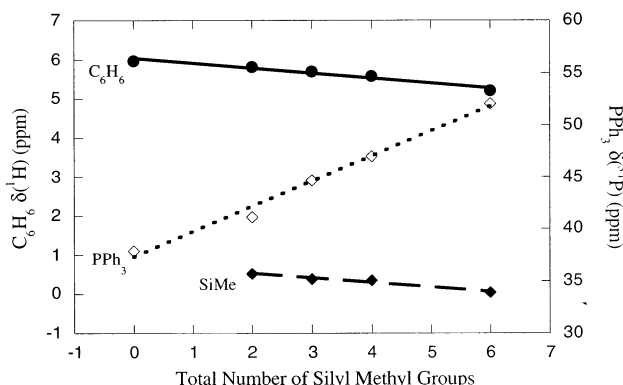


Figure 1. ^1H NMR chemical shifts of the C_6H_6 and SiMe groups and the ^{31}P NMR chemical shift of PPh_3 versus the total number of methyl groups in the ruthenium silyl complexes $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ (**1**–**5**). Average values were used for the SiMe ^1H NMR chemical shifts of **3** and **4**.

by heating *cis*- or *trans*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$ with the appropriate arene in excess of 120°C .¹² The facile synthesis of $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ complexes reported herein will make this class of silyl complexes more readily available for further investigation.

NMR Spectra of $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$. Multi-nuclear NMR characterizations of **1**–**11** were consistent with the formulation and molecular connectivity of these $\eta^6\text{-arene}$ bis(silyl) ruthenium complexes. In ^1H NMR spectra, the $\eta^6\text{-arene}$ 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 SiMe₂Cl 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 ($J_{\text{SiP}} = 25$ – 32 Hz) around 72–79 ppm in the $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR spectra; the only exception was the SiMe₃ group of **5**, which was observed as a doublet ($J_{\text{SiP}} = 26$ Hz) at 10.46 ppm. The PPh_3 groups were observed in the $^{31}\text{P}\{^1\text{H}\}$ 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 $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$. The crystal structures of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ ($\text{SiX}_3 = \text{SiCl}_3$ (**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 $(\eta^6\text{-benzene})\text{ruthenium}$ 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 $(\eta^6\text{-p-Bu}_2\text{C}_6\text{H}_4)\text{Ru}$ –

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiX}_3)_2$ ($\text{SiX}_3 = \text{SiCl}_3$ (**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))	129.2(2) (C(7)) 124.03(13) (C(7))	124.03(13) (C(7)) 112.8(2) (C(8))
	113.71(4) (Cl(2)) 112.03(8) (Cl(1))	112.03(8) (Cl(1)) 112.8(2) (C(8))	112.8(2) (C(8)) 113.45(14) (C(9))
	114.59(5) (Cl(3)) 110.66(8) (Cl(2))	110.66(8) (Cl(2)) 113.45(14) (C(9))	113.45(14) (C(9)) 125.23(13) (C(10))
Ru–Si(2)–X ^c	114.53(4) (Cl(4)) 118.3(2) (C(8))	118.3(2) (C(8)) 125.23(13) (C(10))	125.23(13) (C(10)) 112.8(2) (C(11))
	112.26(4) (Cl(5)) 122.33(8) (Cl(3))	122.33(8) (Cl(3)) 112.8(2) (C(11))	112.8(2) (C(11)) 113.14(14) (C(12))
	125.69(5) (Cl(6)) 112.52(7) (Cl(4))	112.52(7) (Cl(4)) 113.14(14) (C(12))	113.14(14) (C(12)) 100.9(15)
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.

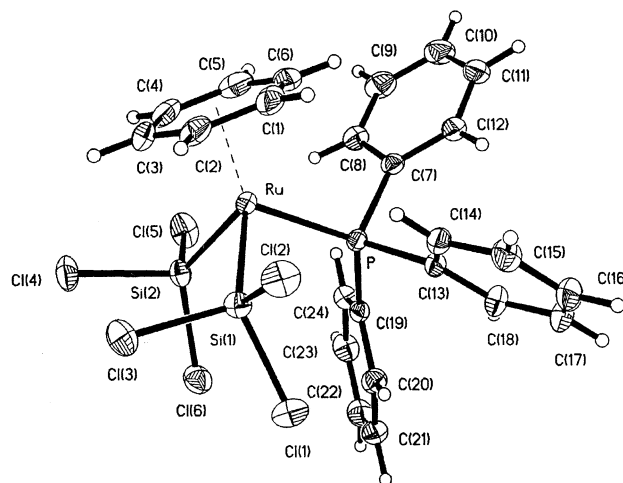


Figure 2. Perspective view of the molecular structure of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiCl}_3)_2$ (**1**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

