

Synthesis and Reactivity of Dinuclear μ -Silyl Complexes of Ruthenium having Three-centre Two-electron Ru–H–Si Interactions

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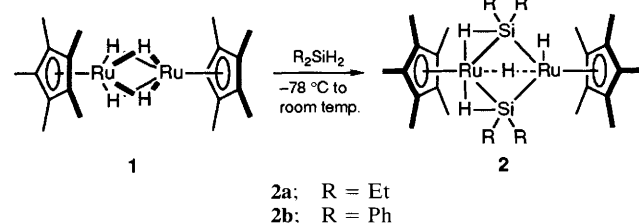
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Reaction of $[(C_5Me_5)Ru(\mu-H)_4Ru(C_5Me_5)]$ with R_2SiH_2 yields the dinuclear μ -silyl complexes $[(C_5Me_5)Ru(\mu-\eta^2-HSiR_2)]_2(\mu-H)(H)$ **2a**, R = Et; **2b**, R = Ph, having three-centre two-electron interactions, and pyrolysis of **2b** in refluxing toluene affords a dinuclear μ -silylene (silanediyl) complex $[(C_5Me_5)Ru(\mu-SiPh_2)]_2(\mu-H)_2Ru(C_5Me_5)$ **3**; the molecular structures of **2a** and **3** have been determined by X-ray diffraction.

Transition metal complexes having metal–silicon bonds have recently attracted considerable interest as key intermediates for transition metal-catalysed hydrosilylation of unsaturated hydrocarbons or polymerization of silanes. Transition metal complexes having both M–H and M–Si bonds are conventionally synthesized by the oxidative addition of hydrosilanes to low-valent coordinatively unsaturated metal centres. Since the first ' η^2 -H-SiR₃' complex was prepared in 1969,¹ many mononuclear complexes having M–H–Si bonds have been synthesized.² While several dinuclear metal complexes with bridging M–H–Si interactions have been reported,³ there is no precedent as far as ruthenium is concerned. We have already reported that coordinatively unsaturated dinuclear species could readily be generated from the dinuclear tetrahydride complex $[(C_5Me_5)Ru(\mu-H)_4Ru(C_5Me_5)]$ **1**.⁴ We report herein the synthesis of dinuclear μ -silyl complexes of ruthenium

having three-centre two-electron (3c–2e) M–H–Si interactions by the reaction of **1** with hydrosilanes. The X-ray structure determination and some reactions of the μ -silyl complexes are also reported.

The dinuclear ruthenium tetrahydride-bridged complex **1** readily reacted with dihydrosilanes R_2SiH_2 (R = Et and Ph) in toluene at low temperature to give the dinuclear μ -silyl complexes $[(C_5Me_5)Ru(\mu-\eta^2-HSiR_2)]_2(\mu-H)(H)$ **2a**, R = Et; **2b**, R = Ph, in excellent yields (Scheme 1).[†]



Scheme 1

[†] Selected spectroscopic data for new compounds: **2a**: ν_{RuH}/cm^{-1} (KBr) 2066; δ_H (500 MHz, 25 °C, $C_6D_5CD_3$) 1.92 (30H, s, C_5Me_5), –13.90 (4H, s, Ru–H–Si, Ru–H and Ru–H–Ru); δ_H (–80 °C) 2.03 (15H, s, C_5Me_5), 1.67 (15H, s, C_5Me_5), –12.81 (1H, s, Ru–H or Ru–H–Ru), –13.54 (2H, s, Ru–H–Si), –15.54 (1H, s, Ru–H–Ru or Ru–H); δ_C (125 MHz, 25 °C, C_6D_6) 93.1 (C_5Me_5), 16.4 (CH_2), 15.3 (CH_2), 12.6 (C_5Me_5), 11.5 (Me), 10.4 (Me).

