

Ruthenium(IV) Silyl Hydride Complexes *via* Reaction of Silanes with 16-Electron $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{X}]$ ($\text{X} = \text{Cl}, \text{CH}_2\text{SiHPh}_2, \text{SiMePh}_2$) Complexes. Hydride Migrations to an η^2 -Silene Ligand

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Reactions of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\eta^2\text{-CH}_2\text{=SiPh}_2)]$ with hydrosilanes occur *via* initial migration of hydride to the silene ligand, and eventually give disilyl hydride or silyl dihydride ruthenium(IV) complexes; the 16-electron chloride $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{Cl}]$ adds mesityl (Mes) silane to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})_2(\text{SiHCIMes})]$ which was crystallographically characterized.

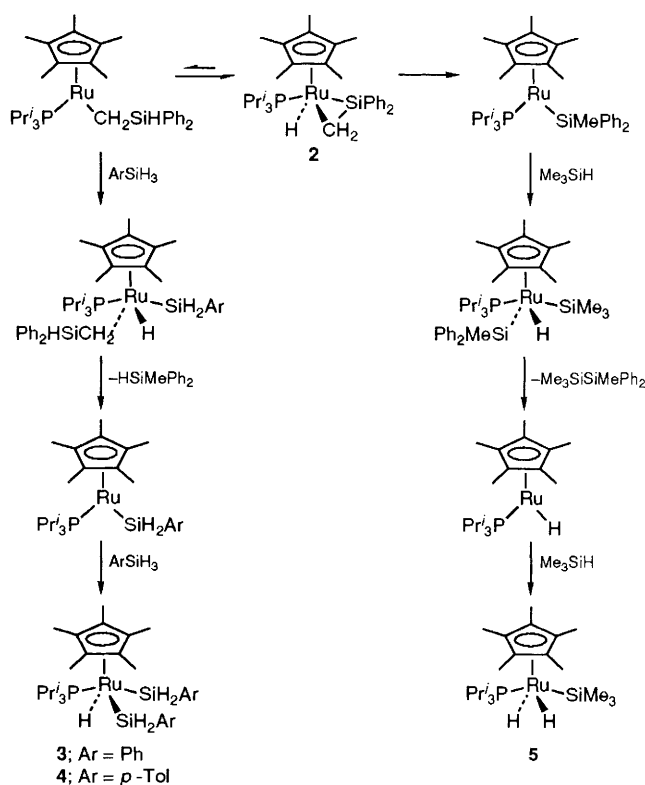
In attempts to develop new transition metal-silicon chemistry, we have synthesized electron-rich, 16-electron ruthenium complexes which readily add Si-H bonds to form stable Ru-Si bonded complexes.¹ For example, intramolecular Si-H oxidative addition (or β -hydrogen transfer) to ruthenium in

$[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{CH}_2\text{SiHPh}_2]$, generated by reaction of $\text{ClMgCH}_2\text{SiHPh}_2$ with $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{Cl}]$ **1**, was used to produce the first isolated η^2 -silene complex, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\eta^2\text{-CH}_2\text{=SiPh}_2)]$ **2**.^{1c} Here we describe reactions of this silene complex with hydrosilanes, which go

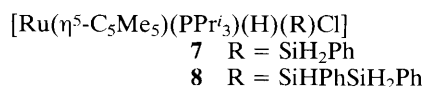
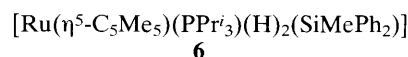
via 16-electron alkyl or silyl derivatives produced by migration of hydride back to the silene ligand. For comparison, we also describe some intermolecular reactions of the 16-electron ruthenium chloride **1** with silanes. The reactions above produce ruthenium(IV) silyl hydride complexes, via sequences of oxidative addition–reductive elimination steps that can lead to disilyl hydride or silyl dihydride complexes.

