Novel Concurrent Formation of Mo–Si and Si–C Bonds by the Reacion between $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ and $PhSiH_3$

Da-Yang Zhou, Makoto Minato, Takashi Ito,* and Mikio Yamasaki[†]
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240
[†]*Rigaku Corporation, Matsubara-Cho, Akishima, Tokyo 196*

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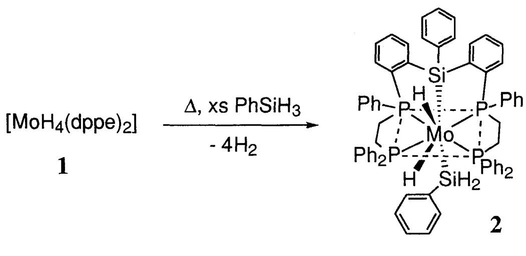
Reaction of $[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ with $PhSiH_3$ in refluxing toluene yielded doubly chelated novel complexes with the Si–C–C–P–Mo framework as a result of the oxidative addition involving Si–H bond cleavage concurrent with the selective activation of the ortho C–H bonds of the dppe ligands.

Studies on the formation and the reactivities of a single or a double bond between a transition metal and a silicon atom constitute one of the most exciting research interests in viewpoints of the useful organic syntheses incorporating silyl groups and of its peculiar bonding properties.[1] One of the typical methods of formation of a transition metal–silicon bond is the oxidative addition of silane derivatives involving either Si–H or Si–Si bond cleavage to a low valent, coordinatively unsaturated transition metal complex.[2]

We have reported versatile reactivities of the coordinatively unsaturated intermediate, $MoH_n(dppe)_2$ (n = 2 or 0; dppe = $Ph_2PCH_2CH_2PPh_2$), which is generated photochemically or thermally from $[MoH_4(dppe)_2]$ (**1**), towards various substrates involving the selective C–H, C–O, O–H, or N–H bond cleavage.[3] Continuing these studies, we found that the thermal reaction of **1** with phenylsilane gives novel complex **2** which possesses an unusual doubly chelated Mo–Si bond in addition to the normal PhH_2Si–Mo moiety (eq 1).



(1)

2

Heating a toluene solution of **1** under reflux in the presence of more than 2 equivalents of $PhSiH_3$ for 3 h afforded a yellow solid of **2**[4] in yield of 78%. Kubas et al. reported that the agostic $Mo\cdots H$–C interaction in $[Mo(CO)\{(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2\}_2]$ is readily displaced by primary or secondary silanes to give η^2-silane complexes, while the reaction of $[Mo(CO)(dppe)_2]$ with $PhSiH_3$ resulted in the equilibrium between the agostic starting complex and the η^2-silane type of coordination product.[5a]

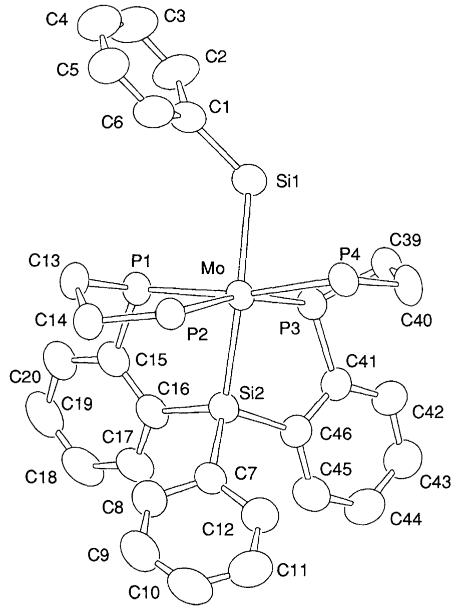
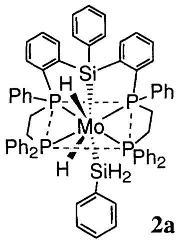
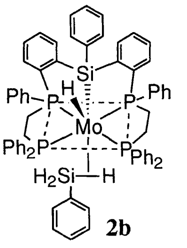