$(\text{CO})(\text{SiCl}_3)_2$ (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 $\text{Cp}(\text{PR}_3)_2\text{Ru}(\text{SiX}_3)$ complexes.^{4,5,24}

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 $166.3 \pm 2.8^\circ$). The silyl group has a distorted-tetrahedral geometry with an average X–Si–X (X = Cl, C) angle of $100.3 \pm 0.7^\circ$ and an average Ru–Si–X angle of $117.3 \pm 2.4^\circ$. The anti Ru–Si–X angles ($125.2 \pm 1.8^\circ$ average) are significantly larger than the non-anti Ru–Si–X angles ($113.4 \pm 0.9^\circ$). 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 $\geq 10^\circ$ larger than Ru–Si–X angles

(21) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rapoport, Z., Eds.; Wiley: New York, 1991; pp 245–307.

(22) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rapoport, Z., Eds.; Wiley: New York, 1991; pp 309–364.

(23) Einstein, F. W. B.; Jones, T. *Inorg. Chem.* **1982**, *21*, 987–990.

(24) Freeman, S. T. N. Thesis, Department of Chemistry & Biochemistry, Ohio University, Athens, OH, 2002; p 194.

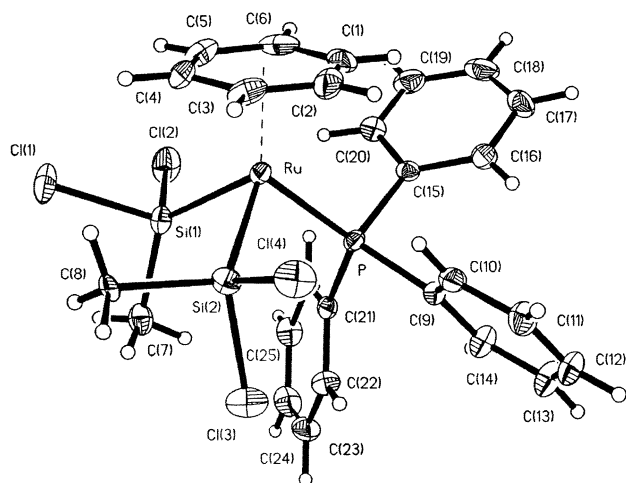


Figure 3. Perspective view of the molecular structure of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMeCl}_2)_2$ (**2**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

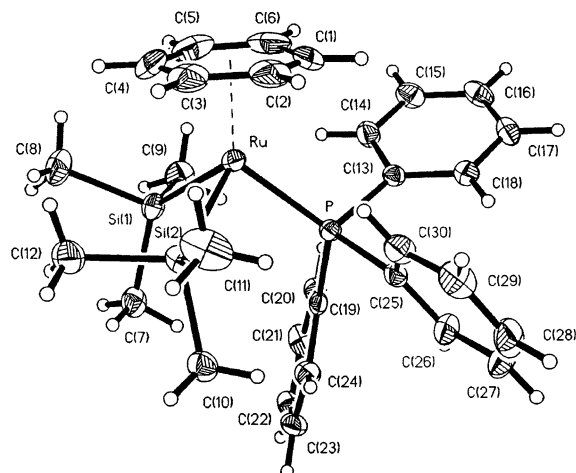


Figure 4. Perspective view of the molecular structure of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_3)_2$ (**5**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

for the other substituents on silicon: $\text{Cp}(\text{PMe}_3)_2\text{RuSiCl}_3$ ($\text{Ru-Si-Cl}(\text{anti}) = 125.6^\circ$ vs $\text{Ru-Si-Cl} = 115.9^\circ$ (av)),⁵ $\text{Cp}(\text{PMe}_3)_2\text{RuSiCl}_2\text{Cp}^*$ ($\text{Ru-Si-Cl}(\text{anti}) = 119.9^\circ$ vs $\text{Ru-Si-Cl} = 109.2^\circ$),³ $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2\text{H}$ ($\text{Ru-Si-H}(\text{anti}) = 112.9^\circ$ vs $\text{Ru-Si-Ph} = 98.8^\circ$ (av)),⁷ and $\text{Cp}^*(\text{PMe}_3)_2\text{RuSiPh}_2\text{OTf}$ ($\text{Ru-Si-OTf}(\text{anti}) = 118.2^\circ$ vs $\text{Ru-Si-Ph} = 96.9^\circ$ (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 $\text{Os}(\text{SiR}_3)\text{Cl}(\text{CO})\text{-(PPh}_3)_2$ ($\text{R} = \text{F, Cl, OH, Me}$), where the Os-Si distances increased from 2.273(6) Å ($\text{R} = \text{Cl}$) to 2.374(2) Å ($\text{R} = \text{Me}$).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 $\text{CpFe}(\text{CO})_2\text{SiR}_3$ ($\text{SiR}_3 = \text{SiCl}_3, \text{SiMe}_3$), 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 ^1H 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 . $^{29}\text{Si}\{^1\text{H}\}$ DEPT (79.5 MHz) was recorded on a Varian VXR 400S spectrometer and externally referenced to SiMe_4 .