Addition of 2 equiv. of a primary silane ArSiH_3 ($\text{Ar} = \text{Ph}$, $p\text{-Tol}$; $p\text{-Tol} = p\text{-MeC}_6\text{H}_4$) to $[\text{H}_6]$ benzene solutions of **2** results in rapid, quantitative formation of the bis(silyl) complexes $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\text{SiH}_2\text{Ar})_2]$ **3**, $\text{Ar} = \text{Ph}$; **4**, $\text{Ar} = p\text{-Tol}$, with elimination of HSiMePh_2 . A preparative scale reaction gave complex **3** as colourless crystals from pentane, in 60% yield.[†] Based on comparison of the $^2J_{\text{PRuH}}$ coupling constants for **3** and **4** (30 and 31 Hz, respectively) with $^2J_{\text{PRuH}}$ values for other $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)(\text{H})(\text{X})(\text{Y})]$ complexes with a *cis*-arrangement of the hydride and phosphine ligands,² we conclude that the silyl ligands in **3** and **4** are *cis* to one another.[‡] Since the reaction of PhSiH_3 with $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{D})(\eta^2\text{-CH}_2=\text{SiPh}_2)]$ $[\text{H}_1]$ -**2** cleanly produces **3** and DSiMePh_2 (by ^1H and ^2H NMR spectroscopy), it appears that formation of **3** proceeds via exclusive migration of deuterium to the silene silicon atom to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{CH}_2\text{SiDPh}_2]$, which then reacts with the silane (Scheme 1).

Reactions of **2** with more sterically hindered silanes are slower, and proceed via a different pathway to mono(silyl) complexes, in addition to other products. For example, reaction of a diethyl ether solution of **2** with Me_3SiH (10 psi) gives two principal ruthenium-containing products (by ^1H NMR spectroscopy) which could not be separated by fractional crystallization from pentane. The major product (*ca.* 60%) was readily identified as $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})_2(\text{SiMe}_3)]$ **5** by its NMR spectra, which are very similar to those for thoroughly characterized $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})_2(\text{SiMePh}_2)]$ **6**.^{1d} Equivalent hydride



