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Accounts

Oxidative Addition Reactions Involving Molybdenum Polyhydrides

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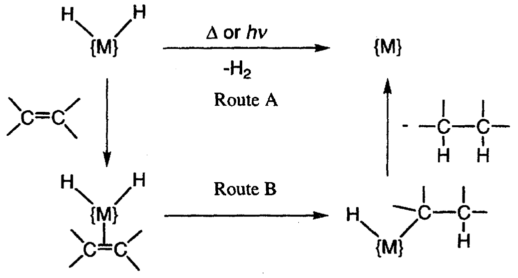
Versatile reactions of tetrahydridomolybdenum, [$MoH_4(dppe)_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$), one of the typical polyhydrido complexes, are shown. It releases one or two moles of dihydrogen on irradiation or heating in solution to give a coordinatively unsaturated intermediate {$MoH_2(dppe)_2$} (**A**) and/or {$Mo(dppe)_2$} (**B**) which reacts with (1) methacrylic esters to cause olefinic C–H bond activation, (2) allyl carboxylates to give an carboxylato-κ^2O complex and propene as a result of C–O bond activation, (3) β-diketones and catechols to give chelated diketonato and catecholato derivatives, respectively, (4) cyclic imines and amides to cleave their N–H bonds to give *N*-acylamido complexes, or finally (5) aryl silanes to give a novel hydrido-silyl complex which has a quinquedentate ligand comprising a P∼P∼Si∼P∼P framework. The last complex was further investigated in view of the reactivity resulting from its unique structure. Most of these reaction products are characterized spectroscopically as well as by X-ray crystallography.

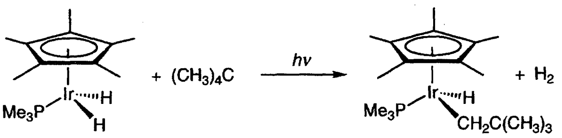
Among early transition metals, molybdenum, which belongs to group 6, is somewhat special because it resides close to the category of the so-called late transition metals in the periodic table. For instance, some molybdenum complexes show the Lewis acidic character which is characteristic of the early transition metals, whereas others exhibit some late transition metal properties. Some typical features of the group 6 transition metals, especially those of molybdenum, are as follows. (1) It can adopt versatile valency states from −2 to +6, each forming stable compounds. (2) It can form complexes with various coordination numbers exceeding 6, which include 7, 8, and even 9. (3) Its complex often shows high oxophilicity as a common feature of the early transition metals. (4) It exists abundantly in nature; hence its compounds are usually environmentally benign. In addition, molybdenum metal is far less expensive as compared with other precious metals such as palladium, ruthenium, rhodium, etc.

Transition metal polyhydrido complexes are known to be potent precursors of the coordinatively unsaturated species because they often release dihydrogen via reductive elimination on light irradiation or heating in solution (Route A in Scheme 1). Alternatively, such coordinatively unsaturated intermediates may be formed from the polyhydride through insertion of the unsaturated compounds such as olefins into one of M–H bonds followed by reductive elimination between M–H and M–C bonds (Route B in Scheme 1).



Scheme 1. Two possible pathways, routes A and B, for generation of the coordinatively unsaturated species {M} from dihydride.

The highly reactive nature of the coordinatively unsaturated intermediate thus generated toward oxidative addition has been amply documented: One typical example is the intermolecular aliphatic C–H bond activation such as shown in Eq. 1.[1]



(1)

Following the first isolation of eight-coordinate molybdenum tetrahydride [MH_4L_4] (M = Mo; L = $PMePh_2$, $PEtPh_2$, 1/2 $Ph_2PCH_2CH_2PPh_2$) by Pennela in 1971,[2] synthetic as well as spectral studies of a series of this type of complexes have been reported for M = Mo and W.[3,4] Among these tetrahydrides, the molybdenum complex with a diphosphine ligand, [$MoH_4(dppe)_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$), which can be prepared either by reduction of [$MoCl_4(dppe)$]

with $NaBH_4$ in the presence of dppe (Eq. 2)[2,4] or by treatment of *trans*-$[Mo(N_2)_2(dppe)_2]$ with H_2[5] or some organic molecules such as 2-propanol, tetrahydrofuran (THF), indoline,[6] 1-alkynes,[7] or acrylonitrile (Eq. 3),[8] is found to be especially interesting because it possesses moderate stability (enabling one to handle it easily under an inert atmosphere) and shows versatile reactivities, some of which are typical of the polyhydrido complexes (vide infra). An X-ray crystallographic study of a single crystal of the THF solvate of **1** has been undertaken[8] to reveal its dodecahedral geometry with the four phosphorus atoms in the *B* sites and the four hydrides in the *A* sites.[9]

$$[MoCl_4(dppe)] + 4\ NaBH_4 + dppe \xrightarrow[\text{EtOH}]{\text{reflux}} [MoH_4(dppe)_2]\ (\mathbf{1}) \tag{2}$$

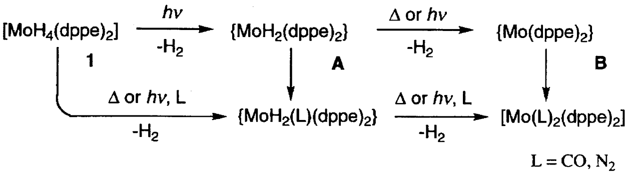
$$\textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] + A\text{—}H \longrightarrow [MoH_4(dppe)_2]\ (\mathbf{1})$$
$$A\text{—}H = H_2,\ (CH_3)_2CHOH,\ \text{tetrahydrofuran, indoline},\ HC{\equiv}CR \tag{3}$$

The investigation of the reaction of **1** has at first been restricted to the electrophilic attack on the hydrido ligand. Thus, Churchill and Rottella reported that the reaction of **1** with triphenylmethyl cation yielded $[Mo(O)(OH)(dppe)_2]^+BF_4^-$ [10] whereas Tatsumi et al. described the formation of *trans*-$[MoF(HNO)(dppe)_2]^+PF_6^-$ and *trans*-$[MoF(NO)(dppe)_2]$ on treatment of **1** with nitrosyl hexafluorophosphate in benzene–methanol.[11] Later we found that protonation of **1** with carboxylic acid afforded a cationic dihydrido(carboxylato) complex of molybdenum(IV) accompanied by evolution of H_2 (Eq. 4).[12]

$$[MoH_4(dppe)_2] + RCOOH \longrightarrow [MoH_2(O_2CR)(dppe)_2]^+[RCO_2]^- + 2\ H_2$$
$$R = CH_3,\ CH_3CH_2,\ CH_2{=}CH\text{-},\ CH_2{=}C(CH_3)\text{-} \tag{4}$$

In 1982, Graff et al. found that irradiation of benzene solution of **1** under either a CO or N_2 atmosphere yielded known complexes *cis*- and *trans*-$[Mo(CO)_2(dppe)_2]$ or *trans*-$[Mo(N_2)_2(dppe)_2]$, respectively.[13] These results suggest the intermediary formation of the coordinatively unsaturated intermediate such as **A** (16e) and/or **B** (14e) in Scheme 2 on irradiation as a result of reductive elimination of H_2 from **1**. Similar results were obtained when **1** was heated to reflux in toluene under analogous conditions.