2b: ν_{RuH}/cm^{-1} (KBr) 2082; δ_H (500 MHz, 25 °C, $C_6D_5CD_3$) 1.78 (30H, s, C_5Me_5), –12.96 (4H, s, Ru–H–Si, Ru–H and Ru–H–Ru); δ_H (–80 °C) 1.94 (15H, s, C_5Me_5), 1.46 (15H, s, C_5Me_5), –11.54 (1H, s, Ru–H or Ru–H–Ru), –12.75 (2H, s, Ru–H–Si), –14.50 (1H, s, Ru–H–Ru or Ru–H); δ_C (125 MHz, 25 °C, $[^2H_8]$ tetrahydrofuran) 146.6 (Ph-*ipso*), 144.9 (Ph-*ipso*), 137.1 (Ph), 135.6 (Ph), 128.3 (Ph), 127.0 (Ph), 126.9 (Ph), 94.8 (C_5Me_5), 12.3 (C_5Me_5).

3: δ_H (270 MHz, 25 °C, C_6D_6) 1.40 (30H, s, C_5Me_5), –19.69 (2H, s, Ru–H–Ru); δ_C (67 MHz, 25 °C, C_6D_6) 90.9 (C_5Me_5), 10.8 (C_5Me_5).

4: ν_{CO}/cm^{-1} (KBr) 1955; δ_H (500 MHz, 25 °C, CD_2Cl_2) 1.52 (30H, s, C_5Me_5); δ_C (67 MHz, 25 °C, CD_2Cl_2) 205.2 (CO), 99.0 (C_5Me_5), 10.7 (C_5Me_5).

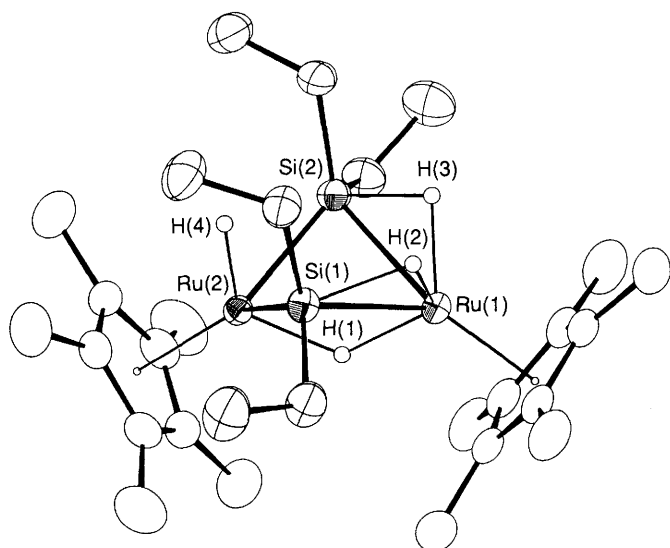


Fig. 1 Molecular structure of $[(C_5Me_5)Ru(\mu-\eta^2-HSiEt_2)_2(\mu-H)(H)]$ **2a**. Selected bond lengths (Å) and angles (°) are as follows: Ru(1)–Ru(2) 2.971(1), Ru(1)–Si(1) 2.544(2), Ru(1)–Si(2) 2.551(2), Ru(2)–Si(1) 2.338(1), Ru(1)–H(1) 1.71(5), Ru(1)–H(2) 1.63(4), Ru(1)–H(3) 1.72(4), Ru(2)–H(1) 1.69(5), Ru(2)–H(4) 1.45(4), Si(1)–H(2) 1.75(4), Si(2)–H(3) 1.68(4); Ru(1)–Si(1)–Ru(2) 74.84(4), Ru(1)–Si(2)–Ru(2) 74.76(4), Si(1)–Ru(1)–Si(2) 80.09(5), Si(1)–Ru(2)–Si(2) 89.09(4).

