Preparation and Structure of a Disilarhodacycle, *fac*-$[\mathrm{\overline{Rh(SiMe_2CH_2CH_2SiMe_2}})\mathrm{H(PMe_3)_3}]$

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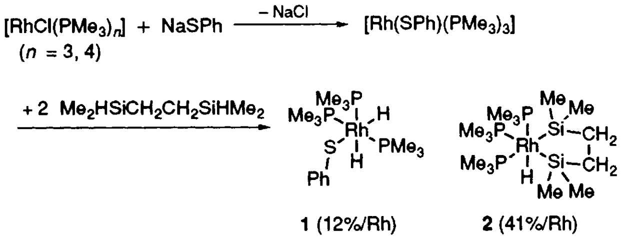
Treatment of $[\mathrm{Rh(SPh)(PMe_3)_3}]$, prepared *in situ* from $[\mathrm{RhCl(PMe_3)}_n]$ (n = 3, 4) and NaSPh, with 1,2-bis(dimethylsilyl)ethane gave a mixture of *cis,mer*-$[\mathrm{RhH_2(SPh)(PMe_3)_3}]$ **1** and *fac*-$[\mathrm{\overline{Rh(SiMe_2CH_2CH_2SiMe_2}})\mathrm{H(PMe_3)_3}]$ **2**; the structure of **2** has been determined by X-ray crystallography.

Although rhodium complexes catalyse various synthetic organic reactions such as hydrosilation, silylformylation and dehydrogenative coupling of hydrosilanes,[1–4] there have been only a limited number of reports on silylrhodium complexes[5] which are regarded to play important roles as intermediates in the above reactions. Recently $[\mathrm{RhCl(PPh_3)_3}]$ catalysed hydrosilation of nitriles, ketones and acetylenes using 1,2-bis(dimethylsilyl)ethane and 1,2-bis(dimethylsilyl)benzene was reported to give unique reaction products or to show a remarkably high reaction rate depending on the kind of the substrates employed.[6] The hydrosilanes react with Fe and Pt complexes to cause elimination of the two Si–H hydrogens giving disilametallacycles.[6a,7] The chelated disilyl ligand of a Fe carbonyl complex reacts with nitrile to give silyl-enamine.[8] Also in the above hydrosilation catalysed by $[\mathrm{RhCl(PPh_3)_3}]$ a mechanism involving a disilarhodacycle intermediate was postulated. In this paper we report the preparation of a novel disilarhodacycle complex by reaction of a $\mathrm{Rh^I}$ complex with $\mathrm{Me_2HSiCH_2CH_2SiHMe_2}$ and the structure determined by X-ray crystallography.

Previously, we have prepared $[\mathrm{Rh(SPh)(PMe_3)_3}]$, which undergoes facile oxidative addition of the S–H bond of thiol and the C–H bond of phenylacetylene to give the corresponding $\mathrm{Rh^{III}}$ complexes, respectively.[9] 1,2-Bis(dimethylsilyl)ethane also reacts smoothly with $[\mathrm{Rh(SPh)(PMe_3)_3}]$, prepared *in situ* from $[\mathrm{RhCl(PMe_3)}_n]$ (n = 3, 4) and NaSPh, to give a mixture of *cis,mer*-$[\mathrm{RhH_2(SPh)(PMe_3)_3}]$ **1** (12%) and *fac*-$[\mathrm{\overline{Rh(SiMe_2CH_2CH_2SiMe_2}})\mathrm{H(PMe_3)_3}]$ **2** (41%) (Scheme 1).† Although the reaction of $[\mathrm{Rh(SPh)(PMe_3)_3}]$ with an excess of 1,2-bis(dimethylsilyl)ethane (> 2 equiv. of Rh) proceeds at room temperature to give the reaction products, an equimolar reaction of the Rh complex with the hydrosilane does not give complex **2**.