When **1** in benzene was irradiated in the presence of CO_2, deep brown crystals, characterized by IR bands at 1360 and 1550 cm^{-1} as being assignable to the carboxylato ligand coordinated to the metal in a η^2-mode, were obtained and were identified as a hydrido(formato) complex $[MoH(O_2CH)(dppe)_2]$. (Eq. 5).[14] The formato complex is thought to be formed via a CO_2 insertion into the Mo–H bond in **A** in Scheme 2 generated by irradiation of **1**.



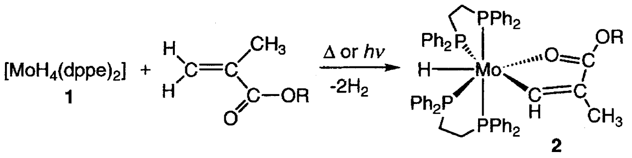
L = CO, N_2

Scheme 2.

$$\underset{\mathbf{1}}{[MoH_4(dppe)_2]} \xrightarrow[-H_2]{h\nu} \underset{\mathbf{A}}{\{MoH_2(dppe)_2\}} \xrightarrow{CO_2} [MoH(O_2CH)(dppe)_2] \tag{5}$$

In expectation that facile oxidative addition involving specific bond cleavage giving new hydridomolybdenum complexes may take place, we have undertaken systematic studies on the photochemical or thermal reactions of a benzene or toluene solution of **1** in the presence of various organic substrates. Here I summarize these results on the oxidative addition involving selective cleavage of C–H, C–O, O–H, N–H, and Si–H bonds to the molybdenum metal in **1**.

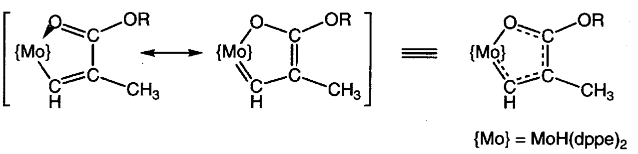
Oxidative Addition Reactions of 1 Involving C–H Bond and C–O Bond Cleavage. The yellow suspension of the tetrahydrido complex **1** in an excess of alkyl methacrylate, $CH_2{=}C(CH_3)COOR$ (R = Et, *i*-Pr, *n*-Bu, and *cyclo*-C_6H_{11}), either with or without aprotic solvent such as toluene and cyclohexane changed to a deep red solution on heating at 80—100 °C or irradiating at room temperature. From this solution a red solid which was analyzed as the alkenyl(hydrido) complex **2** shown in Eq. 6 was isolated.[15]



(6)

Apparently, complex **2** seems to have been formed as a result of oxidative addition of the methacrylate to the intermediate **B** (Scheme 2) involving selective cleavage of the C–H bond (*cis* to the ester group) at the sp^2 carbon of the terminal methylene, just as in the case reported for ruthenium[16] and iron.[17] Observation of alkyl isobutyrate as a by-product in the reaction (Eq. 6) indicates that route B in Scheme 1 took place in generating coordinatively unsaturated intermediate **B** in this case. The ^1H NMR of **2** in C_6D_6 at room temperature exhibits a Mo–H signal at $\delta = -4.25$ as a doublet of quintets as well as a sextet assignable to the sp^2 methine proton at an extremely low field ($\delta = 9.88$). The latter, in accord with the ^{13}C NMR data (in C_6D_6) in which methine carbon appears at $\delta = 251.69$, suggests the carbenoid nature of the alkenyl carbon attached to molybdenum, indicating the presence of resonance structures as shown in Chart 1. The existence of this sort of resonance forms may enhance the stability of **2** giving rise to play an important role for the reaction (Eq. 6) to proceed.

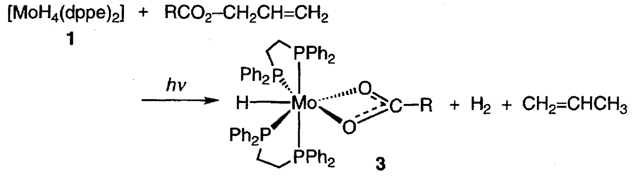
When a tetrahydrido complex **1** in benzene is irradiated in the presence of an excess of allyl carboxylates and



{Mo} = MoH(dppe)$_2$

Chart 1.

carbonates, $RCO_2CH_2CH{=}CH_2$ (R = H, Me, Et, Pr, *i*-Bu, $CH_2{=}C(Me)$, Ph, OMe, OEt), selective cleavage of the bond between allylic carbon and oxygen atoms occurred and the corresponding hydrido(carboxylato/carbonato) complexes of molybdenum(II) $[MoH(O_2CR)(dppe)_2]$ (**3**) were obtained as a main product.[18—20] The reaction was accompanied by evolution of H_2, propene, and CO_2 (only in the case of carbonate), each in an amount corresponding to the yield of **3** (Eq. 7). Although much work has been done on the C–O bond cleavage of unsaturated esters using groups 8—10 transition-metal organometallics, mainly in conjunction with the famous allylic alkylation reactions, less has been studied utilizing group 6 metal complexes.[21]

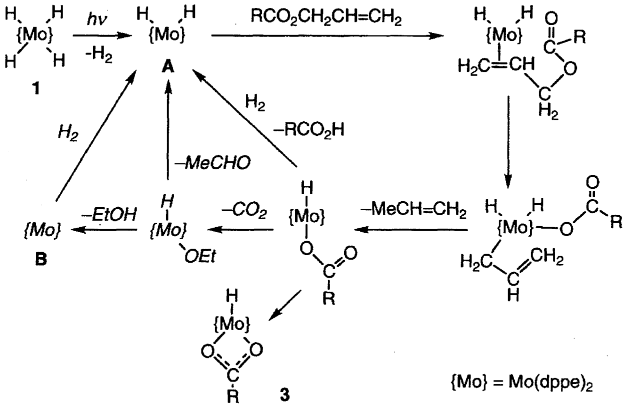


(7)

The seven-coordinate hydrido complexes **3** were characterized spectroscopically as well as by single crystal X-ray analysis for the ethylcarbonato complex (R = OEt, Table 1). In the ^{1}H NMR spectra in C_6D_6, hydrido signals appeared around $\delta = -6$ as a triplet of triplets suggesting pentagonal bipyramidal geometry with two phosphorus atoms at the apical positions and the rest in the equatorial girdle as shown in Eq. 7. ^{31}P NMR data that consist of two triplets and the X-ray molecular structure analysis are consistent with these results.

Since the C–O bond cleavage did not take place when propyl acetate was employed in place of allyl carboxylate, the C=C double bond of an allyl group seems to play an important role in these reactions. As a possible pathway for the reaction (Eq. 7), we can assume the initial coordination of the allyl group to the coordinatively unsaturated intermediate **A** in Scheme 1, followed by oxidative addition involving C–O bond cleavage and reductive elimination between hydrido and 2-propenyl ligands to give propene (Scheme 3). That the release of propene occurs directly from the hydrido-σ-allyl intermediate without an intervening π-allyl intermediate was evidenced by the fact that the reaction of **1** with 1-methylprop-2-enyl acetate and but-2-enyl acetate under similar conditions afforded 1-butene and *trans*-2-butene, respectively, as major C_4 products: No isomerized butenes were observed.[20]

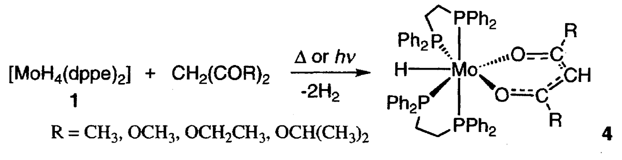
With the increased bulkiness of R, the yield of propene increased significantly, whereas that of H_2 remained unchanged. Thus, when R = *t*-Bu, 1.01 mol/mol of **1** of propene was evolved together with 0.67 mol of H_2. Bubbling of H_2 through the reaction system of **1** and allyl pivalate raised the yield of propene to 2.67 mol/mol of **1**. Furthermore, when the photoreaction of **1** with allyl ethylcarbonate was carried out under a stream of hydrogen, the yield of propene reached 3.0 mol/mol of **1**. These results suggest the possible catalytic hydrogenolysis of the allylic esters and the carbonates (Scheme 3).[19]



Scheme 3. Possible pathway for the photoreaction of allyl carboxylates and carbonates with **1** to give **3**. (Those given in itallics are applied for allyl ethylcarbonate.)

