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Redistribution reactions of hydrosilanes mediated by the unsymmetrical and homometallic phosphido-bridged complex $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ [☆]

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Abstract

Reactions of the unsymmetrical and homobimetallic phosphido-bridged complex $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ (**1**) with various hydrosilanes gave rise to redistribution of the substituents on hydrosilanes. The reaction of **1** with 2 equiv. of secondary silane R_2SiH_2 (R = Ph, *p*-Tol) caused effective aryl scrambling to afford a monoarylsilylene-bridged complex $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}SiRH)(\mu\text{-}PPh_2)$ (**2**, R = Ph; **3**, R = *p*-Tol) and a tertiary silane R_3SiH (R = Ph, *p*-Tol). The signals of ^{29}Si and $^{31}P\{^1H\}$ NMR spectra of these complexes appear at very low field (^{29}Si NMR: **2**, δ 209.1, $^1J(Si\text{-}H) = 185$ Hz, $^2J(Si\text{-}P) = 26$ Hz; **3**, δ 209.1, $^1J(Si\text{-}H) = 185$ Hz, $^2J(Si\text{-}P) = 27$ Hz. ^{31}P NMR: **2**, δ 224.5; **3**, δ 225.0). Complex **2** and Ph_3SiH were also formed by the reaction of **1** with 1 equiv. of dihydrodisilane $HPh_2SiSiPh_2H$. Similarly, the reaction of **1** with alkyldisilane $HMe_2SiSiMe_2H$ proceeded smoothly to give the alkyl-scrambling product $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}SiMeH)(\mu\text{-}PPh_2)$ (**4**) and Me_3SiH. Some intermediates were observed in each reaction by NMR spectroscopy. A reaction mechanism containing silyl(silylene) intermediates is proposed.

Keywords: Phosphorus; Iron; Silane; Carbonyl; Cyclopentadienyl; Silylene

1. Introduction

Dinuclear transition metal complexes supported by some bridging ligands have received considerable attention because of the potential for new reactivity, namely "cooperative reactivity" between two metals, which we could not expect from mononuclear complexes. For example, many intriguing studies concerning the synthesis and reactivity of early–late heterobimetallic complexes have been reported [1], in which the combination of the electron-poor early metal and the electron-rich late metal are expected to make an ideal environment for heterolytic bond cleavage of organic or inorganic substrates. However, at present only a few reactions that show the direct participation of both metals in a reaction with organic substrates have been observed [1a–d] and in most cases reactions occur on a single metal centre, probably because of the too large polarity on the metal–metal bond of the heterometals. Unsymmetrical and homometallic dinuclear complexes are expected to have less polarity on a metal–metal bond, which may effectively give different roles to the two metals in reactions with various substrates.

For these reasons, we became interested in the unsymmetrical and homometallic phosphido-bridged diiron complex $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$, which we have previously prepared by the reaction of the tetramethylfulvene-bridged complex $(\eta^1:\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ with PPh_2H in hot benzene [2]. An analogous complex which has an unsubstituted cyclopentadienyl ligand has been prepared by a completely different method, but the detailed reactivity has not been investigated [3]. We report here the reactions of $(\eta^5\text{-}C_5Me_5)Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ with hydrosilanes in which a stoichiometric redistribution of the substituents on the silicon atoms occurs.

[☆] Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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2. Experimental details

2.1. General procedure

All reactions were carried out in a degassed sealed tube or a glass vessel fitted with Teflon stopcocks and all manipulations were performed using standard Schlenk techniques under a dinitrogen atmosphere or vacuum line techniques owing to the extreme sensitivity of the products to air or moisture. Pentane, benzene, toluene and benzene-d_6 were dried over a potassium mirror and directly transferred into a sealed NMR tube or glass vessels by the trap-to-trap transfer method. Hydrosilanes Ph_2SiH_2 [4], (p-Tol)$_2$SiH$_2$ [4], $HPh_2SiSiPh_2H$ [5] and $HMe_2SiSiMe_2H$ [6] were prepared according to literature methods. The starting material (η^5-C$_5$Me$_5$)Fe$_2$(CO)$_4$(μ-CO)(μ-PPh$_2$) (**1**) was prepared by the previously reported procedure [2].

