Unique Intramolecular Exchange between H of $SiHPh_2$ and SAr in $[RhH(SiHPh_2)(SAr)(PMe_3)_3]$

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mer-$[RhH(SiHPh_2)(SAr)(PMe_3)_3]$, prepared from oxidative addition of H_2SiPh_2 to $Rh(SAr)(PMe_3)_3$, undergoes transfer of the thiolato ligand to the coordinated Si atom to give *fac*-$[RhH_2\{SiPh_2(SAr)\}(PMe_3)_3]$.

Transition-metal complex catalysed dehydrogenative condensation of primary or secondary silanes with alcohols, amines and thiols proceeds under mild conditions,[1,2] and has been applied to preparation of silyl ether and of precursors of silicon containing ceramics [eqn. (1)].

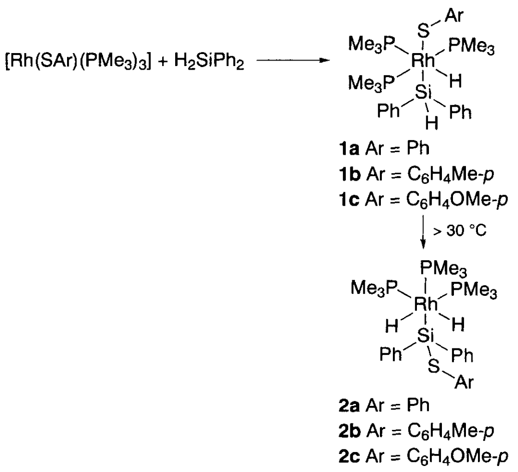
$$R_2SiH_2 + R'YH \xrightarrow[M]{} R_2(H)Si{-}YR' + H_2 \quad (Y = O, NH, S) \qquad (1)$$

Kinetic results on the reaction catalysed by an iridium complex are consistent with the reaction pathway involving nucleophilic reaction of alcohol on the organosilane coordinated to the Ir centre.[3] On the other hand, stoichiometric reaction of alkoxidoruthenium complexes with secondary or tertiary silanes giving the corresponding alkoxysilane suggests a significant role of the alkoxido ligand in the Si–O bond-forming reaction promoted by the metal complexes.[4] Mechanistic details of similar Si–S bond-forming reaction by transition-metal complexes is also intriguing. Although $[RhCl(PPh_3)_3]$ efficiently catalyses the dehydrogenative coupling of secondary silanes and thiols,[1d] stoichiometric reaction of organosilanes with thiolato transition-metal complexes has not been studied in detail. In relation to these catalytic and basic reactions, we report in this work a unique intramolecular exchange between H of coordinated $SiHPh_2$ and coordinated SAr in $[RhH(SiHPh_2)(SAr)L_n]$ type complexes, resulting in formation of the complexes with $SiPh_2(SAr)$ as ligand.

Reactions of H_2SiPh_2 with $[Rh(SAr)(PMe_3)_3]$ (Ar = Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*)[5] at room temperature cause facile oxidative addition of an Si–H bond to the Rh^I centre to give *mer*-$[RhH(SiHPh_2)(SAr)(PMe_3)_3]$ (Ar = Ph **1a**, C_6H_4Me-*p* **1b**, C_6H_4OMe-*p* **1c**) (Scheme 1). The spectroscopic and analytical results are in accord with the structures having three PMe_3 ligands at meridional coordination sites and thiolato and diphenylsilyl ligands at mutually *trans* positions.†

On standing, hexane or benzene solutions of **1a–c** above 30 °C are completely converted into *fac*-$[RhH_2\{SiPh_2(SAr)\}(PMe_3)_3]$ (Ar = Ph **2a**, $C_6H_4Me_{-p}$ **2b**, C_6H_4OMe-*p* **2c**) (Scheme 1).‡ Fig. 1 shows the molecular structure of **2a** as determined by X-ray crystallography.§ The molecule has a distorted octahedral coordination around the rhodium centre. Two hydrido ligands are situated at mutually *cis* positions, and three PMe_3 ligands occupy facial coordination sites. The Rh–Si bond distance [2.342(1) Å] is in the range of values reported for rhodium-(I) and -(III) silyl complexes (2.20–2.39 Å),[6] while the Si–S bond [2.228(1) Å] is longer than the corresponding bond distances of ruthenium, osmium and platinum complexes with thiolato substituents on a silylene ligand (2.07–2.20 Å).[7]