Oxidative Addition Reactions of 1 Involving O–H Bond Cleavage. Organic O–H groups behave as proton donors to a greater or lesser extent; the degree of such behavior depends on the electron withdrawing nature of the group attached to OH. Shubina et al. studied the interaction of several proton donors with the tetrahydride **1** with IR and UV spectroscopy and found that weak proton donors such as PhOH and $(CF_3)_2CHOH$ led to the formation of a molecular hydrogen-bonded complex of the type $\{OH\cdots Mo\}$, whereas the strong proton donor CF_3COOH caused proton transfer to form an ionic H-complex of the type $\{Mo^+H\cdots O^-\}$ and caused hydrogen evolution at room temperature.[22] In accordance with this, we observed that interaction of **1** with acetic, propionic, acrylic, or methacrylic acids affords a protonated carboxylato complex $[MoH_2(O_2CR)(dppe)_2]^+$ accompanied with H_2 evolution as already described above (Eq. 4).[12] When a less acidic OH group is allowed to interact with **1**, oxidative addition involving O–H bond cleavage rather than electrophilic attack may take place. We found that the reactions of β-diketones, malonates and catechols shown below are such examples because these substrates do not show any reactivity toward **1** without heating or irradiation

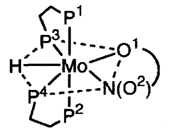
2, 4-Pentanedione (acetylacetone) and dialkyl malonates, known as the active methylene compounds, reacted thermally or photochemically with tetrahydride **1** to give chelated hydrido(2,4-pentanedionato)-[23] or hydrido(malonato)-molybdenum(II) complexes **4** as reddish yellow to reddish brown crystals (Eq. 8).[24] The analogous hydrido(malonato) complexes of tungsten were prepared similarly starting from *trans*-$[W(N_2)_2(dppe)_2]$.[24]

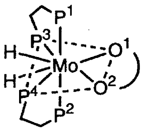


(8)

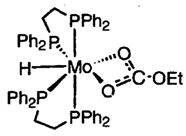
The seven-coordinate hydrido complexes **4** were characterized spectroscopically as well as by single crystal X-ray analysis (Table 1) for the diisopropyl malonato complex

Table 1. Comparison of the Structural Data for the Seven-Coordinate Complexes **3**, **4**, **7a**, and **8a**, and the Eight-Coordinate Complexes **6a** and **6b**





Complex	Mo–H	Mo–P^1 Mo–P^2 Mo–P^3 Mo–P^4	Mo–O^1 Mo–N(O^2)	H–Mo–P^3 P^3–Mo–O^1 N(O^2)–Mo–P^4 P^4–Mo–H	O^1–Mo–N(O^2)	P^1–Mo–P^3 P^2–Mo–P^4
3	1.69	2.507(2) 2.446(2) 2.365(1) 2.357(2)	2.333(4) 2.271(2)	45.0 110.12(11) 106.39(12) 101.59(13)	56.95(13)	77.60(6) 92.04(13)
4	1.64(3)	2.437(1) 2.454(1) 2.425(1) 2.440(1)	2.207(2) 2.225(2)	64(1) 81.78(7) 78.27(6) 57(1)	81.29(9)	79.72(4) 81.23(4)
7a	1.582	2.453(3) 2.510(3) 2.394(2) 2.378(3)	2.354(7) 2.282(6)	115.11 100.28(17) 117.96(23) 74.23	57.38(27)	74.29(9) 77.13(9)
8a	—	2.421(5) 2.447(5) 2.424(5) 2.421(5)	2.24(1) 2.25(1)	— 83.6(3) 93.4(3) —	57.9(4)	98.9(2) 81.9(2) P^3–Mo–P^4 124.8(2)
6a	1.51 1.65	2.511(2) 2.489(1) 2.452(1) 2.466(1)	2.126(3) 2.134(4)	— 73.9(1) 72.2(1) —	76.2(1)	80.78(5) 81.53(5)
6b	1.54 1.64	2.508(2) 2.506(2) 2.454(2) 2.468(2)	2.137(4) 2.127(4)	— 73.6(1) 75.0(1) —	76.0(2)	80.57(5) 80.96(7)



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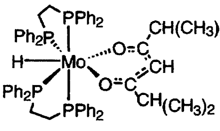
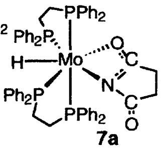
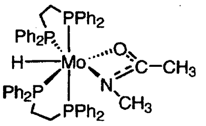


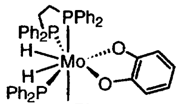
4



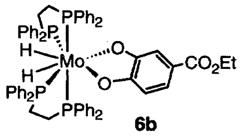
7a



8a



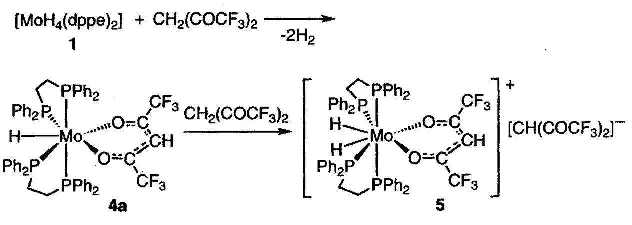
6a



6b

(R = O^{i}Pr) to possess pentagonal bipyramidal geometry with two phosphorus, two oxygen and hydrogen atoms comprising the equatorial girdle. Hydrido signals appeared around $\delta = -5$ as a triplet of triplets in their ^{1}H NMR spectra in C_6D_6.

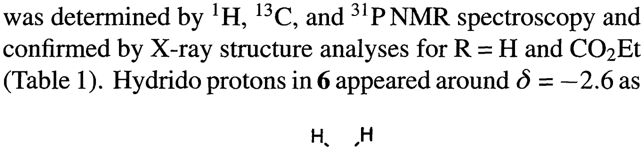
When hexafluoroacetylacetone was employed as a substrate, the reaction proceeded at room temperature in dark to give, depending on the ratio of the substrate to **1**, neutral (hexafluoroacetylacetoanto)hydrido complex **4a** or cationic (hexafluoroacetylacetoanto)dihydrido complex **5** which corresponds to the cationic carboxylato complex shown in Eq. 4 (Eq. 9).[25] Considering the fairly high acidity of hexafluoroacetylacetone (pK_a = 4.35) which is comparable to that of acetic acid (4.56), it is conceivable that hexafluoroacetylacetone behaved similarly to acetic acid rather than to acetylacetone whose acidity is pK_a = 8.80.