Scheme 1



[†] Isolated compounds were characterized by microanalysis and NMR (spectra in C_6D_6) and IR spectroscopy. Selected data: **3**: ^1H NMR (300 MHz): δ -11.40 (d, $^2J_{\text{PH}}$ 30 Hz, RuH), 1.07 (dd, $^3J_{\text{PH}}$ 13 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.48 (s, C_5Me_5), 2.19 (m, PCH), 4.94 (m, SiH), 5.22 (m, SiH), 7.23–7.33 (m, SiPh) and 8.13 (m, SiPh); ^{31}P NMR (121.5 MHz): δ 62.30; IR (Nujol): ν/cm^{-1} 2040 (SiH). **4**: ^1H NMR (300 MHz): δ -11.38 (d, $^2J_{\text{PH}}$ 31 Hz, RuH), 1.10 (dd, $^3J_{\text{PH}}$ 13 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.52 (s, C_5Me_5), 2.20 (s, SiTol), 2.22 (m, PCH), 4.96 (m, SiH), 5.25 (m, SiH), 7.14–7.16 (m, SiTol) and 8.06 (m, SiTol); ^{31}P NMR (121.5 MHz): δ 62.46. **5**: ^1H NMR (300 MHz): δ -12.33 (d, $^2J_{\text{PH}}$ 29 Hz, RuH), 0.62 (s, SiMe), 0.98 (dd, $^3J_{\text{PH}}$ 13 Hz, $^3J_{\text{HH}}$ 8 Hz, PCCH_3), 1.85 (m, PCH) and 1.62 (s, C_5Me_5); ^{31}P NMR (121.5 MHz): δ 81.50. **6**: ^1H NMR (300 MHz): δ -12.17 (d, $^2J_{\text{PH}}$ 28 Hz, RuH), 0.98 (dd, $^3J_{\text{PH}}$ 13 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.12 (s, SiMe), 1.82 (m, PCH) and 1.62 (s, C_5Me_5); ^{31}P NMR (121.5 MHz): δ 81.52. **8**: ^1H NMR (300 MHz): δ -9.80 (br, RuH), 1.10 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.42 (s, C_5Me_5), 2.23 (m, PCH), 4.97 (br, 3 H, SiH), 7.09–7.18 and 7.96 (m, 10 H, SiPh); ^{31}P NMR (121.5 MHz): δ 56.2 (br). The broad peaks at this temperature indicate a rapid dynamic process. IR (Nujol): ν/cm^{-1} 2045 and 2055 (SiH). **9**: ^1H NMR (300 MHz): δ -9.47 (d, $^2J_{\text{PH}}$ 34 Hz, RuH), 1.01 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.37 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.42 (s, SiMe), 1.51 (s, C_5Me_5) and 2.21 (m, PCH); ^{29}Si NMR (59.6 MHz): δ 61.8. **10**: ^1H NMR (300 MHz): δ -12.90 (d, $^2J_{\text{PH}}$ 26 Hz, RuH), -11.44 (d, $^2J_{\text{PH}}$ 26 Hz, RuH), 0.71 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 0.97 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.65 (m, PCH), 1.81 (s, C_5Me_5), 2.14 (s, $\text{C}_6\text{H}_2\text{Me}$), 2.78 (s, $\text{C}_6\text{H}_2\text{Me}_2$), 6.73 (s, C_6H_2) and 6.78 (m, SiH); ^{31}P NMR (121.5 MHz): δ 81.34; IR (Nujol): ν/cm^{-1} 2100 (SiH). **11**: ^1H NMR (300 MHz): δ -12.17 (d, $^2J_{\text{PH}}$ 29 Hz, RuH), 0.90 (dd, $^3J_{\text{PH}}$ 12 Hz, $^3J_{\text{HH}}$ 7 Hz, PCCH_3), 1.49 (m, PCH), 1.80 (s, C_5Me_5), 2.17 (s, $\text{C}_6\text{H}_2\text{Me}$), 2.70 (s, $\text{C}_6\text{H}_2\text{Me}_2$), 4.80 (s, SiH), 6.73 (s, C_6H_2) and 6.78 (m, SiH); ^{31}P NMR (121.5 MHz): δ 83.05.

[‡] The presence of only two SiH resonances in the ^1H NMR spectra for **3** and **4** indicates rapid fluxionality at room temperature that equilibrates the silyl ligands.

ligands for **5** give rise to a doublet in the ^1H NMR spectrum (δ -12.33, $^2J_{\text{PH}}$ 29 Hz) and a triplet in the selectively coupled ^{31}P NMR spectrum (δ 81.50, $^2J_{\text{PH}}$ 29 Hz). A minor product in this reaction, which appears also to be a silyl hydride complex, remains unidentified. In addition, $\text{Me}_3\text{SiSiMePh}_2$ was detected in the reaction mixture by ^1H NMR spectroscopy. It therefore appears that bulkier silanes are able to trap the 16-electron silyl complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{SiMePh}_2]$, which forms by the slower migration of hydride to the carbon atom of the silene ligand^{1d} (Scheme 1). Oxidative addition of silane to this unsaturated complex would give a disilyl hydride, and elimination of $\text{Me}_3\text{SiSiMePh}_2$ would then produce $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)\text{H}]$, a logical precursor to **5**. Initial NMR studies indicate that reactions of Me_2SiH_2 and MeSiH_3 with **2** behave similarly.

