Thermal and Photochemical Reactions of Rhodium(trialkylsilyl)hydride Complexes: NMR and Bonding of Poly(silyl)(hydride) Complexes

Simon B. Duckett and Robin N. Perutz*

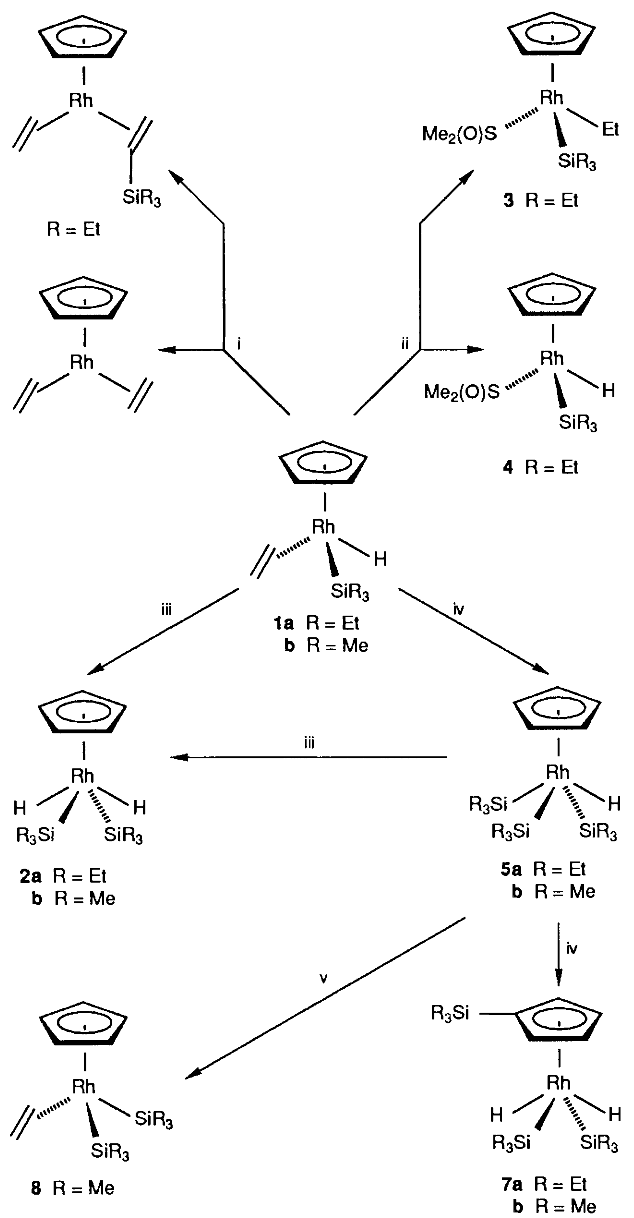
Department of Chemistry, University of York, York YO1 5DD, UK

Thermal reaction of (η^5-C_5H_5)Rh(C_2H_4)(H)(SiR_3) with R'_3SiH (R, R′ = Et, Me) generates the sterically hindered poly(silyl) complexes (η^5-C_5H_5)Rh(SiR'_3)$_2$(SiR_3)H, some of which contain an η^2-silane ligand; these complexes undergo silyl migrations with an excess of silane and also prove photosensitive.

We recently reported the photochemical synthesis of (Cp)Rh(C_2H_4)(H)(SiR_3) **1** (Cp = η^5-C_5H_5, **1a** R = Et, **1b** R = Me) and (Cp)Rh(SiR_3)$_2$(H)$_2$ **2** (**2a** R = Et, **2b** R = Me).[1] The former compounds are ideally set up for hydrosilation and are indeed hydrosilation catalysts. The latter belong to the increasingly numerous group of Rh^V and Ir^V organometallics.[2] Complexes **1** and **2** contain normal 2-centre Rh–Si and Rh–H bonds in contrast to several d^6 η^2-silane complexes.[3] Prior to examining the mechanism of hydrosilation by **1a** and **1b**, we have investigated their photochemical and thermal reactivity towards two-electron donors and trialkylsilanes. These studies have revealed contrasts between thermal and photochemical reactivity, and have generated a new class of sterically hindered poly(silyl) complexes, which probably possess dynamic η^2-silane ligands.