(9)

As for the reaction of the 1,3-dicarbonyl compounds to the coordinatively unsaturated species, there are two possible routes. One is the route via oxidative addition involving O–H bond cleavage of the enol form of the 1,3-dicarbonyl compounds (route C in Scheme 4), whereas the other is the route that accompanies C–H bond cleavage of their diketo form (route D). Taking into account the high concentration of the enol form of acetylacetone, it seems to be reasonable to consider that the reaction of acetylacetone follows route C, although that of malonate is not certain because its tautomeric equilibrium significantly shifts toward the diketo form.

1,2-Dihydroxybenzene (catechol), which has a pK_{a1} value (9.23) a little larger than that of acetylacetone and a large pK_{a2} value (13.0), reacted with **1** under heating at 110 °C in toluene to give chelated catecholato-*O*,*O*′ complex **6** as a result of successive oxidative addition involving two O–H groups (Eq. 10).[26,27]. By a similar reaction of **1** with 2,3-naphthalenediol, the corresponding chelated 2,3-naphtalenediolato-*O*,*O*′ complex was obtained. Essentially the same results were obtained when dinitrogen complex of Mo(0), *trans*-[Mo(N_2)$_2$(dppe)$_2$], was employed in the place of **1**. Tungsten analogs of **6** were obtained also by using *trans*-[W(N_2)$_2$(dppe)$_2$].

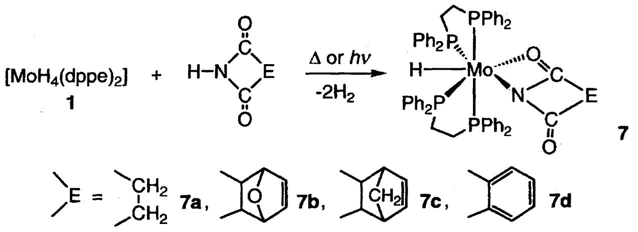


R = H, CH_3, $C(CH_3)_3$, $CO_2CH_2CH_3$

(10)

Catecholato and naphthalenediolato complexes thus obtained are yellow to brown solids. The configuration of the eight coordinate dihydrido complex **6** as shown in Eq. 10 was determined by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and confirmed by X-ray structure analyses for R = H and CO_2Et (Table 1). Hydrido protons in **6** appeared around $\delta = -2.6$ as a quasi-quintet for R = H, CH_3, and $C(CH_3)_3$, and as a triplet of triplets for R = CO_2Et. Observation that the hydrido signal of the last complex changed to a quasi-quintet at higher temperature (50 °C) revealed that the complex is fluxional at fairly high temperature, whereas the rest are fluxional even at room temperature.

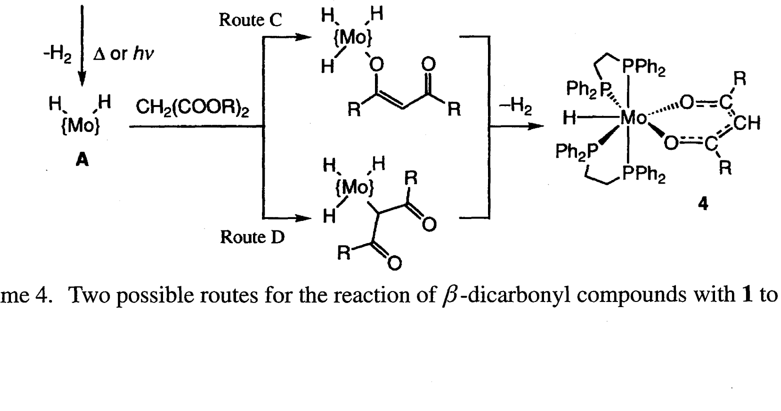
Oxidative Addition Reactions of 1 Involving N–H Bond Cleavage. The reaction of [MoH_4(dppe)$_2$] (**1**) with succinimide in benzene under irradiation gave wine-red colored seven coordinate hydrido(succinimido-*N*,*O*)molybdenum(II) complex **7a** in which the imido ligand is coordinated in a bidentate fashion through its nitrogen atom and one of two carbonyl oxygen atoms. Similar reactions took place for phthalimide and some other substituted succinimides as shown in Eq. 11.[28,29] Photoreaction of *trans*-[Mo(N_2)$_2$(dppe)$_2$] with succinimide in benzene under irradiation also afforded **7a**.



(11)

Succinimide is known to act as a weak acid (pK_a = 9.6) giving rise to ready displacement of the NH proton with an alkali metal. Complex **1** however did not show any indication of reaction with succinimide in benzene at room temperature, but reacted at the elevated temperature or under irradiation to give **7a** as shown in Eq. 11. These observations indicate that the reaction proceeds via direct attack of imide on the coordinatively unsaturated intermediate **A** or **B** in Scheme 2.

IR spectrum (KBr) of succinimido complex **7a** showed two distinct bands at ca. 1700 and 1540 cm^{-1} which may be assignable to the carbonyl stretching of the imido ligand; the lower frequency band to the C=O group coordinated to the metal and the higher one to the free C=O. In the ^{1}H NMR of **7a** at room temperature a hydride signal was observed at $\delta = -6.62$ as a triplet of triplets assignable to an A_2K_2X spin system (A = P_{eq}, K = P_{ax}, X = H). This, together with the coupling constants, resembles the values observed for the carboxylato complex **3** described above. Although the



Scheme 4. Two possible routes for the reaction of β-dicarbonyl compounds with **1** to give **4**.

hydride signals of complexes **7c** and **7d** were similar to that of **7a**, a more complicated pattern consisting of 14 peaks assignable to an ABKMX (A, B = P_{eq}, K, M = P_{ax}, X = H) spin system was observed for **7b**. $^{31}P\{^{1}H\}$ NMR spectra consistent with the ^{1}H NMR results were obtained at 25 °C: e.g. a pair of triplets assignable to an A_2K_2 spin system was observed for **7a**, whereas a complex pattern assignable to an ABKM spin system was observed for the rest. On lowering the temperature of **7a** in THF, the ^{31}P NMR signal gradually broadened and coalesced at about -30 °C. At -82 °C the hyperfine structure appeared, which may be assigned to the ABKM spin system.

Two triplets of A_2K_2 in the ^{31}P NMR of **7a** at room temperature, which are similar to those observed for **3** or $[MoH\{NPhC(O)H\text{-}N,O\}(PMe_3)_4]$,[30] suggest that the complex **7a** in solution is exchanging within the NMR time-scale between **I** and **II** in Chart 2. Thus an interconversion between **I** and **II** which takes place at higher temperatures slows down on lowering the temperature and finally freezes at the intermediate conformation **III** or **III′** which is energetically most favorable, i.e. the sterically least demanding conformation. X-Ray analysis of the wine-red needle of **7a** (Table 1) revealed its solid state molecular structure to be consistent with the low temperature spectral results. In the cases of **7b** and **7c** which carry bulky substituents on the imido ligand, interconversion between **I** and **II** may be hindered and the sterically least-demanding conformation will be predominant even at room temperature, giving rise to the observation of ^{31}P NMR similar to that of **7a** taken at -82 °C.