^{1}H and ^{13}C NMR spectra were recorded on a Bruker UX-300 instrument. ^{31}P NMR spectra were recorded on JEOL FX-90Q or Bruker AC-300 spectrometers referenced to external 85% H_3PO_4. IR spectra were obtained on a Horiba FT-200 spectrometer, and mass or high-resolution mass spectra on a Hitachi M-2500S or JEOL JMS HX-110 mass spectrometer.

Two types of experiments were performed for each reaction. First, (a) designates the experiment in which the reaction was monitored by ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. The yields of the reaction products were determined by the relative intensities of ^{1}H NMR signals against that of the methyl proton of toluene which was added to a reaction tube as an internal standard, except for the reaction of **1** with (p-Tol)$_2$SiH$_2$. In that case, the signal of C_6D_5H which was almost separated from those of aromatic protons was used as a standard. Second, (b) designates the usual preparative experiment involving isolation of the products.

2.2. Reaction of 1 with Ph_2SiH_2

(a) A thick-walled NMR tube (5 mm o.d.) was charged with **1** (10 mg, 0.017 mmol) and Ph_2SiH_2 (16 mg, 0.085 mmol, 5.1 equiv.) and benzene-d_6 (0.5 ml) was added to it by the trap-to-trap transfer technique in vacuo. After the tube had been flame sealed, it was carefully warmed in an oil bath (1 day at room temperature, 2 days at 40 °C and then 3 days at 60 °C). The colour of the solution gradually changed from black to green. The reaction was monitored by ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. After additional warming of the solution for 3 days at 80 °C, its colour finally became dark brown and the ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectra showed signals corresponding to (η^5-C$_5$Me$_5$)Fe$_2$(CO)$_4$(μ-SiPhH)(μ-PPh$_2$) (**2**) (50%) and Ph_3SiH (82%) together with those of excess Ph_2SiH_2 (2.5 equiv.). Some small signals for the intermediates and (η^5-C$_5$Me$_5$)$_2$Fe$_2$(CO)$_4$, a thermolysis product of **1**, were also observed at the final stage. Furthermore, continuous heating caused gradual decomposition of **2**.

(b) A glass vessel (18 mm o.d.) was charged with **1** (108 mg, 0.189 mmol) and Ph_2SiH_2 (59 mg, 0.32 mmol) and benzene (ca. 5 ml) was added. The solution was gradually warmed with stirring from room temperature to 60 °C until the colour of the solution changed to dark green; this took about 5 days. After additional warming for 3 days at 80 °C, the resulting brown solution was transferred into a Schlenk tube in a glove-box and the solvent was removed under reduced pressure to give a dark brown, oily residue. Most of Ph_3SiH and excess starting material Ph_2SiH_2 were extracted with pentane (30 ml) from the residue. The remaining dark brown solid was dissolved in toluene (1.5 ml) and the solution was layered with pentane (3 ml). Keeping it at room temperature for 2 weeks in a glove-box gave brown crystals of **2** in 13% yield (16 mg, 0.025 mmol). Ph_3SiH was identified by ^{1}H, ^{29}Si NMR and mass spectrometry. **2**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.32 (s, 15H, Me), 7.01 (SiH, by Si–H COSY measurement) 6.8–7.8 (m, 10H, Ph). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.9 (Me), 92.6 (C_5Me$_4$), 129.30, 129.35, 129.37, 129.40, 129.8, 130.0 (Ph or PPh$_2$), 133.9 (d, J(P–C) = 11 Hz, PPh$_2$), 134.4 (d, J(P–C) = 9 Hz, PPh$_2$), 136.4 (Ph), 142.0 (d, J(P–C) = 24 Hz, PPh$_2$), 142.7 (d, J(P–C) = 36 Hz, PPh$_2$), 134.4 (Ph), 216.9 (d, ${}^{2}J$(P–C) = 3 Hz, CO), 218.3 (d, ${}^{2}J$(P–C) = 15 Hz, CO). (The ^{13}C{^{1}H non-decoupling} spectrum gave an integral ratio of 3 : 1 for the CO signals at 216.9 ppm and 218.3 ppm.) ^{31}P NMR (C_6D_6): δ 224.5. ^{29}Si NMR (^{1}H non-decoupling, C_6D_6): δ 209.1 (dd, ${}^{2}J$(Si–H) = 185 Hz, ${}^{2}J$(Si–P) = 26 Hz). Mass spectrum (DEI): m/z 650 (3.5, M^+), 622 (9.3, $M^+ - CO$), 566 (5.2, $M^+ - 3CO$), 510 (16, $M^+ - Fe(CO)_3$), 482 (9.8, $M^+ - Fe(CO)_4$). IR (KBr pellet): ν(SiH) 2083 (m); ν(CO) 1983 (vs), 1940 (vs), 1915 (vs), 1902 (vs) cm^{-1}.