It is well known that metal(alkene)hydride complexes undergo a reversible [1,3] H-shift.[4] That complex **1** undergoes such a shift can be demonstrated by selectively generating the deuteriated complexes (Cp)Rh(C_2H_4)(D)(SiR_3) or (η^5-C_5D_5)Rh(C_2D_4)(H)(SiR_3) and following the growth/loss of the hydride resonance by ^{1}H NMR spectroscopy.† We expected, therefore, to be able to trap the resulting intermediate, (Cp)Rh(Et)(SiR$_3$), with a suitable ligand. CO and Bu^{t}NC react instead to displace the ligands from **1** yielding (Cp)Rh(C$_2$H$_4$)L and (Cp)RhL$_2$ (L = CO and Bu^{t}NC).[5] When the substrate is ethene, very slow reaction leads to (Cp)Rh(C$_2$H$_4$)$_2$ and (Cp)Rh(C$_2$H$_4$)(CH$_2$=CHSiEt$_3$) in a ratio of 2.5 : 1.[5] However, with Me$_2$SO, the (Cp)Rh(Et)(SiEt$_3$) intermediate is trapped to form (Cp)Rh(Me$_2$SO)(Et)(SiEt$_3$) **3** together with (Cp)Rh(Me$_2$SO)(H)(SiEt$_3$) **4** in a 1 : 1 ratio.‡ The identity of **4** was confirmed by its independent generation from reaction of **2a** with Me$_2$SO.[6]

The precursors **1a** and **1b**, and the products of reaction with silanes are ideal for NMR, since each element has a spin 1/2 nucleus. We have characterised the reaction products by ^{1}H, ^{13}C, ^{29}Si and sometimes ^{103}Rh NMR. The value of $^2J_{\text{Si-H}}$, characteristic of the bonding of the silane ligands (> 20 Hz in the η^2-SiH complexes), may be probed from the ^{29}Si spectrum or *via* the satellites in the ^{1}H spectrum.[3,7] The photochemical reaction of **1** with R$_3$SiH yields **2**. However, the thermal reaction generates (Cp)Rh(SiR$_3$)$_3$H **5** (**5a** R = Et, **5b** R = Me) and ethane with **2** formed as a minor product (Scheme 1). The



Scheme 1 Reactions of (Cp)Rh(C$_2$H$_4$)(H)(SiR$_3$), **1**. *Reagents and conditions*: i, C$_2$H$_4$; ii, Me$_2$SO; iii, HSiR$_3$, *h*ν; iv, HSiR$_3$, heat; v, *h*ν, C$_2$H$_4$.

Table 1 ^{29}Si NMR parameters for (Cp)Rh(SiR$_3$)$_3$H

Complex	$^2J_{\text{Si-H}}$/Hz	δ	$J_{\text{Rh-Si}}$/Hz
(Cp)Rh(SiEt$_3$)$_3$H **5a**	12.8	29.86	22.9
(Cp)Rh(SiMe$_3$)$_3$H **5b**	13.5	16.4	22.5
(Cp)Rh(SiEt$_3$)$_2$(SiMe$_3$)H	19.3	28.67	19.2 (SiEt$_3$)
6a	<3	17.2	33.3 (SiMe$_3$)
(Cp)Rh(SiEt$_3$)(SiMe$_3$)$_2$H	24.3	28.83	17.9 (SiEt$_3$)
6b	6.0	17.11	26.6 (SiMe$_3$)

---

† The half-life for the exchange of the hydridic proton in (C$_5$D$_5$)Rh(C$_2$D$_4$)(H)(SiR$_3$) is 4 h.