It is rather surprising that even simple amides such as *N*-methylacetamide react smoothly with **1** in benzene or toluene under irradiation at room temperature or heating at 110 °C to give (η^2-*N*-acylamido-*N*,*O*)hydridomolybdenum(II) complex **8**.[27,31] While some examples of the oxidative addition of a highly polarized N–H bond of a cyclic imide, such as those shown above, have been reported,[28,29,32—35] there have been only two precedents for the oxidative addition of simple amides involving N–H bond cleavage to Ru(0) and Fe(0).[36,37] The closely related phenylamide complex $[MoH\{NPhC(O)\text{-}H\text{-}N,O\}(PMe_3)_4]$ has been synthesized by the reaction of phenyl isocyanate with $[MoH_2(PMe_3)_5]$,[30] but the reaction to yield **8** from **1** and amide is, to our knowledge, the first example of the direct oxidative addition of an amide N–H group to the group 6 transition metals.

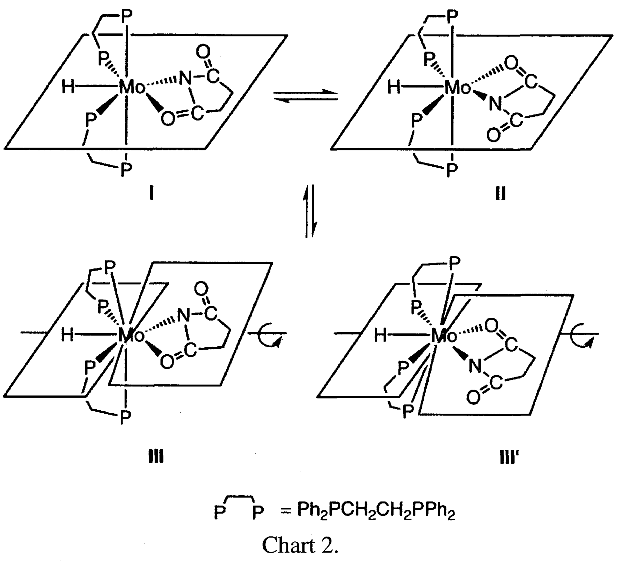
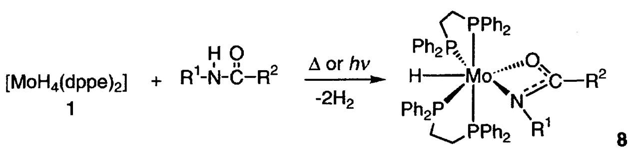


Chart 2.

Irradiation with a 100-W high-pressure mercury lamp at room temperature of a yellow benzene solution containing **1** and an equivalent amount of amides afforded crystalline maroon complexes **8** accompanied by the evolution of H_2 (Eq. 12). Similar results were obtained when **1** and amides were heated at 110 °C in toluene. Tungsten analog of **8** were prepared similarly starting from *trans*-$[W(N_2)_2(dppe)_2]$.[31]



R^1, R^2 = CH_3, CH_3 (**a**); C_6H_5, CH_3 (**b**); CH_3, H (**c**); C_6H_5, H (**d**); $(CH_2)_3$ (**e**); C_6H_5, C_6H_5 (**f**)

(12)

The amide I band in the IR spectrum of **8** shifted to lower frequency by about 100 cm^{-1} as compared with this band in the free amide. This, together with the disappearance of the amide II and the ν(N–H) bands, supports the N–H bond cleavage and the mode of coordination, as shown in Eq. 12. In the ^{1}H NMR spectra, hydride signals appeared at around $\delta = -5$ with the multiplicity corresponding to an ACKMX spin system. These signals are consistent with the four isolated signals in $^{31}P\{1H\}$ NMR spectra each being split into a doublet of doublets of doublets (ACKM spin system).[31]

On the basis of the X-ray analysis of the prismatic single crystal of **8a** (Table 1), the complex is regarded as being in a distorted-pentagonal-bipyramidal configuration with two phosphorus atoms, the nitrogen and the oxygen atoms of the amide ligand, and a hydride ligand comprising the pentagonal girdle. The total of the bond angles around the molybdenum atom $[\angle P^4\text{–}Mo\text{–}P^3+\angle P^3\text{–}Mo\text{–}O+\angle O\text{–}Mo\text{–}N+\angle N\text{–}Mo\text{–}P^4]$ is 359.7°, which suggests a strictly flat equatorial plane. The nitrogen, oxygen, and three carbon atoms of the amide ligand are in a plane with a C–O bond length of 1.29(2) Å, which is longer than the corresponding bond length of free *N*-methylacetamide (1.225 Å) and a C(1)–N bond length of 1.35(2) Å, which is slightly shorter than that of the free ligand (1.386 Å). The Mo–N distance of 2.25(1) Å for **8a** is shorter than the average value of the σ-donating Mo–N bond distance of 2.33 Å,[38] whereas the Mo–O distance (2.24(1) Å) is close to those of the related complex $[MoH(O_2COEt\text{-}O,O')(dppe)_2]$ (**3**, R = OEt) (2.271(2) and 2.333 (3) Å).[19] These structural features strongly suggest the following resonance form of the η^2-amide ligand of **8** (Chart 3).

It is noteworthy that *N*-acylamido complexes **8** are highly susceptible to the electrophilic attack by organic acids. Thus, the reaction of **8f** with acetic acid in benzene at room tem-

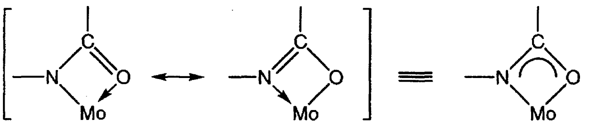
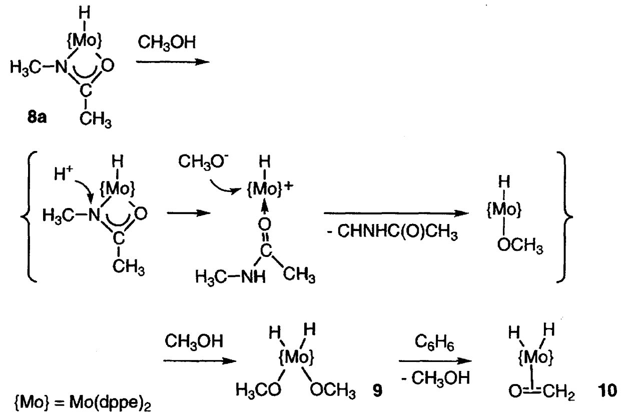


Chart 3.

perature gave $[MoH(O_2CCH_3)(dppe)_2]$ **3**, which has been prepared by photoreaction of **1** with allyl acetate (Eq. 7), together with *N*-phenylbenzamide, while that of **8b** with hexafluoroacetylacetone under similar conditions afforded $[MoH\{CH(COCF_3)_2\text{-}O,O'\}(dppe)_2]$ **4a** and *N*-phenylacetamide.

Furthermore, such a weak acid as methanol reacts with **8a** at ambient temperature to give eight-coordinate dihydridodimethoxomolybdenum complex **9** together with *N*-methylacetamide both in quantitative yield (Scheme 5). Dimethoxo complex **9** gradually changes into the formaldehyde complex **10** in benzene, the conversion being significantly retarded in toluene.