2.3. Reaction of 1 with (p-Tol)$_2$SiH$_2$

(a) An NMR tube (5 mm o.d.) was charged with **1** (10 mg, 0.017 mmol) and (p-Tol)$_2$SiH$_2$ (16 mg, 0.075 mmol, 4.4 equiv.) and benzene-d_6 (0.5 ml) was added. After the tube had been flame sealed, the solution was warmed as described in Section 2.2(a) and the reaction was monitored by ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. The ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectra of the resulting brown solution showed signals corresponding to (η^5-C$_5$Me$_5$)Fe$_2$(CO)$_4$(μ-Si-p-TolH)(μ-PPh$_2$) (**3**) (45%) and (p-Tol)$_3$SiH (76%) together with those of excess (p-Tol)$_2$SiH$_2$ (2.0 equiv.).

(b) In a manner similar to the reaction of **1** with Ph_2SiH_2, a solution of **1** (100 mg, 0.175 mmol) and (p-Tol)$_2$SiH$_2$ (185 mg, 0.871 mmol) was heated in toluene (ca. 5 ml) and then worked up. Dark brown crystals of **3** containing a small amount of impurity were obtained in 12% yield (14 mg, 0.021 mmol). **3**: ^{1}H NMR (300 MHz, C_6D_6): δ 1.33 (s, 15H, Me), 1.99 (s, 3H, *p*-C_6H_4*Me*), 6.8–7.8 (m, 14H, Ph and *p*-C_6*H_4*Me), 7.04 (SiH, by Si–H COSY measurement). ^{13}C NMR (75.5 MHz, C_6D_6): δ 9.9 (Me), 21.0 (*p*-C_6H_4*Me*), 95.6 (*C_5*Me_4), 125–130 (Ph), 133.9 (d, *J*(P–C) = 11 Hz, PPh_2), 134.5 (d, *J*(P–C) = 9 Hz, PPh_2), 136.6 (Ph), 142.0 (d, *J*(P–C) = 24 Hz, PPh_2), 142.7 (d, *J*(P–C) = 36 Hz, PPh_2), 217.1 (d, ^2J(P–C) = 3 Hz, CO), 218.2 (d, ^2J(P–C) = 15 Hz, CO). ^{31}P NMR (C_6D_6): δ 225.0. ^{29}Si NMR (^{1}H non-decoupling, C_6D_6): δ 209.1 (dd, ^2J(Si–H) = 185 Hz, ^2J(Si–P) = 27 Hz). Mass spectrum (DEI): *m/z* 664 (0.4, M^+), 636 (1.5, $M^+ -$ CO, 608 (2.6, $M^+ -$ 2CO), 580 (2.7, $M^+ -$ 3CO), 552 (2.9, $M^+ -$ 4CO), 376 {100, (C_5Me_5)Fe(PPh_2)}. IR (KBr pellet): ν(SiH) 2077 (m); ν(CO) 1984 (vs), 1938 (vs), 1917 (vs), 1902 (sh, vs), 1896 (vs) cm^{-1}.