‡ Selected spectroscopic data for **3–8**. NMR spectra were recorded in [^{2}H$_8$]-toluene at 300 MHz (^{1}H). ^{13}C and ^{29}Si spectra (see Table 1 for **5** and **6**) were recorded either using the DEPT enhancement techniques or with decoupling only during data acquisition. ^{103}Rh spectra were recorded at 12.59 MHz.

3, ^{1}H: δ 4.93 (d, 5H, J_{RhH} 0.6 Hz, C$_5$H$_5$), 2.51 (q, 3H, $J_{\text{RhH}} = J_{\text{HH}} =$ 0.6 Hz, Me$_2$SO), 2.48 (m, 3H, Me$_2$SO), 1.97 (m, 1H, CH_{A}H$_{\text{B}}$CH$_3$), 1.47 (m, 4H, CH$_{\text{A}}H_{\text{B}}$CH_3), 1.19 (m, 9H, SiEt$_3$) and 1.07 (m, 6H, SiEt$_3$); ^{13}C{^{1}H} δ 92.68 (d, J_{RhC} 2.3 Hz, C$_5$H$_5$), 58.23 (d, J_{RhC} 2.1 Hz, Me$_2$SO), 55.72 (s, Me$_2$SO), 26.01 (d, J_{RhC} 1.5 Hz, RhCH$_2$CH$_3$), 11.7 (s, J_{SiC} 42.4 Hz, SiCH$_2$CH$_3$), 11.0 (s, SiCH$_2$CH$_3$) and 2.18 (d, J_{RhC} 26.7 Hz, RhCH$_2$CH$_3$). The ethyl group of (Cp)Rh(*Et*)(SiEt$_3$)(CD$_2$-SOCD$_3$) in CD$_3$SOCD$_3$ was identified by ^{1}H COSY at 360 MHz: δ 1.76 (m, 1H), 1.42 (t, 3H) and 1.35 (m, 1H); (*m/z* 284 (12%), 254 (27), 246 (34) and 196 (33); satisfactory C, H analysis.

4, ^{1}H: δ 4.97 (t, 5H, $J_{\text{RhH}} = J_{\text{HH}} =$ 0.5 Hz, C$_5$H$_5$), 2.54 (m, 3H, Me$_2$SO), 2.46 (d, 3H, J_{RhH} 0.6 Hz, Me$_2$SO), 1.21 (t, 9H, J_{HH} 7.2 Hz, SiCH$_2$CH_3), 1.03 (m, 6H, SiCH_2CH$_3$) and −13.45 (d, 1H, J_{RhH} 33.0 Hz, RhH); ^{13}C{^{1}H} δ 89.06 (d, J_{RhC} 1.3 Hz, C$_5$H$_5$), 59.79 (d, J_{RhC} 2.8 Hz, Me$_2$SO), 59.44 (s, Me$_2$SO), 13.05 (s, SiCH$_2$CH$_3$) and 10.71 (s, SiCH$_2$CH$_3$).

5a ^{1}H: δ 5.26 (dd, 5H, J_{RhH} 0.5 Hz, J_{HH} 0.2 Hz, C$_5$H$_5$), 1.06 (t, 27H, J_{HH} 8.0 Hz, SiCH$_2$CH_3), 0.98 (q, 18 H, J_{HH} 8.0 Hz, SiCH_2CH$_3$) and −13.18 (d, 1H, J_{RhH} 35.3 Hz, RhH); ^{13}C{^{1}H} δ 93.01 (d, J_{RhC} 2.1 Hz, C$_5$H$_5$), 15.34 (d, J_{RhC} 1.6 Hz, SiCH$_2$CH$_3$) and 11.16 (s, SiCH$_2$CH$_3$).