We have previously reported the oxidative addition of PhSiH_3 to **1**, which affords $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\text{SiH}_2\text{Ph})\text{Cl}]$ **7**.^{1a} We find that the analogous reaction occurs with $\text{Ph}_2\text{SiSiH}_2\text{Ph}$ and HSiMeCl_2 , but not with Bu_2SiH_2 , Ph_2SiHCl or PhMeHSiSiHMePh . The complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\text{SiHPhSiH}_2\text{Ph})\text{Cl}]$ **8** was isolated as a slightly impure, low-melting yellow solid that was identified by comparison of its NMR spectra with those for **7**. The compound $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})(\text{SiMeCl}_2)\text{Cl}]$ **9** was prepared by addition of HSiMeCl_2 to **1** in diethyl ether, and was isolated as yellow crystals from diethyl ether in 76% yield.

Reaction of **1** with MesSiH_3 ($\text{Mes} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$) in benzene gives the unexpected chlorosilyl complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}^i_3)(\text{H})_2(\text{SiHClMes})]$ **10** as colourless crystals from toluene (75% yield). The chiral silicon centre in **10** is

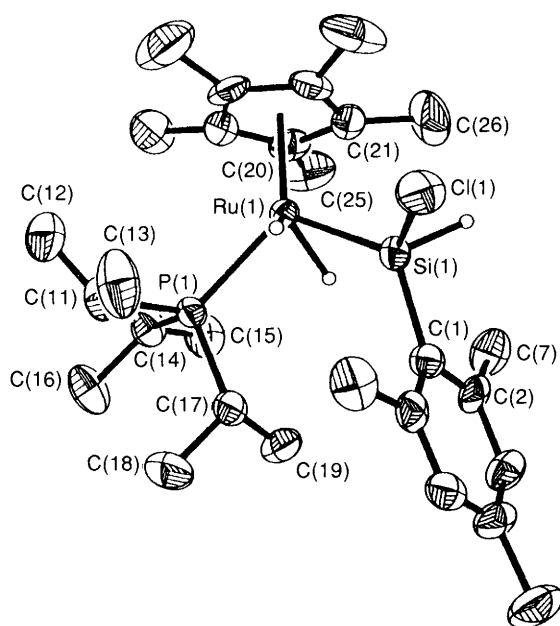
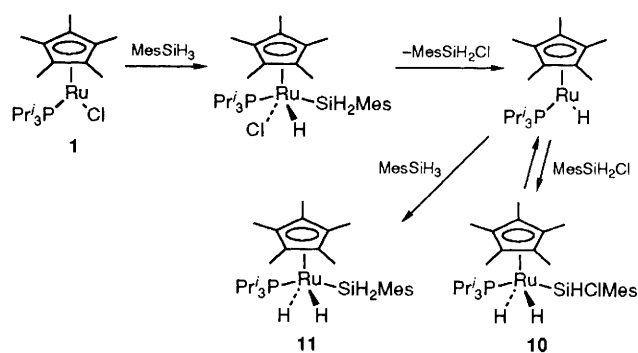


Fig. 1 ORTEP view of complex **10**. Selected distances (Å) and angles (°): Ru(1)–Si(1) 2.302(3), Ru(1)–P(1) 2.351(3), Ru(1)–H(1a) 1.50(9), Ru(1)–H(1b) 1.59(7), Si(1)–Cl(1) 2.170(4), Si(1)–H(2) 1.48(8), Si(1)–C(1) 1.904(11); H(1a)–Ru(1)–H(1b) 107.5(4), P(1)–Ru(1)–H(1a) 78.4(3), P(1)–Ru(1)–H(1b) 78.7(3), P(1)–Ru(1)–Si(1) 107.7(1), H(1a)–Ru(1)–Si(1) 64.3(3), H(1b)–Ru(1)–Si(1) 59.7(3), Ru(1)–Si(1)–Cl(1) 116.3(1), Ru(1)–Si(1)–H(2) 109.8(3), Ru(1)–Si(1)–C(1) 126.3(3), Cl(1)–Si(1)–C(1) 102.9(3).