2.4. Reaction of 1 with $HPh_2SiSiPh_2H$

(a) An NMR tube (5 mm o.d.) was charged with **1** (10 mg, 0.017 mmol) and $HPh_2SiSiPh_2H$ (8 mg, 0.02 mmol, 1.4 equiv.) and benzene-d_6 (0.5 ml) was added. After the tube had been flame sealed, the solution was warmed (1 day at room temperature, 1 day at 40°C, 2 days at 60°C and then 2 days at 80°C) as described in Section 2.3(a), resulting in a similar colour change from black to dark green, and then to dark brown. The reaction was monitored by ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. The ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectra of the resulting brown solution showed signals corresponding to **2** (60%) and Ph_3SiH (75%) together with those of excess $HPh_2SiSiPh_2H$ (0.4 equiv.).

(b) In a manner similar to the reaction of **1** with Ph_2SiH_2, a solution of **1** (80 mg, 0.14 mmol) and $HPh_2SiSiPh_2H$ (70 mg, 0.18 mmol) was heated in benzene (ca. 2 ml) and then worked up. Dark brown crystals of **2** containing a small amount of impurity were obtained in 16% yield (13 mg, 0.023 mmol).

2.5. Reaction of 1 with $HMe_2SiSiMe_2H$

(a) An NMR tube (5 mm o.d.) was charged with **1** (10 mg, 0.017 mmol) and $HMe_2SiSiMe_2H$ (3 mg, 0.03 mmol, 1.7 equiv.) and benzene-d_6 (0.5 ml) was added. After the tube had been flame sealed, the solution was warmed (1 day each at room temperature and 40°C, 3 days at 60°C and then 1 day at 80°C) and monitored by ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy. During this period, a colour change from black to greenish brown and then to reddish brown was observed. The ^{1}H, ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR spectra of the resulting reddish brown solution showed signals corresponding to (η^5-C_5Me_5)$Fe_2(CO)_4$(μ-SiMeH) (μ-PPh_2) (**4**) (73%) and Me_3SiH, together with those of excess $HMe_2SiSiMe_2H$ (0.5 equiv.).

(b) A glass vessel (18 mm o.d.) was charged with **1** (100 mg, 0.175 mmol) and $HMe_2SiSiMe_2H$ (104 mg, 0.875 mmol) and benzene (ca. 3 ml) was added. The solution was heated as described in (a). Removal of volatiles gave a reddish brown oily residue, which was then washed with pentane and dried under vacuum to afford a brown powder. Attempts to purify this powder by recrystallization were unsuccessful owing to the extreme instability of **4**, especially in solution, even if it was handled in a glove-box. Therefore, most of spectral data for **4** were obtained from the reaction mixture. **4**: ^{1}H NMR (300 MHz, C_6D_6): δ 0.87 (d, ^3J(H–H) = 3.9 Hz, 3H, Me), 1.35 (s, 15H, Me), 6.69 (d of q, ^3J(P–H) = 1.6 Hz, ^3J(H–H) = 3.9 Hz, 1H, SiH), 6.8–7.2, 7.5–7.8 (m, 10H, Ph). ^{13}C NMR (75.5 MHz, C_6D_6): δ 6.9 (Me), 10.1 (C_5*Me_5*), 95.4 (*C_5*Me_4), 125–145 (Ph), 217.7 (d, ^2J(P–C) = 2.5 Hz, CO). ^{31}P NMR (C_6D_6): δ 231.0. ^{29}Si NMR (C_6D_6): δ 202.8 (d, ^2J(Si–P) = 21 Hz). Mass spectrum (DEI): *m/z* 588 (1.4, M^+), 560 (3.2, $M^+ -$ CO), 532 (6.1, $M^+ -$ 2CO), 504 (8.2, $M^+ -$ 3CO), 476 (8.3, $M^+ -$ 4CO). Exact mass calcd. for $C_{27}H_{29}Fe_2O_4PSi$: 588.0271. Found: 588.0268.