5b, ^{1}H: δ 5.00 (dd, 5H, J_{RhH} 0.5, J_{HH} 0.3 Hz, C$_5$H$_5$), 0.43 (dd, 27H, J_{RhH} 0.5, J_{HH} 0.3, J_{SiH} 6.4 Hz, SiMe$_3$) and −12.78 (d, 1H, J_{RhH} 36.6, RhH); ^{13}C{^{1}H} δ 94.5 (d, J_{RhC} 2.1 Hz, C$_5$H$_5$), 11.61 (d, J_{RhC} 0.9, J_{SiC} 46.9 Hz, SiMe$_3$); *m/z* 388 (0.02%, M$^+$), 372 (0.14), 357 (0.54), 341 (0.8), 314 (3.6), 298 (30), 242 (36), 240 (23), 226 (100), 211 (6.0), 196 (8.7) and 168 (6.6).

6a, ^{1}H: δ 5.06 (dd, 5H, J_{HH} 0.3, J_{RhH} 0.5 Hz, C$_5$H$_5$), 1.03 (t, J_{HH} 9 Hz, SiCH$_2$CH_3), 0.94 (q, J_{HH} 9 Hz, SiCH_2CH$_3$), 0.45 (dd, 18H, J_{HH} 0.2, J_{RhH} 0.5 Hz, SiMe$_3$) and −12.96 (d, 1H, J_{RhH} 35.9, RhH); ^{13}C{^{1}H} δ 94.02 (d, J_{RhC} 2.3 Hz, C$_5$H$_5$), 14.65 (s, SiCH$_2$CH$_3$), 12.13 (d, J_{RhC} 1.2 Hz, SiMe$_3$) and 10.48 (s, SiCH$_2$CH$_3$).

6b, ^{1}H: δ 5.13 (dd, 5H, J_{HH} 0.3, J_{RhH} 0.5 Hz, C$_5$H$_5$), 1.07 (t, J_{HH} 8 Hz, SiCH$_2$CH_3), 1.01 (dq, SiCH_2CH$_3$), 0.30 (s, 9H, SiMe$_3$) and −13.10 (d, 1H, J$_{\text{RhH}}$ 35.4, RhH); ^{13}C{^{1}H} δ 93.6 (d, J_{RhC} 2 Hz, C$_5$H$_5$), 15.24 (s, SiCH$_2$), 12.05 (d, J_{RhC} 1.2 Hz, SiMe$_3$) and 10.75 (s, SiCH$_2$CH$_3$).

7a, ^{1}H: δ 5.16 (m, 2H, C$_5$H$_4$) 5.13 (m, 2H, C$_5$H$_4$), 1.06 (t, 18H, J_{HH} 8 Hz, RhSiCH$_2$CH_3), 1.02 (t, 9H, J_{HH} 8 Hz, SiCH$_2$CH_3), 0.84 (q, 12H, J_{HH} 8 Hz, SiCH_2CH$_3$), 0.75 (q, 6H, J_{HH} 8 Hz, SiCH$_2$CH$_3$) and −14.08 (d, 2H, J_{RhH} 37.2, $^2J_{\text{SiH}}$ 7.0 Hz, RhH); ^{13}C{^{1}H} δ 98.93 (d, J_{RhC} 2.7 Hz, CH), 98.40 (d, J_{RhC} 2.3 Hz, *C*SiEt$_3$), 91.62 (d, J_{RhC} 2.5 Hz, CH), 14.88 (d, J_{RhC} 1Hz, RhSiCH$_2$) 9.99 (s, SiCH$_2$CH$_3$), 8.87 (s, SiCH$_2$CH$_3$) and 6.35 (s, SiCH$_2$); ^{29}Si{^{1}H} δ 37.35 (d, J_{SiRh} 16.8 Hz, RhSi) and −0.85 (s, C$_5$H$_4$Si); ^{103}Rh (^{1}H-INEPT) δ −1908 (−1,0,+1, J_{RhH} 37.3 Hz); *m/z* 398 (5%), 338 (9), 310 (16), 282 (8), 254 (8), 227 (8) and 196 (7); satisfactory C, H analysis.