The ^{1}H NMR spectrum of the complex **1** agrees well with the proposed structure.‡ Fig. 1 shows the molecular structure of complex **2** determined by X-ray crystallography.§ The molecule has a distorted octahedral coordination around the rhodium centre. The Rh–Si bond distances [2.383(2) and 2.389(2) Å] are larger than those of the rhodium complexes with chloro or phenyl substituted silyl ligands [2.203(4) and 2.298(2) Å][5a,e] and are comparable to that of the triethylsilylrhodium(v) complex [2.379(2) Å].[5b] The chelate ring structure is considerably distorted from the gauche chelate conformation common in five-membered chelating compounds. Dihedral angles P(1)–Rh–Si(1)–C(10) [73.7(3)°], P(2)–Rh–Si(2)–C(14) [68.8(3)°], P(1)–Rh–Si(1)–C(12) [49.6(4)°] and P(2)–Rh–Si(2)–C(15) [57.7(5)°] seem to indicate that the four methyl carbons on the Si atoms occupy positions between the ideal equatorial and axial positions. ^{1}H and ^{13}C{^{1}H} NMR



Scheme 1

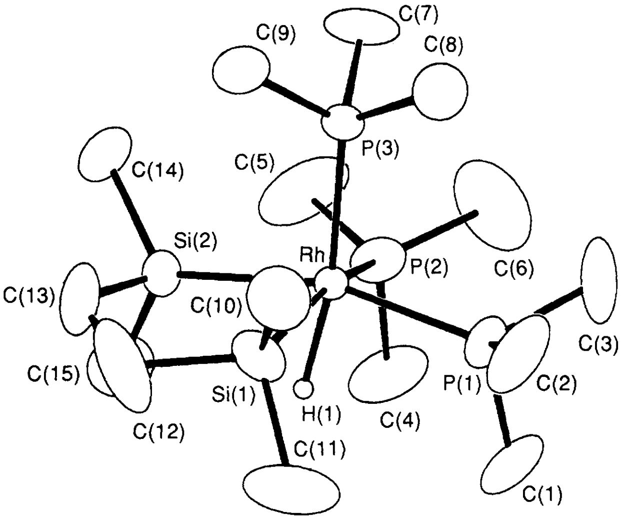


Fig. 1 A perspective drawing of complex **2**. Selected bond distances (Å) and angles (°): Rh–Si(1) 2.383(2), Rh–Si(2) 2.389(2), Rh–H(1) 1.53(4), Si(1)–C(12) 1.837(9), Si(2)–C(13) 1.933(11), Si(1)–Rh–Si(2) 80.46(7), Rh–Si(1)–C(12) 112.2(3), Rh–Si(2)–C(13) 108.5(3).

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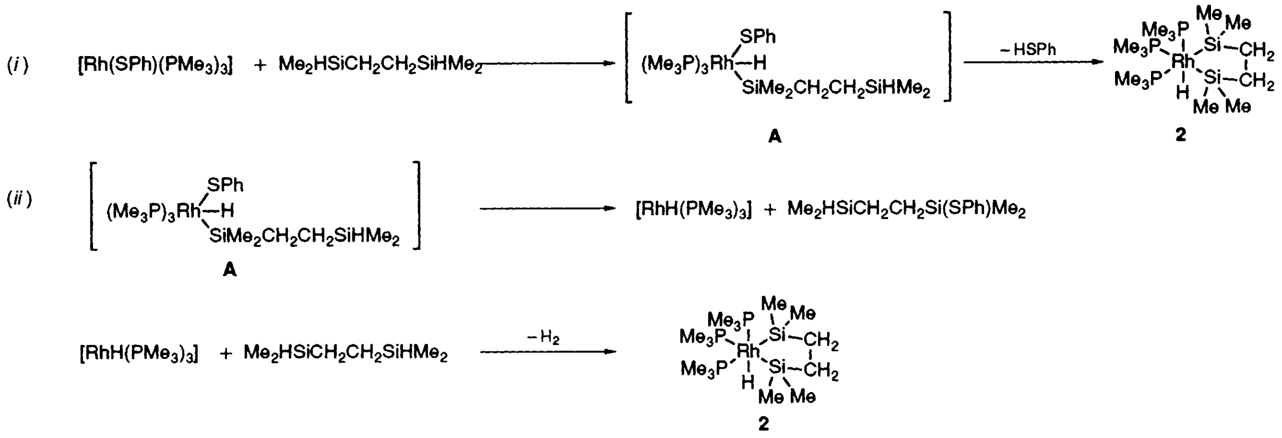
† *Detailed experimental procedure* for preparation of **2**: A mixture of $[\mathrm{Rh(PMe_3)_4}]$Cl (460 mg, 1.0 mmol) and NaSPh (180 mg, 1.3 mmol) was stirred in hexane (45 cm^3) under Ar for 24 h. After removal of NaCl by filtration 1,2-bis(dimethylsilyl)ethane (0.50 cm^3, *ca.* 3.0 mmol) in hexane (5 ml) was added to the reaction mixture. Stirring the reaction mixture for 7 days caused precipitation of **1** (51 mg, 12%) which was separated by filtration. The filtrate was condensed to *ca.* 20 cm^3 *in vacuo* to give a small amount of white solid. Gentle heating of the reaction mixture to dissolve the solid formed followed by cooling the resulting solution gave colourless crystals of **2** (140 mg, 28%). Condensation of the filtrate afforded **2** (64 mg, 13%) as a colourless solid. Preparation of **2** starting from $[\mathrm{RhCl(PMe_3)_3}]$ was carried out analogously.