3. Results and discussion

3.1. Reaction of 1 with dihydrosilane R_2SiH_2 (R = Ph, p-Tol)

The unsymmetrical phosphido-bridged diiron complex **1** reacted with 2 equiv. of a secondary silane R_2SiH_2 (R = Ph, *p*-Tol) on warming in benzene or toluene to afford a brown monoarylsilylene-bridged complex (η^5-C_5Me_5)$Fe_2(CO)_4$(μ-SiRH)(μ-PPh_2) (**2**, R = Ph; **3**, R = *p*-Tol) and a tertiary silane R_3SiH (R = Ph, *p*-Tol) (Eq. (1)). The ^{29}Si NMR signal of **2** appears at 209.1 ppm as a doublet of doublets with coupling constants of ^1J(Si–H) = 185 Hz and ^2J(Si–P) = 26.2 Hz, which apparently shows that **2** has a μ-SiPhH ligand [7]. The signal of **3** also appears at very low field (209.1 ppm, ^1J(Si–H) = 185 Hz and ^2J(Si–P) = 26.6 Hz). The Si–H signals of both **2** and **3** in the ^{1}H NMR spectrum overlap with the phenyl signals, but ^{29}Si–^{1}H COSY measurements clearly display them as a cross peak at 7.01 and 7.04 ppm, respectively. The ^{31}P{^{1}H} NMR spectra of **2** and **3** show signals at 224.5

(1)

1

2 : R = Ph
3 : R = *p*-Tol

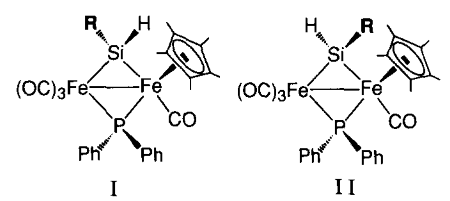
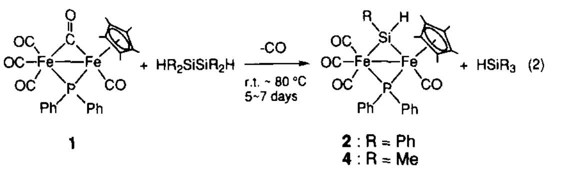


Fig. 1. Possible geometric isomers for **2** and **3**.



and 225.0 ppm. This marked low-field shift denotes that the phosphido ligand bridges across a metal–metal bond [8]. The IR spectra of **2** and **3** also support the structure described in Eq. (1): for example, **2** clearly shows a Si–H stretching band ν(Si–H) at 2083 cm^{-1} and terminal carbonyl bands ν(CO) at 1983, 1940, 1915 and 1902 cm^{-1}. The ^{13}C{^{1}H non-decoupling} NMR spectrum of **2** shows two signals in the carbonyl region, at 216.9 ppm (^2J(P–C) = 3 Hz) and 218.3 ppm (^2J(P–C) = 15 Hz) with an intensity ratio of 3 : 1, which are assigned to three carbonyls and one carbonyl on each metal, respectively. This also supports the structure of **2**. To our knowledge, **2** and **3** are the first examples of complexes having both μ-phosphido and μ-silylene ligands.

There are two possible geometric isomers for each of **2** and **3**, as shown in Fig. 1, but only one of them exists according to the spectral data. Although we have no experimental evidence so far, considering the large steric repulsion expected between R and η^5-C_5Me_5 groups in **II**, isomer **I** may be more favourable. As we shall show in the next section, when a substituent on a silicon atom is a less hindered methyl group, both geometric isomers **I** and **II** are possible.

3.2. Reaction of 1 with dihydrodisilane HR_2SiSiR_2H (R = Ph, Me)

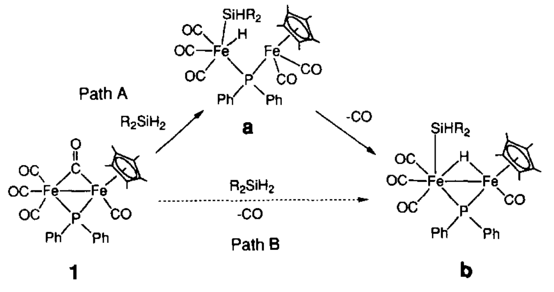
Interestingly, **2** and Ph_3SiH were also formed by the reaction of **1** with 1 equiv. of dihydrodisilane $HPh_2SiSiPh_2H$ (Eq. (2)). ^{1}H, ^{29}Si and ^{31}P NMR spectra of the reaction mixture showed the signals of **2** and Ph_3SiH almost cleanly.