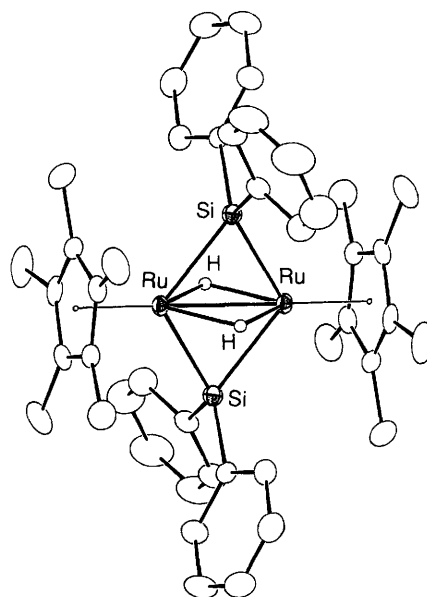
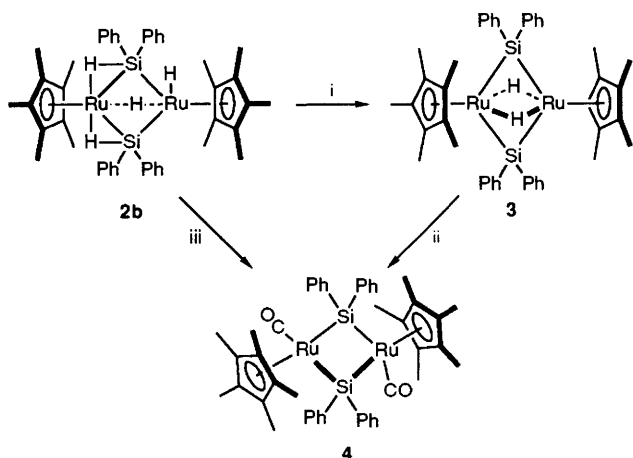


Fig. 2 Molecular structure of $[(C_5Me_5)Ru(\mu-SiPh_2)(\mu-H)]_2$ **3**. Selected bond lengths (Å) and angles (°) are as follows: Ru–Ru' 2.665(0), Ru–Si 2.364(1), Ru–Si' 2.360(1), Ru–H 1.73(3), Ru–H' 1.72(3); Ru–Si–Ru' 68.70(3), Si–Ru–Si' 111.30(3), H–Ru–H' 79(1), Ru–H–Ru' 101(1).

The structure of **2a** was determined by X-ray diffraction.‡ The asymmetric unit involves two equivalent molecules. The two independent molecular units are almost identical, and the very slight structural differences between them may reflect the influence of packing force. The structure of one of the two independent units is shown with the numbering scheme in Fig. 1. The hydrogen atoms were located in a difference Fourier map at a distance of 1.64 Å (average) from Ru and 1.68 Å (average) from Si and bridging the longer of the two Ru–Si bonds. While the shorter Ru–Si distance in **2a** lies in the



Scheme 2 Reagents and conditions: i, toluene, 110 °C, 4 h; ii, CO (10 atm), toluene, 150 °C, 30 min; iii, CO (10 atm), toluene, 150 °C, 4 h

Both complexes are very soluble in toluene and can be isolated as red-orange prisms from cold pentane. At 25 °C the 1H NMR spectra showed the hydride ligands to be equivalent. However, at –80 °C the 500 MHz 1H NMR spectra of **2a** and **b** showed a 1 : 2 : 1 ratio of hydride ligands. The T_1 values of the hydride ligands determined separately at –80 °C at 500 MHz; 0.81, 0.80 and 0.84 s for **2a** and 2.04, 2.02 and 2.06 s for **2b**, showed that complexes **2a** and **b** are not η^2-H_2 complexes but σ -bonded hydride complexes without bonding interactions between the hydride ligands. While the resonances for the two C_5Me_5 ligands in **2** were equivalent at 25 °C, inequivalent (1 : 1) C_5Me_5 groups were observed in the low-temperature spectra.

Although spectroscopic evidence for Ru–H–Si three-centred bonds in **2** is lacking, the crucial hydrides were located in the X-ray structure determinations and, therefore, the occurrence of the Ru–H–Si three-centred bonds was proved.