Figure 1. ORTEP drawing of **2**. Phenyl rings attached to P1 – P4 and all hydrogen atoms are omitted for clarity.
Selected distances [Å] and angles [°] : Mo–P1 2.455 (2), Mo–P2 2.490 (2), Mo–P3 2.451(2), Mo–P4 2.487 (2), Mo–Si1 2.620 (2), Mo–Si2 2.559 (2), Si1–C1 1.898 (9), Si2–C7 1.899 (8), Si2–C16 1.913 (8), Si2–C46 1.913 (8); P1–Mo–P2 81.08 (7), P2–Mo–P4 100.67(7), P1–Mo–P3 101.39 (7), P3–Mo–P4 79.44 (7), Si1–Mo–Si2 143.91 (7), Mo–Si1–C1 124.4 (3), Mo–Si2–C7 126.2 (2).

An X-ray crystallographic study was performed on a yellow crystal of **2** obtained from hexane/toluene solution (Figure 1). There are two Si atoms in the molecule: one (Si1) is what constitutes a usual terminal SiH_2Ph ligand and another (Si2) contains bonds between silicon and the ortho carbons of the phenyl groups of the dppe ligand. Interestingly, Si2 bonds selectively to the ortho carbons of the phenyl groups attached to P1 and P3. Mo–Si2 was found to be shorter than Mo–Si1 by 0.06 Å. Although the hydrido ligand was not able to be located directly in the molecular structure, its presence was confirmed by means of ^1H-NMR spectroscopy.[4] The presence of two sets of hydrido signals of identical intensities at least at and below room temperature[7] may indicate that these two hydrides are located separately in both sides of the pseudo-equatorial plane comprised of four phosphorus atoms (formula **2a**). Alternatively, the formula like **2b**, for instance, where two hydrides are NMR spectroscopically differentiated from each other by way of the mode of coordination may also be conceivable.[5b,8]

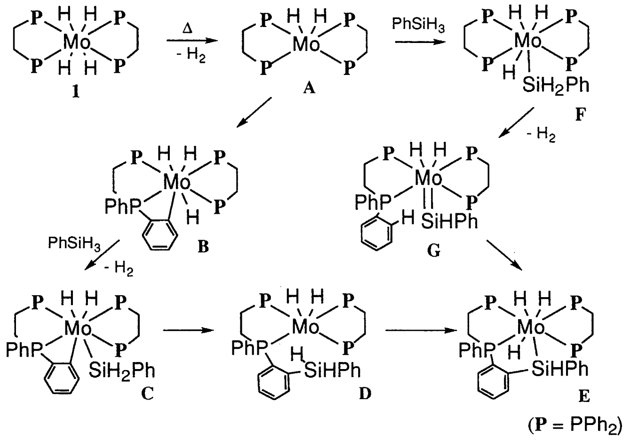


2a



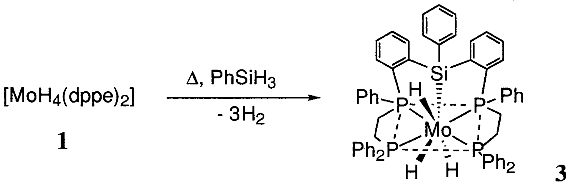
2b

A possible pathway of the formation of **2** from **1** is a route that incorporates a sequence of reactions involving oxidative addition of the ortho C–H bond of dppe ligand to the 16-electron reactive intermediate **A** to give **B**, the oxidative addition of $PhSiH_3$ to give **C**, reductive elimination from **C** to generate new Si–C bond (**D** in the Scheme), and intramolecular oxidative addition of Si–H bond in **D** to give the chelate **E**. An alternative path in which intervention of the silylene intermediate like **G** in Scheme below, however, cannot be ruled out.[9]



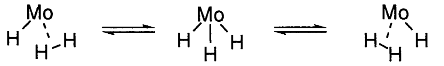
Scheme. Two possible pathways for the chelate formation.