We also examined whether the Si–C bond of alkylsilane can be activated or not by **1**. The reaction of $HMe_2SiSiMe_2H$ with **1** proceeded smoothly to give (η^5-C_5Me_5)$Fe_2(CO)_4$(μ-SiMeH)(μ-PPh_2) (**4**) and Me_3SiH (Eq. (2)). Both the ^{29}Si and ^{31}P NMR spectra of **4** show the signals at very low field (^{29}Si{^{1}H} NMR in C_6D_6 202.8 ppm with ^2J(Si–P) = 20.7 Hz; ^{31}P{^{1}H} NMR 231.0 ppm) in accord with the structure. Unlike the Si–H signals of **2** and **3**, which overlap the phenyl signals, the corresponding signal of **4** appears cleanly at 6.69 ppm as a doublet of quartets with ^3J(P–H) = 1.6 Hz and ^3J(H–H) = 3.9 Hz, which further supports the existence of a μ-SiMeH ligand. In addition to these signals, the ^{1}H NMR spectrum of the reaction mixture clearly indicates the existence of another minor geometric isomer of **4**: a doublet and a singlet appear at 0.66 ppm (^3J(H–H) = 3.6 Hz) and 1.41 ppm, respectively. On the basis of the similarity of the signals to those of the major isomer of **4**, these can be assigned to a methyl group of μ-SiMeH and a pentamethylcyclopentadienyl group for the minor geometric isomer of **4**. The isomer ratio is about 8 : 1 according to the ^{1}H NMR spectrum.

The fact that the reaction of **1** with 2 equiv. of secondary silane and that with 1 equiv. of dihydrosilane give the same products, a tertiary silane and a monosubstituted silylene-bridged complex, implies that the reaction pathways join each other at a certain step in the mechanism. The detailed reaction mechanism will be discussed later.

3.3. Observation of intermediates

The ^{1}H, ^{29}Si and ^{31}P NMR spectra clearly show the existence of some reaction intermediates in the reactions of **1** with hydrosilanes. Two of the intermediates at the early stage of the reaction are thought to have the structures shown in Scheme 1: one is **a**, which has a terminal hydrido, a silyl and a bridging phosphido ligand, and the other is **b**, which has both bridging hydrido and phosphido ligands and a silyl group. For example, when the colour of the solution containing **1** and Ph_2SiH_2 changed from black to dark green after warming it to 40°C, the ^{1}H NMR spectrum showed signals corresponding to new complexes **a** and **b** (R = Ph in Scheme 1) besides those of **1** in an approximate ratio of **a** : **b** : **1** = 3 : 1 : 5. Then, after additional heating for about 2 days at 60°C, the ratio changed to **a** : **b** : **1** = 1 : 9 : 8. After further heating for 1 day at 60 °C, **a** almost disappeared and the signal of **b** increased. Some new signals were observed on further heating, but the



Scheme 1.