Materials. $\text{RuCl}_2(\text{PPh}_3)_3$ was prepared by the published method²⁸ or used as received from Pressure Chemical (Lot #026588001). Hexanes, pentane, benzene, and toluene (Fisher) were deoxygenated with concentrated H_2SO_4 , distilled from potassium/benzophenone, and stored over $[\text{Cp}_2\text{TiCl}_2]_2\text{ZnCl}_2$.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 $[\text{Cp}_2\text{TiCl}_2]_2\text{ZnCl}_2$.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 $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiR}_3)_2$ ($\text{SiR}_3 = \text{SiCl}_3$ (1**), SiMeCl_2 (**2**)).** In a typical experiment, a 25 mL reaction vessel was charged with $\text{RuCl}_2(\text{PPh}_3)_3$ (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 $\text{RuCl}_2(\text{PPh}_3)_3$ than HSiCl_3 , possibly due to the decreased solubility of SiCl_3 -containing species. **1:** ^1H NMR (CD_2Cl_2) δ 7.45, 7.64 (m, 15 H, PPh_3), 5.97 (s, 6H, C_6H_6); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 134.90, 131.20, 128.21 (s, Ph), 101.5 (d, $J_{\text{PC}} = 32.1$ Hz, C_6H_6); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) insufficient solubility of **1** to obtain spectrum; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 37.87 (s, Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{Cl}_6\text{PRuSi}_2$: C, 40.58; H, 2.98. Found: C, 40.40; H, 3.21. **2:** ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 136.50, 134.96, 130.80, 128.05 (m, Ph), 100.30 (d, $J_{\text{PC}} = 25.2$ Hz, C_6H_6), 18.70 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$

(26) Lichtenberger, D. L.; Rai-Chaundhuri, A. *J. Am. Chem. Soc.* **1991**, *113*, 2923–2930.

(27) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(28) Komiya, S., Ed. *Synthesis of Organometallic Compounds: A Practical Guide*; Wiley: New York, 1997.

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

(30) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.

(25) Hübler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076–5083.

DEPT NMR (CD_2Cl_2) δ 77.26 (d, $J_{\text{SiP}} = 29.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 41.13 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{Cl}_4\text{PRuSi}_2$: 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 $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})_2$ (3**) and $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_2\text{Cl})(\text{SiMeCl}_2)$ (**4**).** A mixture of complexes **3**, **4**, and **2** was obtained from the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ 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 $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ (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 $\text{RuCl}_2(\text{PPh}_3)_3/\text{HSiMe}_2\text{Cl}$ 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); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 72.31 (d, $J_{\text{SiP}} = 23.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ 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); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 79.31 (d, $J_{\text{SiP}} = 33.0$ Hz), 73.27 (d, $J_{\text{SiP}} = 26.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 44.67 (s).

Synthesis of $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{SiMe}_3)_2$ (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); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 134.40, 129.36, 127.51 (m, Ph), 92.18 (d, $J_{\text{PC}} = 2.3$ Hz, C_6H_6), 11.04 (s, SiMe_3); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 10.46 (d, $J_{\text{SiP}} = 25.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ 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 $(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)(\text{SiMeCl}_2)_2$ (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 $\text{RuCl}_2(\text{PPh}_3)_3$ (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, $J_{\text{HH}} = 5.9$ Hz, 2H, CH),