7b, ^{1}H: δ 5.05 (m, 4H, C$_5$H$_4$), 0.42 (dt, 18H, J_{RhH} 0.6, J_{HH} 0.4 Hz, RhSiMe$_3$), 0.20 (s, 9H, J_{SiH} 6.75 Hz, SiMe$_3$) and −13.90 (d, 2H, J_{RhH} 39.2, $^2J_{\text{SiH}}$ 7.1, RhH); ^{13}C{^{1}H} δ 98.84 (d, J_{RhC} 2.8 Hz, CH), 91.55 (d, J_{RhC} 2.8 Hz, CH), 13.61 (d, J_{RhC} 1.6, J_{SiC} 47 Hz, RhSiMe$_3$) and 1.97 (s, J_{SiC} 52.6 Hz, C$_5$H$_4$Si*Me*$_3$); ^{29}Si{^{1}H} δ 6.61 (d, J_{SiRh} 0.4 Hz, C$_5$H$_4$Si) and 18.44 (d, J_{SiRh} 15.2 Hz, RhSi).

8, ^{1}H: δ 4.87 (d, 5H, J_{RhH} 0.5 Hz, C$_5$H$_5$), 2.18 (d, 4H, J_{RhH} 1.7 Hz, C$_2$H$_4$) and 0.30 (d, 18H, J_{RhH} 0.4, J_{SiH} 6 Hz, SiMe$_3$); ^{13}C{^{1}H} δ 94.0 (d, J_{RhC} 2.4 Hz, CH) 37.2 (d, J_{RhC} 11.6 Hz, CH$_2$) and 9.66 (d, J_{RhC} 0.9, J_{SiC} 44.7 Hz, SiMe$_3$); ^{29}Si{^{1}H} δ 23.95 (d, J_{SiRh} 30.5 Hz, SiMe$_3$).

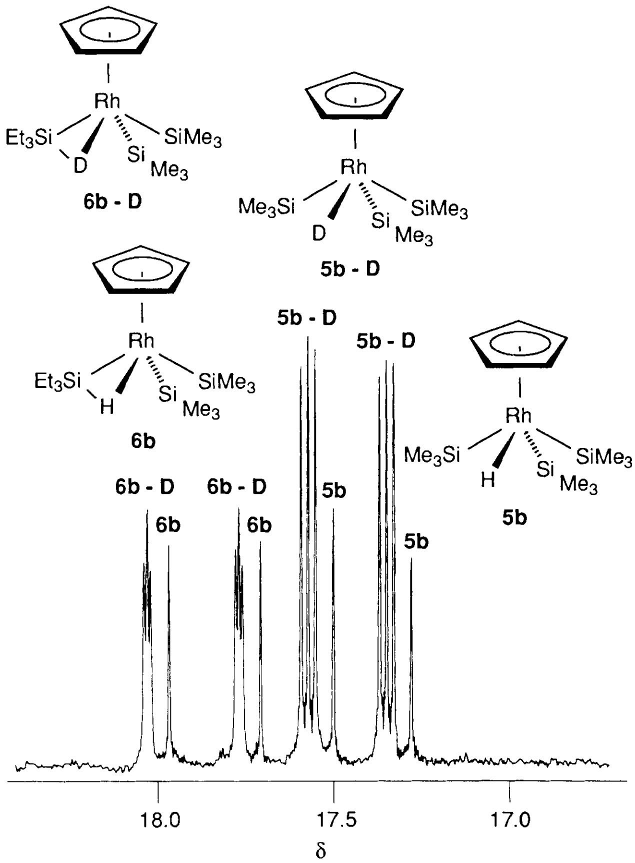
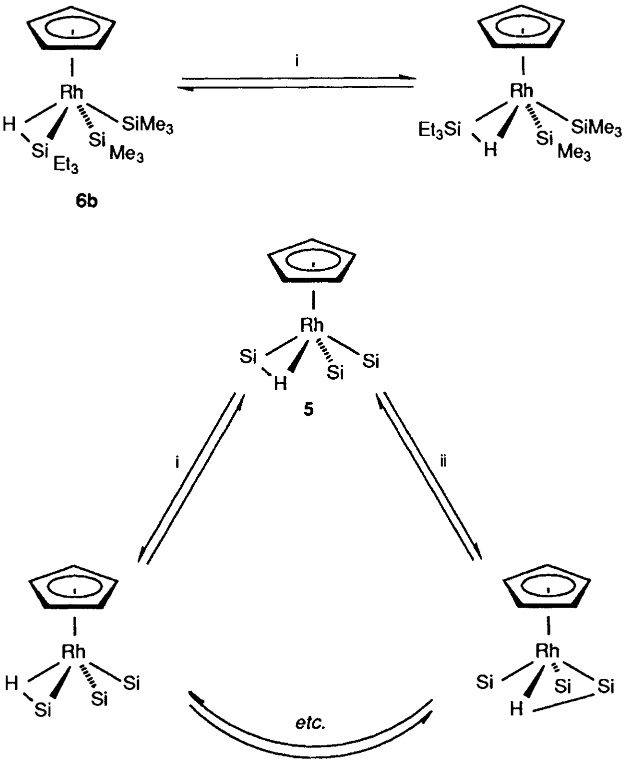


