Preparation and Structure of a Disilarhodacycle, *fac*-[$\overline{Rh(SiMe_2CH_2CH_2Si}Me_2)H(PMe_3)_3$]

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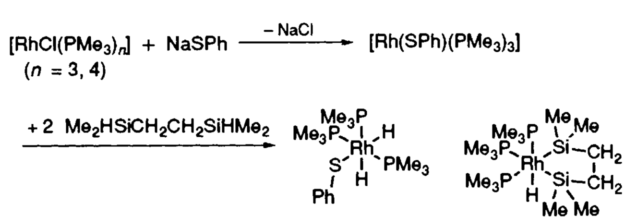
Treatment of [$Rh(SPh)(PMe_3)_3$], prepared *in situ* from [$RhCl(PMe_3)_n$] (n = 3, 4) and NaSPh, with 1,2-bis(dimethylsilyl)ethane gave a mixture of *cis,mer*-[$RhH_2(SPh)(PMe_3)_3$] **1** and *fac*-[$\overline{Rh(SiMe_2CH_2CH_2Si}Me_2)H(PMe_3)_3$] **2**; the structure of **2** has been determined 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 [$RhCl(PPh_3)_3$] 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 [$RhCl(PPh_3)_3$] a mechanism involving a disilarhodacycle intermediate was postulated. In this paper we report the preparation of a novel disilarhodacycle complex by reaction of a Rh^I complex with $Me_2HSiCH_2CH_2SiHMe_2$ and the structure determined by X-ray crystallography.

Previously, we have prepared [$Rh(SPh)(PMe_3)_3$], which undergoes facile oxidative addition of the S–H bond of thiol and the C–H bond of phenylacetylene to give the corresponding Rh^{III} complexes, respectively.[9] 1,2-Bis(dimethylsilyl)ethane also reacts smoothly with [$Rh(SPh)(PMe_3)_3$], prepared *in situ* from [$RhCl(PMe_3)_n$] (n = 3, 4) and NaSPh, to give a mixture of *cis,mer*-[$RhH_2(SPh)(PMe_3)_3$] **1** (12%) and *fac*-[$\overline{Rh(SiMe_2CH_2CH_2Si}Me_2)H(PMe_3)_3$] **2** (41%) (Scheme 1).† Although the reaction of [$Rh(SPh)(PMe_3)_3$] 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 ^1H 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. ^1H and $^{13}C\{^1H\}$ NMR



1 (12%/Rh) **2** (41%/Rh)

Scheme 1

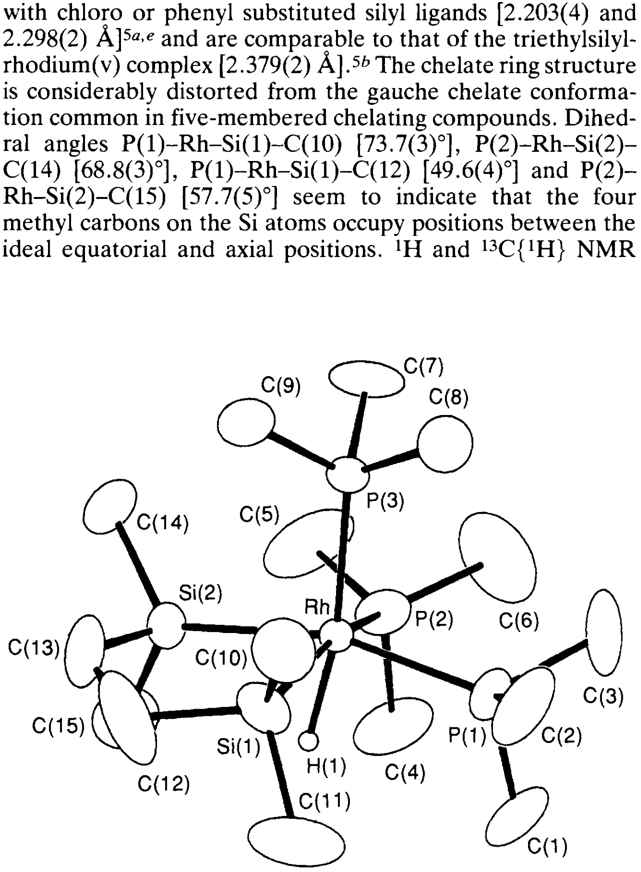


Fig. 1 A perspective drawing of complex **2**. Selected bond distances (Å) and angles (°): Rh–Si(1) 2.383(2), Rh–Si(2) 2.389(2), Rh–H(1) 1.53(4), Si(1)–C(12) 1.837(9), Si(2)–C(13) 1.933(11), Si(1)–Rh–Si(2) 80.46(7), Rh–Si(1)–C(12) 112.2(3), Rh–Si(2)–C(13) 108.5(3).

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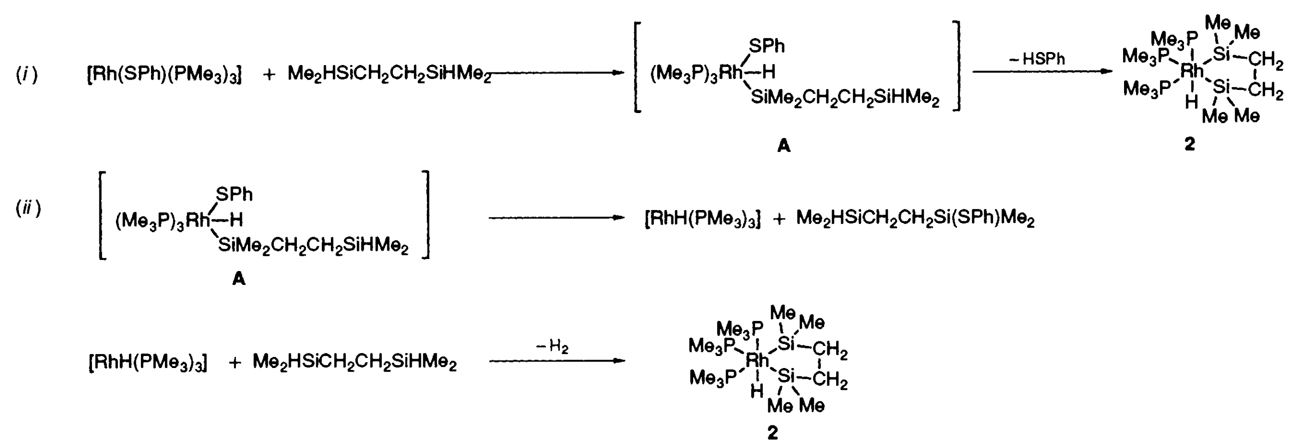
† *Detailed experimental procedure* for preparation of **2**: A mixture of [$Rh(PMe_3)_4$]Cl (460 mg, 1.0 mmol) and NaSPh (180 mg, 1.3 mmol) was stirred in hexane (45 cm^3) under Ar for 24 h. After removal of NaCl by filtration 1,2-bis(dimethylsilyl)ethane (0.50 cm^3, *ca.* 3.0 mmol) in hexane (5 ml) 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 [$RhCl(PMe_3)_3$] was carried out analogously.

‡ *Spectroscopic data* for **1**: ^1H NMR (100 MHz, 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_6H_5).

§ *Crystal data* for **2**: $C_{15}H_{44}P_3RhSi_2$, 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 $F_o > 3\sigma(F_o)$. 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**: ^{1}H 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).

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