Ethanol reacted similarly with **8a** to give diethoxodihydridomolybdenum complex, which is less stable than **9** and changes to the known carbonyl complex *cis*-$[Mo(CO)_2(dppe)_2]$ in solution at slightly elevated temperatures accompanied with evolution of methane and H_2. Treatment of **8a** with 2-propanol at room temperature afforded the parent tetrahydrido complex **1** quantitatively with accompanying formation of acetone. A β-hydrogen elimination from the initially formed isopropoxo intermediate might have been taken place as shown in Scheme 6.

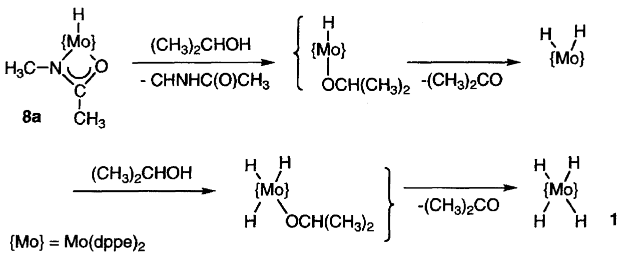


Scheme 5. Possible pathway for the formation of formaldehyde complex **10** from **8a** through dihydridodimethoxo complex **9**.

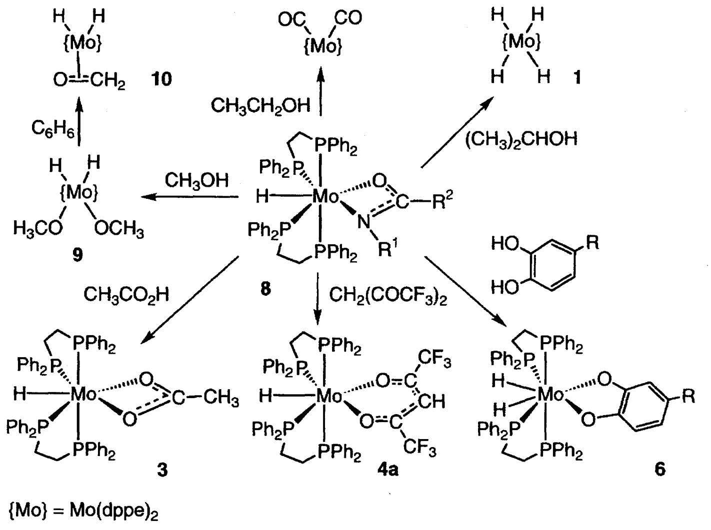
Treatment of **8a** with phenol in toluene at room temperature gave a certain product, which was unable to be characterized due to its poor solubility. Catechols and 2,3-naphthalenediol, on the other hand, reacted with **8a** under ambient conditions to give corresponding catecholato (Eq. 10) and naphthalenediolato complexes **6**, respectively,[27] the same complexes as those obtained from **1** under heating in toluene.

Reactions of (*N*-acylamido-*N*,*O*)hydrido complex **8** with various electrophiles, all of which proceeded under ambient temperature, are summarized in Scheme 7. Complex **8** thus proved to be a useful starting complex for versatile hydridomolybdenum complexes.

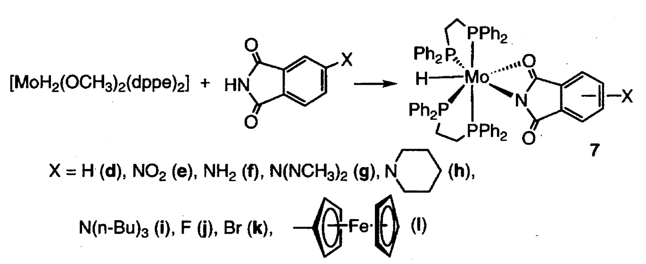
The dihydridodimethoxo complex **9** obtained above is found to be much more susceptible to the electrophilic attack than (*N*-acylamido-*N*,*O*)hydrido complex **8**. By use of this characteristic feature of **9**, a series of hydrido complexes with substituted phthalimido ligand **7d**—**7k**, some of which were unable to be prepared via other methods due to various kinds of limitations, was successfully synthesized (Eq. 13).[39]



Scheme 6. Reaction of *N*-acetylamido complex **8a** with 2-propanol to give tetrahydride **1**.



Scheme 7. *N*-Aceylamido complex **8** as a source of variety of hydridomolybdenum complexes.



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(13)

The electron withdrawing or donating effect of the substituent on the imido-phenyl ring in complexes **7** is expected to resonate with the central metal through the phthalimido framework constructing the zwitter ionic canonical formula as shown in Chart 4. In fact, complex **7** with the electron donating substituent, complex **7e** for example, showed solvatochromism in the UV-vis. absorption spectra measured in *N*,*N*-dimethylformamide and toluene.[39]

Oxidative Addition Reactions of 1 Involving Si–H Bond Cleavage. 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 with reference to the organic syntheses incorporating silyl groups as well as to its peculiar bonding properties. A typical method 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 (Scheme 8). Various kinds of transition metal silyl or silylene complexes have so far been synthesized via this method.[40]

In contrast to the rich chemistry of the late transition metal complexes with M–Si bond, the limited number of the syntheses of group 6 metal complexes with M–Si bond has been reported as follows.[40c,41]

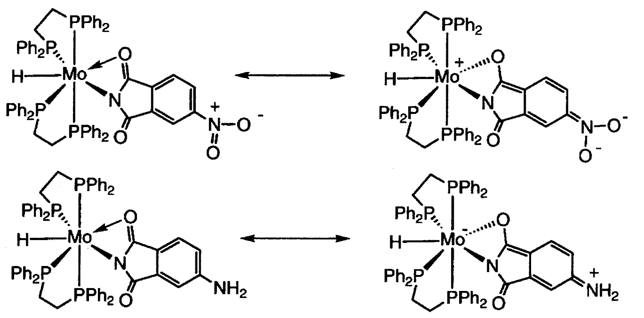
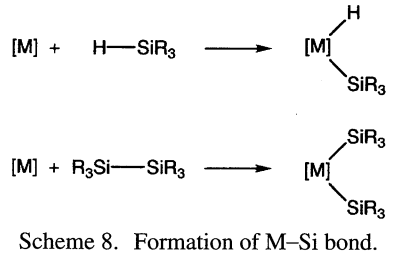
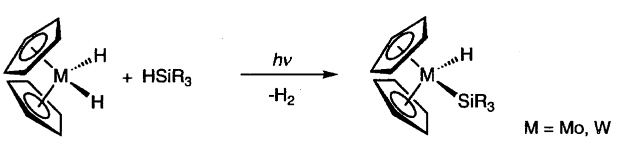


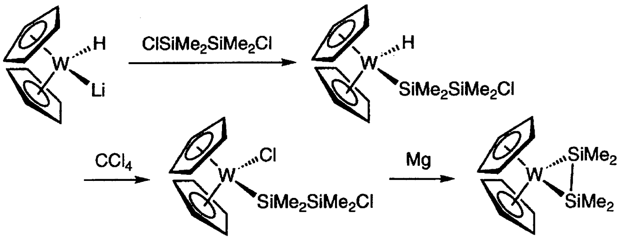
Chart 4.



Scheme 8. Formation of M–Si bond.