responsible for inequivalent hydride ligands (by ^1H NMR spectroscopy), and diastereotopic methyl groups for the phosphine ligand. The SiH resonance (δ 6.78) experiences a considerable downfield shift relative to that for MesSiH_3 (δ 4.21), apparently because of the electronegative chlorine substituent. Molecules of **10** (Fig. 1) adopt a four-legged piano stool geometry, with a *trans*-arrangement for the hydride ligands. § Hydrogens on ruthenium and silicon were located and refined. The average Ru–H distance of 1.55 Å is

§ *Crystal data* for **10**: $\text{C}_{28}\text{H}_{50}\text{ClPRuSi}$, monoclinic, $P2_1/n$, $a = 10.293(2)$, $b = 19.038(4)$, $c = 16.071(4)$ Å, $\beta = 106.57(1)^\circ$, $U = 3018.6(10)$ Å 3 , $Z = 4$, $D_c = 1.28$ g cm $^{-3}$, $F(000) = 1232$, $\mu = 0.7$ mm $^{-1}$, Mo-K α radiation ($\lambda = 0.71073$ Å). Data were collected at *ca* 23 °C on a Nicolet R3m/ μ automated diffractometer using θ – 2θ scans and were corrected for absorption. Of 6209 reflections collected ($5^\circ \leq 2\theta \leq 50^\circ$), 5333 were independent ($R_{\text{int}} = 2.15\%$), and 3253 were considered observed [$F_o > 6\sigma(F)$]. The data were corrected for Lorentz and polarization effects, and for a decay in the intensity of 3 check reflections of approximately 4.5%. A semi-empirical absorption correction based on the Ψ scan method was employed. The minimum and maximum transmission factors for the correction were 0.781 and 0.953, respectively. Systematic absences uniquely determined the space group $P2_1/n$. The structure was solved via a Patterson map and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized, calculated positions, with a fixed thermal parameter approximately equal to 1.2 times the isotropic thermal parameter of the attached carbon atom. $R_F = 6.34$, $R_{wF} = 7.39$, $\text{GOF} = 1.96$ data/parameter = 10.9, largest $\Delta/\sigma = 0.000$, largest difference peak = 3.40 e Å $^{-3}$, located 0.42 Å from Ru. Calculations employed the Siemens SHELXTL PLUS computing package (Siemens Analytical X-ray Instruments, Inc., Madison, WI). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 2

comparable to the distance of 1.53 Å reported for $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)_3\text{H}]$.³ Interestingly, the Ru–Si distance of 2.302(3) Å is short compared to other Ru–Si distances, which in general range from 2.3 to 2.5 Å.⁴

We suggest that formation of the dihydride **10** also proceeds via the 16-electron intermediate $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2\text{H}]$, which is generated by Si–Cl reductive elimination from $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2(\text{H})(\text{Cl})(\text{SiH}_2\text{Mes})]$ (Scheme 2). The coordinatively unsaturated hydride would then be trapped by Si–H addition of MesSiH_2Cl . Support for this reaction scheme is provided by the fact that **1** reacts with an excess of MesSiH_3 (10 equiv.) to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2(\text{H})_2(\text{SiH}_2\text{Mes})]$ **11** and free MesSiH_2Cl . Complex **10** also reacts with excess of MesSiH_3 to give **11**. Therefore, in contrast to complex **7** which is stable in refluxing benzene, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2\text{H}(\text{Cl})(\text{SiH}_2\text{Mes})]$ and **10** are unstable with respect to reductive elimination of silane.

In summary, reactions of **2** with silanes are dominated by initial migration of hydride to the silene ligand. The resulting alkyl or silyl derivative reacts with hydrosilanes to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2(\text{SiR}_3)_2\text{H}]$ or $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPr}_3)_2(\text{H})_2(\text{SiR}_3)]$ complexes, depending (largely) on the steric bulk of the incoming silane. These processes involve both Si–H and Si–Si reductive eliminations. The reaction of **1** with MesSiH_3 involves chlorination of silicon, in a stoichiometric process that may be mechanistically related to commonly observed metal-mediated redistribution reactions at silicon, which are not well understood.⁵

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