Fig. 1 $^{29}Si\{^{1}H\text{-INEPT}\}$ NMR spectrum showing the $SiMe_3$ region of products from the reaction of **1a** with Me_3SiD. Resonances for **5b**, **6b** and their deuteriated counterparts **5b-D** and **6b-D** each appear as doublets due to Rh coupling. The additional 1:1:1 triplet fine structure arises from Si–D coupling in $(Cp)Rh(SiMe_3)_3D$, **5b-D**, the exchange product and $(Cp)Rh(SiMe_3)_2(SiEt_3)D$ **6b-D**. The $^{2}J_{Si-D}$ couplings are significantly smaller than those for the $SiEt_3$ group in **6b-D**.

methyl product **5b** is stable at room temperature, but its ethyl analogue **5a** is thermally sensitive.‡ These tris(trialkylsilyl) complexes are probably formed by trapping of $(Cp)Rh(Et)(SiR_3)$ by R_3SiH followed by elimination of ethane and oxidative addition of a second molecule of R_3SiH (eqn. 1).

$$\underset{\mathbf{1}}{(Cp)Rh(C_2H_4)(SiR_3)H} \longrightarrow (Cp)Rh(Et)(SiR_3) \xrightarrow{R_3SiH} (Cp)Rh(Et)(H)(SiR_3)_2 \xrightarrow{-C_2H_6} (Cp)Rh(SiR_3)_2 \xrightarrow{R_3SiH} \underset{\mathbf{5}}{(Cp)Rh(SiR_3)_3H} \quad (1)$$

The M^{V} complexes $(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2$ and $(\eta^5\text{-}C_5Me_5)Ir(H)_3(SiMe_3)$, have been shown to adopt piano-stool configurations,[2] usually a rigid structure.[8] If this were true of **5b**, we would expect the $SiMe_3$ group *trans* to the hydride to be shifted relative to the two mutually *cis* $SiMe_3$ groups. However, the equivalence of all the ^{1}H, ^{13}C and ^{29}Si NMR resonances of the silyl groups, even at 197 K, requires either that this complex adopts a trigonal bipyramidal structure, or that it undergoes a rapid exchange process.§ Gilbert *et al.* observed such an exchange in the trihydrides $(\eta^5\text{-}C_5Me_5)IrH_3(SnR_3)$ (R = Ph and Me) and $(\eta^5\text{-}C_5Me_5)IrH_3(SiMe_3)$, but did not postulate an exchange mechanism.