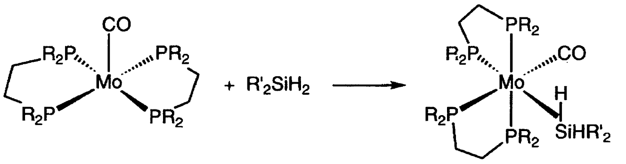


(14)



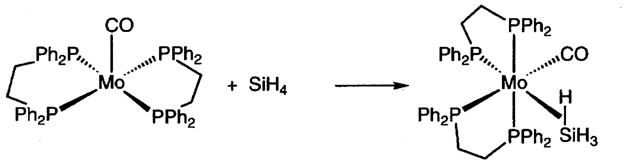
(15)

Luo et al. reported isolation of the novel η^2-silane complexes by the reaction of carbonyl complexes of molybdenum(0) with silanes (Eqs. 16 and 17).[42,43]



R = Et, CH_2Ph; $SiHR'_2$ = SiH_2Ph, $SiH_2(n\text{-}C_6H_{13})$, $SiHPh_2$

(16)



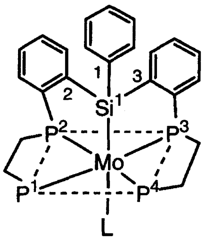
(17)

In expectation of getting oxidative addition products of the general formula, H–{Mo}–SiR_3, which are easily conceivable from the series of reactions described above, we examined the thermal reactions of tetrahydride **1** with silanes. In the reaction of **1** with phenylsilane $PhSiH_3$ in refluxing toluene, an oxidative addition reaction involving Si–H bond cleavage to give Mo–Si bond did in fact occur, although the final isolated product was a little more complicated than what was expected from the simple oxidative addition.[44]

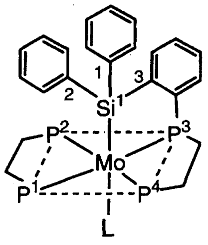
Thus, heating the toluene solution of **1** under reflux in the presence of more than 2 equiv of phenylsilane for 3 h afforded a yellow solid in yield of 78%, which was characterized as **10** shown in Scheme 9 spectroscopically as well as by the X-ray crystallographic study (Table 2). Complex **10** represents the first example of the simultaneous activation of a Si–H bond and two aromatic C–H bonds giving rise to the formation of a quinquedentate ligand which consists of a P∼P∼Si∼P∼P girdle.[44]

Later, the detailed study of this reaction revealed that reaction of **1** with only one equivalent of $PhSiH_3$ under the similar conditions afforded a greenish yellow solid, which was assignable to the trihydride **11a** in yield of 87%. Complex **10** was also derived from trihydride **11a** by its reaction with excess $PhSiH_3$ in refluxing toluene. When *o*- or *p*-tolyl silanes were used in place of phenylsilane, trihydride complexes **11b** and **11c**, respectively, were obtained, although

Table 2. Comparison of the Structural Data for the Complexes **10**, **13**, **14**, and **17** with the P~P~Si~P~Si Quinquidentate Ligand and **12**, with the P~P~Si Tridentate Ligand



10 13 14



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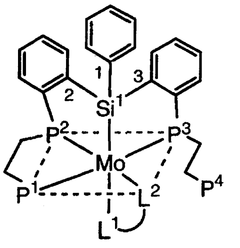

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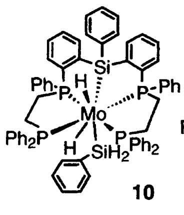
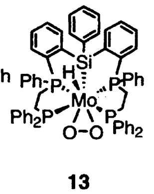
Complex	Mo–Si^1 Mo–L	Mo–P^1 Mo–P^2 Mo–P^3 Mo–P^4	Si^1–C^1 Si^1–C^2 Si^1–C^3	P^1–Mo–P^2 P^2–Mo–P^3 P^3–Mo–P^4 P^4–Mo–P^1	Mo–Si^1–C^1 C^2–Si^1–C^3	Others
10	2.559(2) L=Si^2 2.620(2)	2.487(2) 2.451(2) 2.455(2) 2.490(2)	1.899(8) 1.913(8) 1.913(8)	79.44(7) 101.39(7) 81.08(7) 100.67(7)	126.2(2) 106.6(3)	Si^1–Mo–L 143.91(7)
13	2.554(5) L=O 2.12(1) 2.11(2)	2.495(5) 2.434(5) 2.422(5) 2.497(5)	1.93(2) 1.91(2) 1.85(2)	80.9(2) 99.2(2) 80.0(2) 102.6(2)	124.2(5) 104.9(7)	Si^1–Mo–O^1 151.6(5) Si^1–Mo–O^1 144.9(5)
14	2.515(7) L=O 2.17	2.496(2) 2.466(2) 2.485(2) 2.507(2)	1.869(8) 1.887(7) 1.911(7)	80.16(2) 101.77(2) 80.31(6) 96.32(6)	122.7(2) 102.7(3)	Si^1–Mo–O 143.7(1)
17	2.519(3) L1, L2 2.156(6) 2.167(6)	2.454(3) 2.358(3) 2.470(3) —	1.88(1) 1.89(1) 1.90(1)	80.5(1) 104.93(10) P^3–Mo–L^2 89.7(2) L^2–Mo–P^1 90.9(2)	117.4(3) 102.7(5)	Si^1–Mo–L^1 149.1(2)
12	2.541(2) —	2.460(5) 2.477(2) 2.418(5) 2.503(4)	1.919(7) 1.909(6) 1.917(6)	79.1(1) 95.4(1) 79.2(2) 100.5(2)	121.6(2) 100.9(3)	



10



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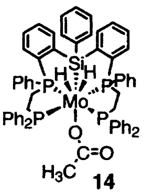

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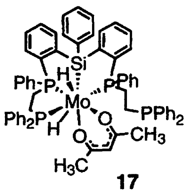

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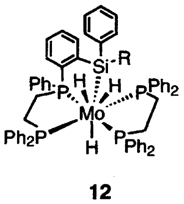
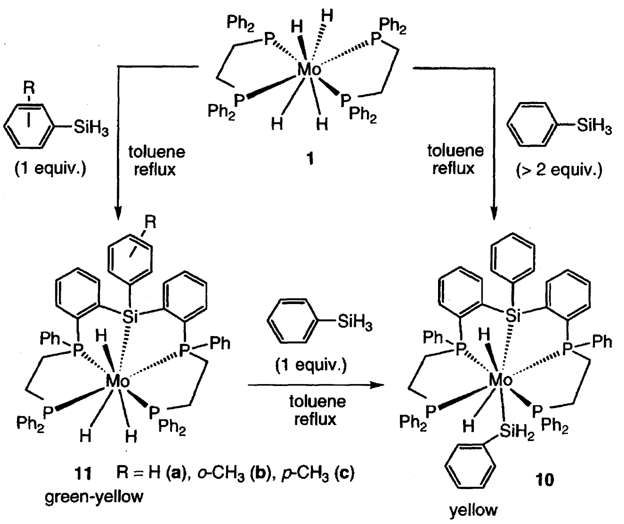


12

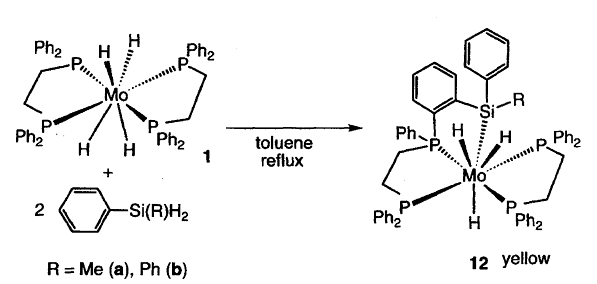
a disilyl complex corresponding to **10** was found to be too unstable to be isolated for these tolylsilanes (Scheme 9).[45]