1.90 (s, 3H, Me), 0.48 (s, 6H, SiCl_2Me); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 136.24 (d, $J_{\text{PC}} = 45.0$ Hz, PPh_3 *ipso*-C), 135.32 (d, $J_{\text{PC}} = 10.7$ Hz, PPh_3 *o*-C), 130.82 (s, PPh_3 *p*-C), 128.04 (d, $J_{\text{PC}} = 10.0$ Hz, PPh_3 *m*-C), 118.93 (s, *CMe*), 101.99, 99.87, 97.66 (s, toluene CH), 19.49 (s, *CMe*), 18.90 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 77.86 (d, $J_{\text{SiP}} = 29.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 44.27 (s). Anal. Calcd for $\text{C}_{29}\text{H}_{27}\text{Cl}_4\text{PRuSi}_2$: 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); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 135.52 (d, $J_{\text{PC}} = 10.7$ Hz, PPh_3 *o*-C), 130.74 (d, $J_{\text{PC}} = 1.5$ Hz, PPh_3 *p*-C), 127.93 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3 *m*-C), 117.30 (s, *CMe*), 103.21 (s, xylene CH), 97.60 (s, xylene CH), 18.96 (s, *CMe*), 17.90 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 78.82 (d, $J_{\text{SiP}} = 29.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 45.66 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{Cl}_4\text{PRuSi}_2$: 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, $J_{\text{HH}} = 6.1$ Hz, 1H, CH), 5.76 (d, $J_{\text{HH}} = 6.1$ Hz, 2H, CH), 4.94 (s, 1H, CH), 2.06 (s, 6H, Me), 0.44 (s, 6H, SiCl_2Me); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 135.67 (d, $J_{\text{PC}} = 10.8$ Hz, PPh_3 *o*-C), 130.83 (d, $J_{\text{PC}} = 2.3$ Hz, PPh_3 *p*-C), 127.97 (d, $J_{\text{PC}} = 9.9$ Hz, PPh_3 *m*-C), 117.64 (s, *CMe*), 106.90 (s, xylene CH), 99.65 (d, $J_{\text{PC}} = 2.3$ Hz, xylene CH), 97.52 (d, $J_{\text{PC}} = 2.3$ Hz, xylene CH), 19.68 (s, *CMe*), 19.08 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 77.87 (d, $J_{\text{SiP}} = 30.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 46.37 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{Cl}_4\text{PRuSi}_2$: 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); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 137.01 (d, $J_{\text{PC}} = 45.8$ Hz, PPh_3 *ipso*-C), 135.42 (d, $J_{\text{PC}} = 10.7$ Hz, PPh_3 *o*-C), 130.65 (d, $J_{\text{PC}} = 2.3$ Hz, PPh_3 *p*-C), 127.92 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3 *m*-C), 117.34 (s, *CMe*), 100.49 (d, $J_{\text{PC}} = 3.0$ Hz, xylene CH), 19.80 (s, *CMe*), 19.76 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 78.67 (d, $J_{\text{SiP}} = 29.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 44.61 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{31}\text{Cl}_4\text{PRuSi}_2$: 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); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 135.82 (d, $J_{\text{PC}} = 9.7$ Hz, PPh_3 *o*-C), 130.82 (s, PPh_3 *p*-C), 127.84 (d, $J_{\text{PC}} = 9.9$ Hz, PPh_3 *m*-C), 112.88 (s, *CMe*), 105.72 (d, $J_{\text{PC}} = 1.5$ Hz, mesitylene CH), 19.84 (s, *CMe*), 19.13 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 77.46 (d, $J_{\text{SiP}} = 31.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 46.49 (s). Anal. Calcd for $\text{C}_{29}\text{H}_{33}\text{Cl}_4\text{PRuSi}_2$: 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, $J_{\text{HH}} = 6.1$ Hz, 2H, CH), 5.37 (m, 3H, CH), 3.33 (s, 3H, OMe), 0.50 (s, 6H, SiCl_2Me); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 135.38 (d, $J_{\text{PC}} = 10.8$ Hz, PPh_3 *o*-C), 130.78 (d, $J_{\text{PC}} = 2.2$ Hz, PPh_3 *p*-C), 127.92 (d, $J_{\text{PC}} = 9.8$ Hz, PPh_3 *m*-C), 114.22 (s, *CMe*), 103.41 (d, $J_{\text{PC}} = 2.2$ Hz, anisole CH), 89.10 (d, $J_{\text{PC}} = 3.1$ Hz, anisole CH), 84.78 (s, anisole CH), 56.59 (s, OMe), 18.67 (s, SiCl_2Me); $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR (CD_2Cl_2) δ 78.91 (d, $J_{\text{SiP}} = 28.7$ Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_4\text{OPRuSi}_2$: 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>.