Scheme 2 Fluxional motion of $(Cp)Rh(SiR_3)_3H$, **5** and **6**. i, η^2-Si–H rotation; ii, η^2-interchange.

As a further probe of the structure we synthesised the two mixed silyl complexes $(Cp)Rh(SiEt_3)_2(SiMe_3)H$ **6a** and $(Cp)Rh(SiMe_3)_2(SiEt_3)H$ **6b** by addition of the appropriate 'cross silane' to **1**.¶ In these complexes, the two different silyl groups within the same molecule exhibit very different $^{2}J_{Si-H}$ couplings, with the coupling to the $SiEt_3$ group far exceeding those to the $SiMe_3$ groups (Table 1 and Fig. 1). However, the pairs of $SiEt_3$ groups in **6a** still retain identical ^{1}H, ^{13}C and ^{29}Si resonances; the same applies to the $SiMe_3$ groups of **6b**. The spectra of both **5** and **6** can be understood if we postulate that each contains an η^2-silane group and that a dynamic process places different silyl groups in the η^2-position (see Scheme 2). In keeping with this hypothesis, the mean coupling $^{2}J_{Si-H}$ of **6b** is almost identical to that of **5**. The values for $^{2}J_{Si-H}$ of the mixed complexes show a strong preference for placing an ethyl group rather than a methyl group in the η^2-position, in accordance with Schubert's predictions.[2,7] The M^{V} complexes $[\{HB(3,5\text{-}Me_2pz)_3\}Rh(H)_2(H_2)]$ and $[(PPh_3)_2Ir(H)_2(Et_3SiH)_2]^+$ involve similar non-classical bonding interactions.[9]

Complex **5** also undergoes two distinct reactions in the presence of an excess of silane depending on the mode of activation. The photochemical product is $(Cp)Rh(H)_2(SiR_3)_2$ **2**, while the thermal product is its ring-substituted analogue $(C_5H_4SiR_3)Rh(H)_2(SiR_3)_2$ **7** (**7a** R = Et, **7b** R = Me). Whereas **7a** is formed from **5a** at 298 K, the corresponding reaction of **5b** occurs only above 373 K. Direct thermal reaction of $(Cp)Rh(C_2H_4)_2$ with Et_3SiH at 383 K provides an

---

§ Complexes of the type $CpMo(CO)_2(L)R'$ (L = PR_3, $P(OR)_3$, R' = alkyl, H, halide) adopt piano-stool (square pyramidal) structures, but are fluxional. A trigonal bipyramidal intermediate is postulated in the exchange process (J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, 1970, **92**, 5852).

¶ Simple silane exchange complicates this reaction and leads to the generation of **5** in addition to **6**.

alternative route to **7a**. Unlike other silyl group migrations,[10] the migration observed for **5** requires no proton-abstracting agent.[11] Although we have not yet established the mechanism of conversion of **5** into **7**, we surmise that the thermal reaction of (Cp)Rh(C_2H_4)$_2$ with R_3SiH generates **7** *via* **1** and then **5**.

Preliminary studies of the effect of irradiation on **5b** reveal that it is highly photosensitive. In the presence of ethene the major photolysis product is the new rhodium(III) complex (Cp)Rh(C_2H_4)($SiMe_3$)$_2$ **8** resulting from Me_3SiH elimination and ethene coordination.‡

These experiments provide an insight into the reaction routes open to a metal(ethene)silyl(hydride) complex (Scheme 1), illustrating how simple ligand dissociation from **1** predominates photochemically, while the thermal reactions reflect competition between [1,3] H-shifts, ethene dissociation and reductive elimination of trialkylsilane. The characterisation of the highly hindered Rh^V complex (Cp)Rh(SiR_3)$_3$H **5** poses stereochemical problems similar to those for trihydride/hydrido (dihydrogen) complexes.[12] The use of different silyl groups as in **6**, provides evidence for the presence of an η^2-silane ligand, which undergoes dynamic rearrangement. This may also prove to be the key to the structures of **5** and the fluxional iridium complexes.[2] Complex **5** also reacts with an excess of silane: a silyl migration leads to the formation of ($C_5H_4SiR_3$)Rh(SiR_3)$_2$(H)$_2$, **7** in the thermal reaction, whereas the unsubstituted product (C_5H_5)Rh(SiR_3)$_2$(H)$_2$ **2** is obtained by photolysis.