First-order plots of the reaction of **1b** giving **2b** are linear up to *ca.* 80% conversion as shown in Fig. 2. From the temperature dependence of the rate constants the following activation parameters are obtained: $\Delta G^\ddagger$ = 98.6 kJ mol^{-1}, $\Delta H^\ddagger$ = 94.9 kJ mol^{-1} and $\Delta S^\ddagger$ = −12.3 J mol^{-1} K^{-1} at 298 K. The reactions of **1a** and of **1c** also obey first-order kinetics. The above results are consistent with an intramolecular reaction pathway for the Si–S bond-forming reaction rather than an intermolecular pathway involving nucleophilic attack of thiolato ligand of a molecule on an $SiHPh_2$ ligand of other



Scheme 1 Reaction of H_2SiPh_2 with thiolato rhodium complexes

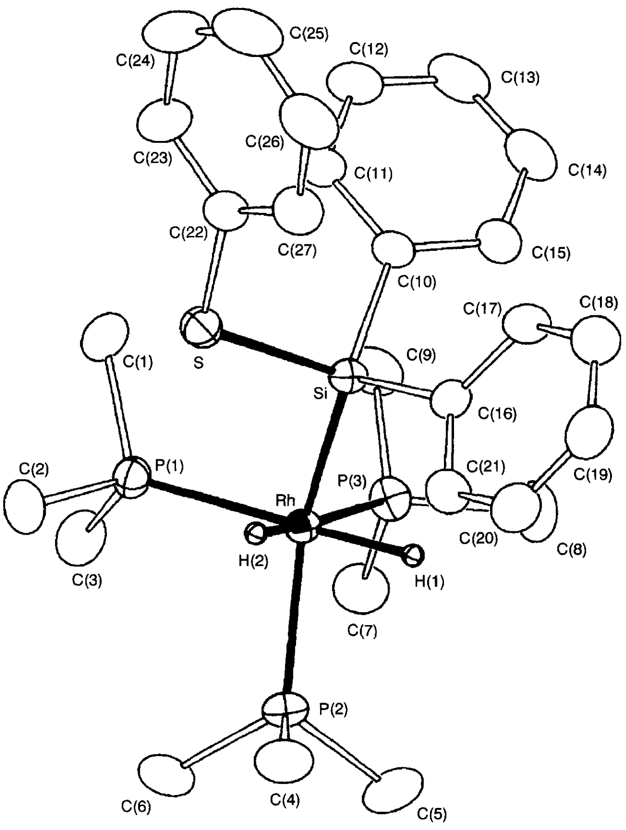


Fig. 1 A perspective drawing of complex **2a**. Selected bond lengths (Å) and angles (°): Rh–P(1) 2.326(1), Rh–P(2) 2.336(1), Rh–P(3) 2.331(1), Rh–Si 2.342(1), Rh–H(1) 1.57(2), Rh–H(2) 1.63(2), Si–S 2.228(1), Si–C(10) 1.907(2), Si–C(16) 1.913(2), P(1)–Rh–P(2) 100.00(5), P(1)–Rh–P(3) 96.24(5), P(1)–Rh–Si 100.74(5), P(1)–Rh–H(1) 173.6(8), P(1)–Rh–H(2) 89.2(8), P(2)–Rh–P(3) 100.95(5), P(2)–Rh–Si 145.62(3), P(2)–Rh–H(1) 81.4(8), P(2)–Rh–H(2) 84.7(8), P(3)–Rh–Si 103.70(5), P(3)–Rh–H(1) 89.6(8), P(3)–Rh–H(2) 171.3(8), H(1)–Rh–H(2) 85(1), Si–Rh–H(1) 75.2(8), Si–Rh–H(2) 68.5(8), Si–S–C(22) 110.70(8).