‡ Crystal data for **2a**: $C_{28}H_{54}Si_2Ru_2$, $M = 649.05$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.533(5)$, $b = 36.137(5)$, $c = 16.534(5)$ Å, $\beta = 92.11(3)^\circ$, $U = 6289(6)$ Å³, $Z = 8$, $D_c = 1.466$ g cm^{–3}, $\lambda(Mo-K\alpha) = 0.71069$ Å, $\mu(Mo-K\alpha) = 10.30$ cm^{–1}, $F(000) = 2704$, final R value 0.0287, $R_w = 0.0381$ for 8842 reflections with $F_o > 3\sigma(F_o)$. Intensity data were collected at 23 °C on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo–K α radiation in the $5^\circ < 2\theta < 50^\circ$ range. Data processing was performed on a Micro VAX II computer by using TEXSAN crystallographic software package.⁶ Metal atoms were located using direct methods. All non-hydrogen atoms and four hydrogen atoms bonded to the metal atoms were located by sequential difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Four metal-bonded hydrogen atoms were refined isotropically.

Crystal data for **3**: $C_{44}H_{52}Si_2Ru_2$, $M = 839.21$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.771(3)$, $b = 11.286(4)$, $c = 10.728(4)$ Å, $\alpha = 120.48(3)$, $\beta = 92.98(3)$, $\gamma = 113.09(2)^\circ$, $U = 980.5(7)$ Å³, $Z = 1$, $D_c = 1.421$ g cm^{–3}, $\lambda(Mo-K\alpha) = 0.71069$ Å, $\mu(Mo-K\alpha) = 8.44$ cm^{–1}, $F(000) = 432$, final R value 0.0308, $R_w = 0.0284$ for 3193 reflections with $F_o > 3\sigma(F_o)$. Intensity data were collected at 25 °C on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo–K α radiation in the $2^\circ < 2\theta < 55^\circ$ range. Data processing was performed on a FACOM A-70 computer by the using R-CRYSTAN structure solving program library obtained from Rigaku Corp. The unique Ru atom was located by direct methods. The remaining non-hydrogen atoms were located in difference Fourier maps and refined anisotropically by full-matrix least-squares. A difference map revealed a bridging hydrogen atom which was refined isotropically.

Atomic coordinates, bond lengths and angles, and thermal parameters for **2a** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

range expected for an Ru–Si single bond, the longer second Ru–Si distance may be attributed to an Ru–H–Si three-centre bond.

Some reactions of the μ -silyl complex **2b** are summarized in Scheme 2. The products **3** and **4** were identified by means of IR, ^1H NMR and ^{13}C NMR spectroscopy.[†]

While **2a** is thermally very stable, **2b** liberates two hydride ligands as molecular hydrogen in refluxing toluene to give a dinuclear μ -silylene complex **3** in which two hydrides bridge ruthenium centres.

The ^1H and ^{13}C NMR spectra show that both hydrides and C_5Me_5 groups are equivalent to each other. The di- μ -silylene complex **3** is sparingly soluble in most organic solvents. Its crystal structure was determined for a crystal from cold pentane, and confirmed the proposed structure.[‡] Fig. 2 shows the molecular structure of **3** with the numbering scheme. The molecule is centrosymmetric and the Ru–Ru distance of 2.665 Å is longer than that in $[(\text{C}_5\text{Me}_5)\text{Ru}(\mu\text{-H})_4\text{Ru}(\text{C}_5\text{Me}_5)]$ (2.463 Å)⁴ but shorter than that expected for an Ru–Ru single bond (2.75–2.93 Å).⁵ The shortening of the Ru–Ru distance in **3** compared with an Ru–Ru single bond may be explained by electronic reasons; the 18-electron rule applied to the dinuclear complex **3** required a double bond between the two ruthenium centres.

Treatment of **3** with carbon monoxide at 150 °C gave a carbonylated di- μ -silylene complex **4**, $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{CO})(\mu\text{-SiPh}_2)_2\text{Ru}(\text{CO})(\text{C}_5\text{Me}_5)]$. The spectroscopic data indicate that the two C_5Me_5 rings are mutually *trans* with respect to the Ru–Ru vector.

Complex **4** can be directly derived from **2b** by treatment with carbon monoxide (10 atm) at 150 °C for 4 h.

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