# Unique Intramolecular Exchange between H of SiHPh₂ and SAr in [RhH(SiHPh₂)(SAr)(PMe₃)₃]

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*mer*-[RhH(SiHPh₂)(SAr)(PMe₃)₃], prepared from oxidative addition of H₂SiPh₂ to Rh(SAr)(PMe₃)₃, undergoes transfer of the thiolato ligand to the coordinated Si atom to give *fac*-[RhH₂{SiPh₂(SAr)}(PMe₃)₃].
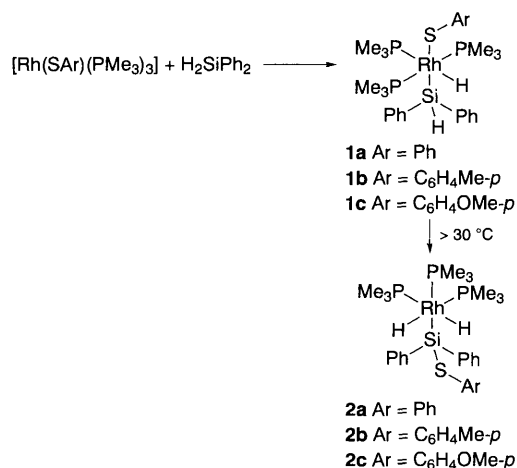
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Transition-metal complex catalysed dehydrogenative condensation of primary or secondary silanes with alcohols, amines and thiols proceeds under mild conditions,[1,2] and has been applied to preparation of silyl ether and of precursors of silicon containing ceramics [eqn. (1)].

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

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(PPh₃)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 SiHPh₂ and coordinated SAr in [RhH(SiHPh₂)-(SAr)Lₙ] type complexes, resulting in formation of the complexes with SiPh₂(SAr) as ligand.

Reactions of H₂SiPh₂ with [Rh(SAr)(PMe₃)₃] (Ar = Ph, C₆H₄Me-*p*, C₆H₄OMe-*p*)[5] at room temperature cause facile oxidative addition of an Si–H bond to the Rh¹ centre to give *mer*-[RhH(SiHPh₂)(SAr)(PMe₃)₃] (Ar = Ph **1a**, C₆H₄Me-*p* **1b**, C₆H₄OMe-*p* **1c**) (Scheme 1). The spectroscopic and analytical results are in accord with the structures having three PMe₃ 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*-[RhH₂{SiPh₂-(SAr)}(PMe₃)₃] (Ar = Ph **2a**, C₆H₄Me-*p* **2b**, C₆H₄OMe-*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 PMe₃ ligands occupy facial coordination sites. The Rh–Si bond distance [2.342(1) Å] is in the range of values reported for rhodium-(ɪ) and -(ɪɪɪ) 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 SiHPh₂ ligand of other
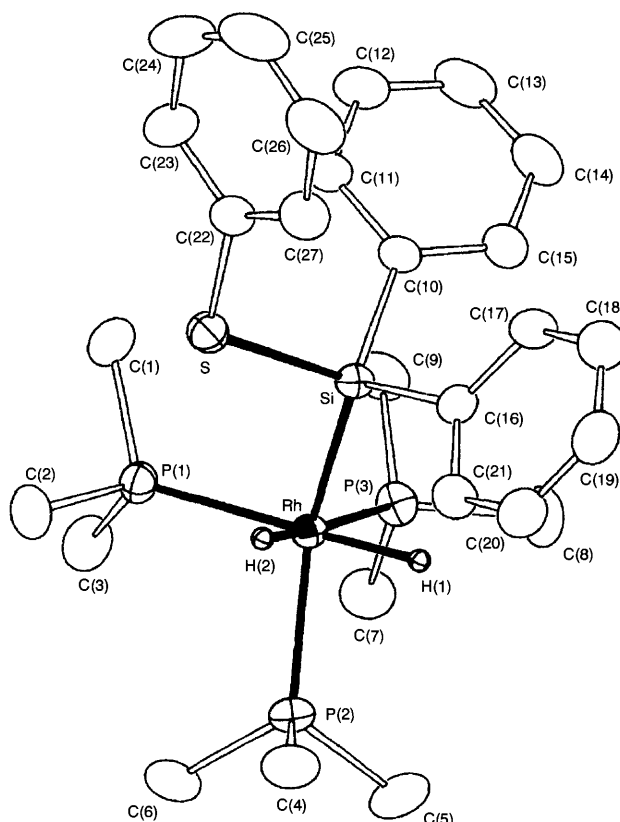


Fig. 1 A perspective drawing of complex **2a**. Selected bond lengths (Å) and angles (°): Rh–P(1) 2.326(1), Rh–P(2) 2.336(1), Rh–P(3) 2.331(1), Rh–Si 2.342(1), Rh–H(1) 1.57(2), Rh–H(2) 1.63(2), Si–S 2.228(1), Si–C(10) 1.907(2), Si–C(16) 1.913(2), P(1)–Rh–P(2) 100.00(5), P(1)–Rh–P(3) 96.24(5), P(1)–Rh–Si 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).

[Rh(SAr)(PMe₃)₃] + H₂SiPh₂ ⟶

Me₃P﹣Rh﹣PMe₃ (S–Ar top, Me₃P, H bottom, Si, Ph Ph H)

**1a** Ar = Ph
**1b** Ar = C₆H₄Me-*p*
**1c** Ar = C₆H₄OMe-*p*

↓ > 30 °C

Me₃P﹣Rh﹣PMe₃ (PMe₃ top, H H, Si, Ph Ph, S–Ar)

**2a** Ar = Ph
**2b** Ar = C₆H₄Me-*p*
**2c** Ar = C₆H₄OMe-*p*
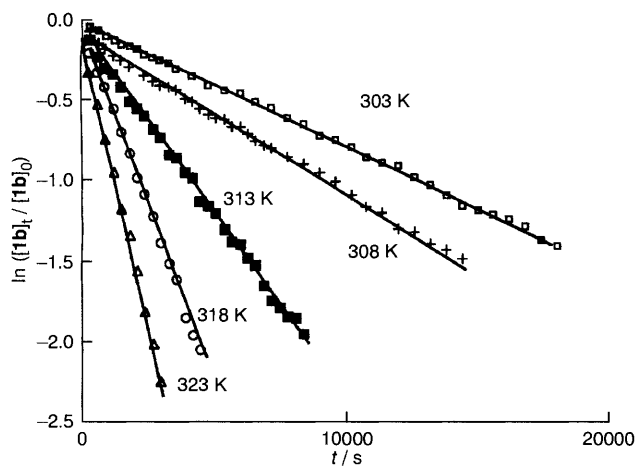
Scheme 1 Reaction of H₂SiPh₂ with thiolato rhodium complexes

Fig. 2 First-order plots of conversion of **1b** to **2b** obtained from change of $^1$H 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$_2$SiPh$_2$ (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%). $^1$H NMR (100 MHz, C$_6$D$_6$) 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$_6$H$_5$). $^{31}$P{$^1$H} NMR (40 MHz, C$_6$D$_6$, ext. 85% H$_3$PO$_4$) 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.

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