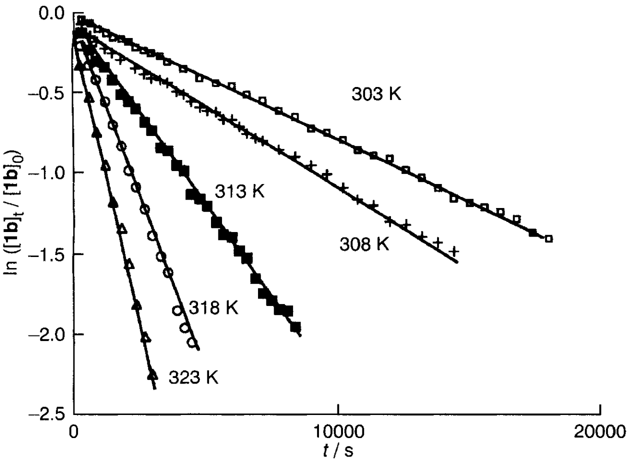


Fig. 2 First-order plots of conversion of **1b** to **2b** obtained from change of ^1H NMR peak intensity of Me hydrogens of the thiolato ligand of **1b**

molecules. Structural change of **1**, such as *trans–cis* isomerisation, seems to occur prior to the Si–S bond-forming reaction since direct intramolecular reaction of thiolato and $SiHPh_2$ ligands in mutually *trans* positions is not feasible. The present study provides the first intramolecular reaction between thiolato and secondary silyl ligands of transition-metal complexes resulting in Si–S bond formation.

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Footnotes

† *Preparation procedure and spectroscopic data* for **1a**. To a hexane (20 cm^3) solution of $[Rh(SPh)(PMe_3)_3]$ (240 mg, 0.55 mmol) was added H_2SiPh_2 (100 mg, 0.54 mmol) in hexane (3 cm^3). Stirring the mixture led to a change of colour of the solution from orange to pale yellow over a few minutes accompanied by formation of a colourless solid. Filtration of the resulting solid product after 3 h gave **1a** (260 mg, 79%). ^1H NMR (100 MHz, C_6D_6) δ −8.97 (ddt, *J* 16, 18 and 153 Hz, 1 H, Rh–H), 0.96 [d, *J* 7 Hz, 9 H, $P(CH_3)_3$], 1.19 [apparent triplet due to virtual coupling, 18 H, $P(CH_3)_3$], 5.47 (dt, *J* 10 and 11 Hz, 1 H, Si–H), 6.5–8.2 (m, 15 H, C_6H_5). $^{31}P\{^1H\}$ NMR (40 MHz, C_6D_6, ext. 85% H_3PO_4) δ −12.2 (dd, *J* 32 and 97 Hz), −28.0 (dt, *J* 32 and 91 Hz). IR (KBr) ν(RhH) 1966, ν(SiH) 2038 cm^{-1}. Complexes **1b** and **1c** were prepared similarly and gave satisfactory analytical and spectroscopic results.

‡ *Preparation procedure and spectroscopic data* for **2a**. Complex **1a** (60 mg, 0.096 mmol) was dissolved in hexane (20 cm^3) by gentle heating. The initial colourless solution turned gradually yellow. After stirring the solution for 48 h the mixture was cooled at −20 °C to give pale yellow crystals of **2a** (24 mg, 40%). ^1H NMR (100 MHz, C_6D_6) δ −10.05 (m, *J* 117 Hz, 2 H, Rh–H), 1.05 [d, *J* 7 Hz, 27 H, $P(CH_3)_3$], 6.5–8.2 (m, 15 H, C_6H_5). $^{31}P\{^1H\}$ NMR (40 MHz, C_6D_6, ext. 85% H_3PO_4) δ −18.4 (dd, *J* 23 and 102 Hz), −24.1 (dt, *J* 23 and 91 Hz). IR (KBr) ν(RhH) 1920 and 1930 cm^{-1}. Complexes **2b** and **2c** were prepared similarly and gave satisfactory analytical and spectroscopic results.

§ *Crystal data* for **2a**: $C_{27}H_{44}P_3RhSSi$, M_r = 624.63, triclinic, space group $P\bar{1}$ (no. 2), a = 10.856(5), b = 14.134(6), c = 10.842(5) Å, α = 97.07(4), β = 106.64(5), γ = 80.10(4)°, U = 1055 Å^3, Z = 2, D_c = 1.325 g cm^{-3}, μ = 8.030 cm^{-1}, $F(000)$ = 652, 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 = 0.022, R_w = 0.035 using 6519 reflections with $F_o \geqslant 3\sigma(F_o)$. All calculations were carried out by using the teXsan program system.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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