‡ *Spectroscopic data* for **1**: ^{1}H NMR (100 MHz, $\mathrm{C_6D_6}$) δ –14.1 (ddtd, J 6, 14, 20 and 19 Hz, 1H, Rh–H), –9.2 (ddtd, J 6, 16, 21 and 165 Hz, 1H, Rh–H), 1.0 (d, J 7 Hz, 9H, P–CH$_3$), 1.2 (apparent triplet due to virtual coupling, J 3 Hz, 18H, P–CH$_3$), 6.9–8.3 (m, 5H, S–C$_6$H$_5$).

§ *Crystal data* for **2**: $\mathrm{C_{15}H_{44}P_3RhSi_2}$, M_r = 476.52, monoclinic, $P2_1/a$, a = 16.160(2), b = 9.3307(9), c = 16.442(2) Å, β = 90.47(1)°, U = 2479 Å^3, Z = 4, D_c = 1.275 g cm^{-3}, μ = 9.58 cm^{-1}, $F(000)$ = 1008, graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques to R = 0.035, R_w = 0.040 using 3094 reflections with F_o > 3σ(F_o). All calculations were carried out by using a program TEXSAN (P. N. Sweptson, 1986) on a DEC Micro VAXII. 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 Possible reaction pathways for the formation of **2**

spectra of **2**¶ show two sets of signals due to the hydrogen and carbon atoms of the Si–Me groups, respectively. The signals can be assigned to the two methyl groups situated on the same side of the Rh–Si(1)–Si(2) plane.

Scheme 2 shows two possible pathways [(*i*) and (*ii*)] for the formation of **2**. Path (*i*) involves initial oxidative addition of an Si–H bond of $Me_2HSiCH_2CH_2SiHMe_2$ to $[Rh(SPh)(PMe_3)_3]$ to give the intermediate Rh^{III} complex **A** that undergoes reductive elimination of HSPh and ensuing oxidative addition of the H–Si bond remaining in the silyl ligand. The other pathway (*ii*) involves the reductive elimination of $Me_2HSiCH_2CH_2Si(SPh)Me_2$ from the intermediate **A** to give $[RhH(PMe_3)_3]$ which undergoes further reaction with $Me_2HSiCH_2CH_2SiHMe_2$ to give **2** and H_2. Si–S bond formation by $[RhCl(PPh_3)_3]$ catalysed reaction of the thiol with hydrosilane has already been reported.[10] Pathway (*i*) involving formation of HSPh seems to be less plausible since the formation of $[RhH(SPh)_2(PMe_3)_3]$ which would be formed from the reaction of HSPh with $[Rh(SPh)(PMe_3)_3]$[9] was not observed in the reaction mixture. However, we cannot show unambiguously whether mechanism (*i*) or (*ii*) is operative in the above formation of **2** at present.

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¶ *Spectroscopic data* for **2**: ^1H NMR (500 MHz, C_6D_6) δ –11.12 (ddt, *J* 15, 15, 20 and 133 Hz, 1H, Rh–H), 0.52 (s, 6H, Si–CH_3), 0.64 (s, 6H, Si–CH_3), 1.04 (d, *J* 7 Hz, 9 H, P–CH_3), 1.09 (m, 18H, P–CH_3), 1.19 (s, 4H, Si–CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 9.09 (ddd, *J* 6.6, 7.4 and 7.4 Hz, Si–CH_3), 13.00 (dddd, *J* 2.5, 5.0, 5.8 and 5.8 Hz, Si–CH_3), 22.07 (ddd, *J* 3.3, 5.8 and 5.8 Hz, Si–CH_2), 25.05 (ddd, *J* 3.3, 8.5 and 10.2 Hz, P–CH_3), 23.77 (ddd, *J* 6.1, 6.1 and 19.0 Hz, P–CH_3).