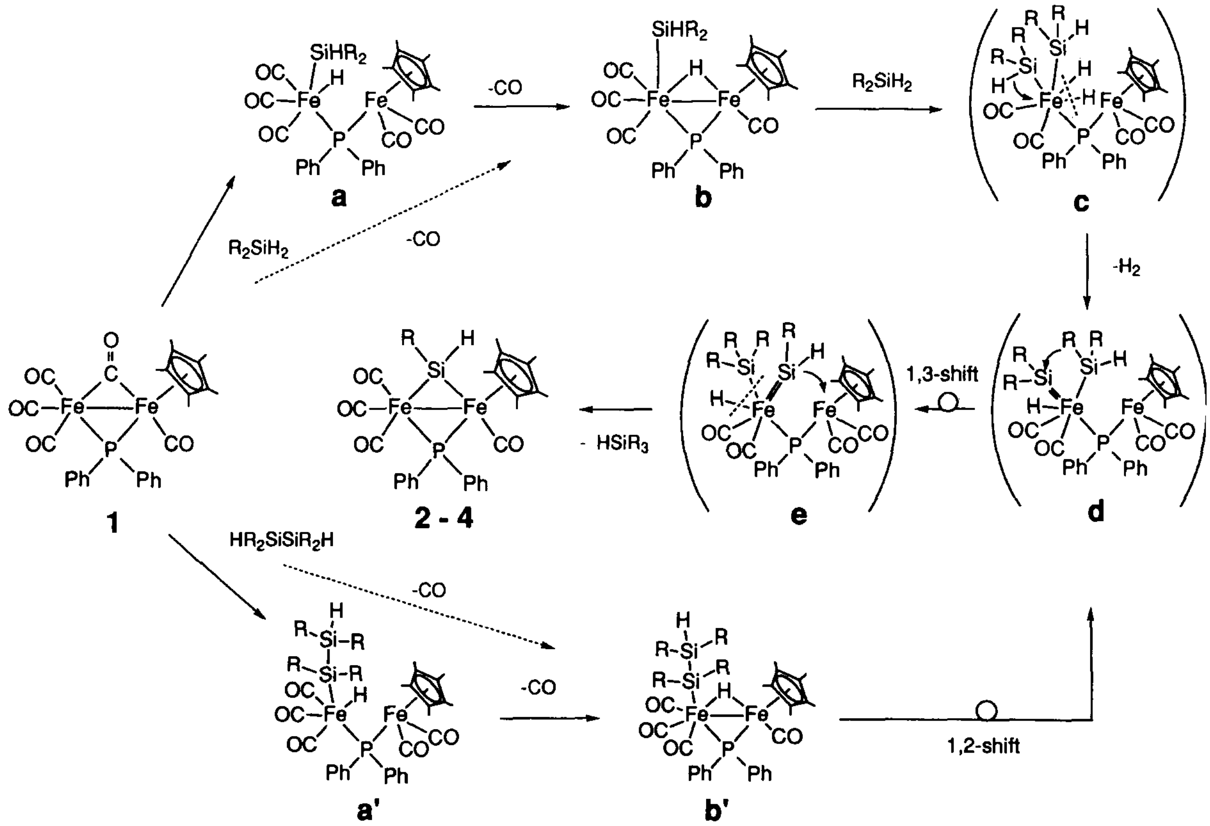
intensity of these signals also decreased, and finally the signals of **2** remained as a major product.

In the ^{1}H NMR spectrum at the early stage of the reaction, the signals at 1.09 (Me), 6.06 (^3J(P–H) = 2.2 Hz, Si–H) and −8.63 ppm (^2J(P–H) = 33.3 Hz, Fe–H) can be assigned to **a**, while the signals at 1.40 (Me), at 6.45 (Si–H), and −17.50 ppm (^2J(P–H) = 31.2 Hz, μ-H) can be assigned to **b**. Especially the upfield hydride resonance at −17.50 ppm in **b** is consistent with a bridging hydrido ligand [9]. The ^{31}P NMR spectrum shows two signals at 54.9 and 176.5 ppm for **a** and **b**, respectively, in addition to that of **1** (169.9 ppm). It is known that the μ-phosphido ligands bridging across metal–metal bonds generally show ^{31}P NMR resonances at relatively low field (δ 50–300) whereas the corresponding resonances are observed at higher field (δ −200 to 50) for compounds in which the μ-phosphido ligand bridges two metals not bound with a metal–metal bond [8]. Therefore, the chemical shifts strongly suggest that **a** has a phosphido ligand bridging two metals with no metal–metal bond, whereas **b** has a phosphido ligand bridging across a metal–metal bond. Analogous intermediates **a** and **b** were also observed in the reaction of **1** with other hydosilanes.

The intermediate **a** can be produced by oxidative addition of hydrosilane to **1**, accompanied by metal–metal bond cleavage. The intermediate **b** can be formed from **a** by CO dissociation. This two-step path A is consistent with the observations in the ^{1}H NMR spectra mentioned above but, at present, we cannot rule out path B in which CO dissociation and oxidative addition of silane occur without metal–metal bond cleavage, because **b** can be observed even just after mixing **1** and Ph_2SiH_2.