Reaction of **1** with only one equivalent of $PhSiH_3$ under the conditions similar to the one described above afforded a greenish yellow solid which was assigned to the trihydride **3** in yield of 87% (eq 2).



(2)

The ^1H-NMR spectrum of **3** in benzene-d_6 at room temperature showed the multiplet signal between -3.9 and -4.7 ppm assignable to Mo–H protons. The ratio of the total intensity of these signals to that of the CH_2CH_2 signals in dppe ligand was 3/8. The multiplet signal was analyzed as a set of a broad triplet at -4.15 ppm with apparent coupling constant of 33 Hz and a broad quintet at -4.45 ppm with J = 35 Hz with the integration ratio 1:2. On raising the temperature in toluene-d_8 these signals gradually accumulated and finally became a simple quintet at 90 °C. There were virtually no changes in the $^{31}P\{H\}$ NMR of **3** in toluene-d_8 measured at room temperature and at 90 °C, which showed a couple of doublets at 110.2 and 81.4 ppm with $^2J(P\text{-}P)$ = 60.6 Hz. The T_1 values measured at room temperature at 400 MHz were found to be 90 ms for the signal at -4.45 ppm and 96 ms for the signal at -4.15 ppm. The results suggest that the η^2-hydrogen mode of coordination may contribute to some extent to each of three hydrides, which plays a key role for the fluxionality of the hydrido ligands (eq 3).[10]



(3)

Although complex **3** was too sensitive to air to be isolated in an analytically pure state, its formulation was further confirmed by deriving it to **2** by the reaction with excess phenylsilane (eq 4). The fact that **3** and **2** were obtained in a stepwise manner starting from **1** strongly suggests that **2** was formed via oxidative addition of the second molecule of $PhSiH_3$ to **3** (eq 4).

$$\mathbf{3} + PhSiH_3 \xrightarrow[110\ °C]{\text{toluene}} \mathbf{2} + H_2 \qquad (4)$$

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4 Complex **2**: Yellow crystals. ^1H NMR (benzene-d_6, 270 MHz): δ -4.5 (br. m, 1H, Mo–*H*), -5.4 (br. quint, 1H, Mo–*H*), 4.2 (s, 2H, Si–*H*). IR (KBr): ν(Si–H) 2086 cm^{-1}, ν (Mo–H) 1738 cm^{-1}. Anal. Found: C, 72.85; H, 5.93%. Calcd for $C_{78}H_{76}P_4MoSi_2$ (**2**•2toluene): C, 72.65; H, 5.94%.

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6 Crystal data for **2** : yellow prism; 0.30 × 0.24 × 0.24 mm; $C_{64}H_{58}MoP_4Si_2 \cdot 2C_7H_8$, F.M. = 1287.45 ; orthorhombic, space group *P*bca (No. 61); a = 44.862(5) Å, b = 23.072(4) Å, c = 12.859(5) Å, V = 13309(4) Å^3, Z = 8 ; Dcalcd = 1.285 g/cm^3 ; Rigaku AFC7R diffractometer; 298 K; Mo Kα radiation (λ = 0.71069 Å); scan method ω; data collection range 23.3–29.4°; total number of reflections measured 9544; number of independent reflections 9542 (R_{int} = 2.047); number of observed reflections 4646 ($I > 3.00\sigma(I)$); R = 0.045, R_w = 0.047; GOF = 1.47.

7 No change was observed for the signals on lowering the temperature in toluene-d_8 down to -60 °C. When the NMR was measured at 80 °C, the multiplet at -3.9 – -4.7 ppm appeared which is characteristic of **3** and did not resume their original pattern on cooling the solution to room temperature. This transformation of the complex **2** to **3** in solution was evidenced by $^{31}P\{H\}$ NMR of **2** taken in THF-d_8.

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