We are grateful to Dr B. E. Mann for recording ^{103}Rh NMR spectra, and to Dow Corning Ltd, British Gas, The Royal Society, the SERC, and the EEC for support. We also appreciated extensive discussions with Professor P. M. Maitlis.

Received, 28th August 1990; Com. 0/03884I

References

1 S. B. Duckett, D. M. Haddleton, S. A. Jackson, R. N. Perutz, M. Poliakoff and R. K. Upmacis, *Organometallics*, 1988, **7**, 1526.

2 M. J. Fernandez, P. M. Bailey, P. O. Bentz, J. H. Ricci, J. Ruiz, T. F. Koetzle and P. M. Maitlis, *J. Am. Chem. Soc.*, 1984, **106**, 5458; M. J. Fernandez and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 310; J. Ruiz, B. E. Mann, C. M. Spencer, B. F. Taylor and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1987, 1963; T. M. Gilbert, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 3508; T. M. Gilbert, R. G. Bergman, *Organometallics*, 1983, **2**, 1458; R. Tanke and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1990, 1056.

3 U. Schubert, G. Scholz, J. Müller, K. Ackermann, B. Worle and R. F. D. Stansfield, *J. Organomet. Chem.*, 1986, **306**, 303 and references cited therein; H. Rabaa, J.-Y. Saillard and U. Schubert, *J. Organomet. Chem.*, 1987, **330**, 397.

4 B. J. Burger, B. D. Santarsiero, M. S. Trimmer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1988, **110**, 3134; M. Brookhart and D. M. Lincoln, *J. Am. Chem. Soc.*, 1988, **110**, 8719.

5 S. T. Belt, S. B. Duckett, D. M. Haddleton and R. N. Perutz, *Organometallics*, 1989, **8**, 748.

6 Compare (η^5-C_5Me_5)Rh(Me_2SO)(Me)$_2$: A. V. Miguel, K. Isobe, B. E. Mann, M. Gomez, B. F. Taylor and P. M. Maitlis, *Organometallics*, 1983, **2**, 1724.

7 U. Schubert, *Adv. Organomet. Chem.*, 1990, **30**, 151.

8 P. Kubacek, R. Hoffmann and Z. Havlas, *Organometallics*, 1982, **1**, 180.

9 U. E. Bucher, T. Lengweiler, D. N. W. von Philipsborn and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 548; X.-L. Luo and R. H. Crabtree, *J. Am. Chem. Soc.*, 1989, **111**, 2527.

10 K. H. Pannell, S. P. Vincenti and R. C. Scott, *Organometallics*, 1987, **6**, 1593; J. Cervantes, S. P. Vincenti, R. N. Kapoor and K. H. Pannell, *Organometallics*, 1989, **8**, 744; P. Pasman and J. J. M. Snel, *J. Organomet. Chem.*, 1986, **301**, 329.

11 U. Schubert and A. Schenkel, *Chem. Ber.*, 1988, **121**, 939.

12 M. D. Heinekey, J. M. Millar, T. F. Koetzle, N. G. Payne and K. W. Zilm, *J. Am. Chem. Soc.*, 1990, **112**, 909; J. K. Burdett, J. R. Phillips, M. R. Pourian, M. Poliakoff, J. J. Turner and R. Upmacis, *Inorg. Chem.*, 1987, **26**, 3054.