3.4. Possible mechanism for the redistribution reaction

Metal-mediated redistribution and dispropotionation at silicon atoms have been known for many years [10], but the mechanism has not been well investigated. Pannell and co-workers [11] and our group [12] reported alkyl scrambling in the photolysis of the disilanyl complexes $Cp(CO)_2FeSiR_2SiR'_3$ and suggested a mechanism involving silyl(silylene) intermediates of the type $Cp(CO)_2Fe(=SiR_2)(SiR'_3)$ in which an alkyl group migrates between silyl and silylene centres. Our group further obtained results which strongly support the existence of the silyl(silylene) intermediate, that is, isolation and structural characterization of bis(silylene) complexes of the type $L_nM\{SiR_2 \ldots O(Me) \ldots SiR_2\}$ (M = Fe, Mn) [13]. We also found that a bis(silylene)ruthenium complex can be prepared by a thermal reaction which indicates that the formation of silyl(silylene) species can be also induced thermally [14]. Recently,



Scheme 2.

Pestana et al. [15] reported the thermal redistribution of methyl groups in bis(silyl)tungsten complexes and proposed a mechanism involving a cationic silyl(silylene) tungstenocene intermediate.

In consideration of such examples, the driving force of the redistribution reaction of substituents on silicon atoms in our system also seems to be the formation of silyl(silylene) intermediates. The formation of a silylene-bridged complex and a tertiary silane in the reactions of Eqs. (1) and (2), in fact, can be rationalized according to the reaction sequence shown in Scheme 2. The upper route in Scheme 2 illustrates the process for dihydrosilanes and the lower route shows that for dihydrodisilanes.

The first step in both cases involves the oxidative addition of hydrosilanes, giving a hydrido- and phosphido-bridged silyl complexes as described in Section 3.3. In the case of dihydrosilanes, the next step is the second oxidative addition of another silane to the intermediate **b**, probably accompanied by a metal–metal bond breaking, and subsequent reductive elimination of H_2 (via intermediate **c**). Then a [1,2]-shift of a hydrogen atom from one of the silicon atoms to a metal would produce a silyl(silylene) intermediate **d**. Esteruelas et al. [16] recently suggested that a similar [1,2]-shift (or an α-elimination) of hydrogen could lead to the formation of a silylene intermediate in the alcoholysis of hydrosilanes in the presence of an iridium complex. Then, an aryl group on the silyl ligand migrates directly to a silylene group by a [1,3]-shift, leading to the formation of another silyl(silylene) intermediate **e**. Finally a bulky tertiary silyl group is reductively eliminated as a tertiary silane, and a very reactive terminal silylene ligand bridges two metals to stabilize, giving a silylene- and phosphido-bridged complex.

If the silylene ligand ($Fe{=}SiR_2$) in intermediate **d** bridges the metals, a diarylsilylene-bridged complex and a secondary silane would be formed, but we could not obtain any evidence for the formation of such a silylene-bridged complex by NMR spectroscopy. In addition, when **1** was treated with only 1 equiv. of Ph_2SiH_2, **2** and unreacted **1** were observed in about a 1:1 ratio in the ^1H NMR spectrum after the signal of Ph_2SiH_2 had almost disappeared. This is well in accord with the mechanism shown in Scheme 2.

Selective elimination of a tertiary silane and formation of a monoarylsilylene-bridged complex can be explained by consideration of steric effects. It is naturally expected that the repulsion between a pentamethylcyclopentadienyl group (Cp′) and a diphenylsilylene ligand is larger than that between Cp′ and a monophenylsilylene ligand. Furthermore, the reductive elimination of a bulky tertiary silane would be easier than that of a secondary silane.

In the case of the reaction of **1** with dihydrodisilane, a similar process containing silyl(silylene) intermediates can be also proposed. The difference between the reaction of **1** with monosilanes and that with disilanes is that disilanyl intermediate **b′** is converted into the intermediate **d** by an intramolecular [1,2]-shift of the terminal silyl group, analogous to the photolysis of disilanyl(carbonyl) complexes mentioned above.

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