When secondary silanes such as Ph(Me)SiH$_2$ or Ph$_2$SiH$_2$ were employed in the similar reaction with **1**, the trihydrido complex **12** with a tridentate ligand P~P~Si, which was structurally characterized by X-ray analysis (Table 2), was isolated instead of **11** (Scheme 10).[45]

The X-ray crystallographic study of complex **10** revealed that there are two Si atoms in the molecule: One (Si^2) constitutes a usual terminal SiH$_2$Ph ligand and the other (Si^1) contains bonds between silicon and the *ortho* carbons of the phenyl groups of the dppe ligand. Interestingly, the mode of bonding between Si^1 and two *ortho* carbons is not symmetrical in respect of the equatorial P^1–P^2–P^3–P^4 plane. Mo–Si^1 was found to be shorter than Mo–Si^2 by 0.06 Å. Although the hydrido ligand was unable to be located directly in the molecular structure, its presence was confirmed by means of ^{1}H NMR spectroscopy as follows. The high-field region of the ^{1}H NMR spectrum of **10** in C$_6$D$_6$ at room temperature showed two resonances with integration 1 : 1; a broad multiplet at $\delta = -4.5$ and a broad, apparent triplet at $\delta = -5.4$. The results indicate that there are two sets of magnetically inequivalent protons that may be assignable to two hydrido ligands, at least at and below room temperature. The most



Scheme 9. Thermal reactions of **1** with primary arylsilanes.



Scheme 10. Thermal reactions of **1** with secondary arylsilanes.

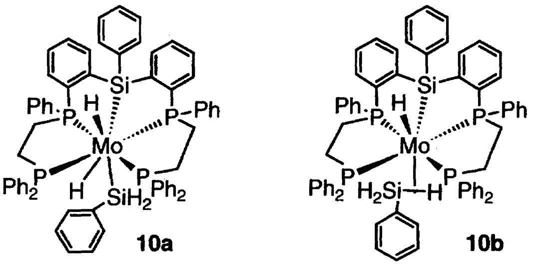


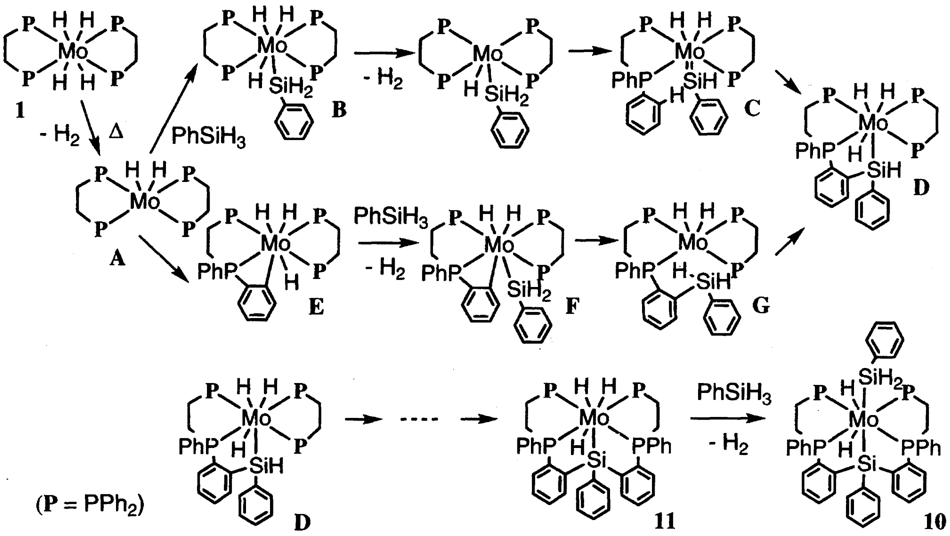
Chart 5.

straightforward explanation for these NMR results may be that these two hydrides reside separately on both sides of the pseudo-equatorial plane comprised of four phosphorus atoms (formula **10a** shown in Chart 5). Alternatively, the formula like **10b**, where two hydrides are differentiated from each other by NMR by way of the mode of coordination, that is, the normal terminal hydride and the η^2-silane type of coordination, may also be conceivable. We are unable to decide the precise configuration of the hydride ligands in **10** at the present stage.[44]

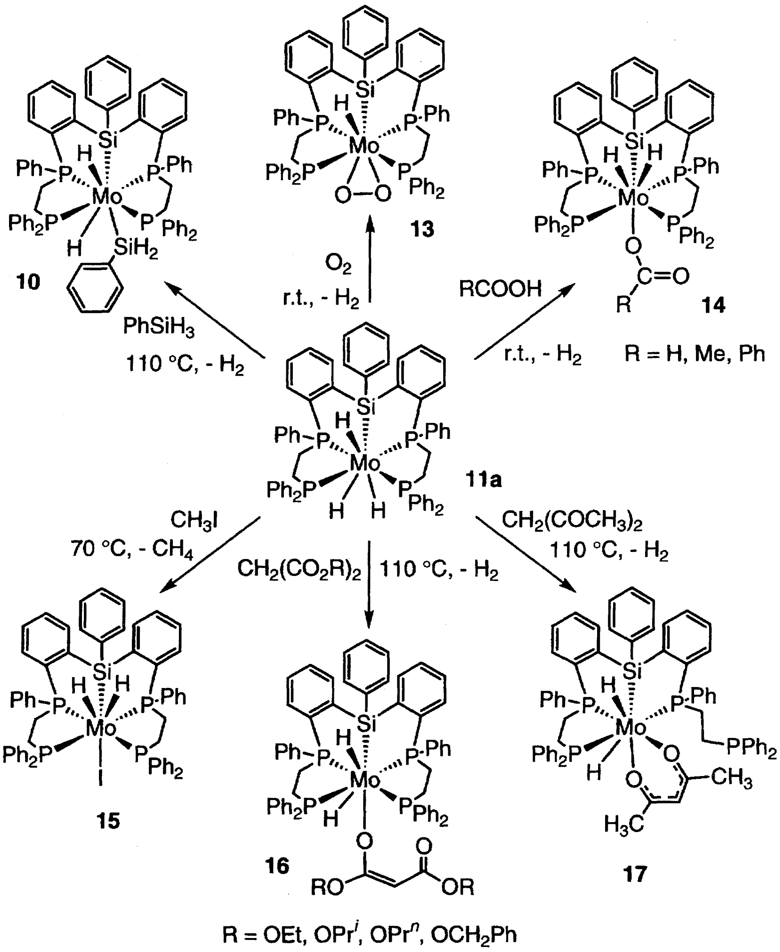
It is intriguing to speculate on the reaction path from **1** to **10**. As is shown in Scheme 11, the first molecule of $PhSiH_3$ may oxidatively add to the 16-electorn reactive intermediate **A**, which was generated thermally from **1** releasing one mole of H_2, to give a phenylsilyl-molybdenum intermediate **B**. Since the direct substitution of the ortho hydrogens of phenyl groups in the dppe ligand with Si in the coordinated SiH_2Ph ligand seems to be less likely, the intervention of the silylene intermediate like **C** in the Scheme 11 seems to be more plausible. The successive activation of ortho C–H bonds in the phenyl groups of dppe ligands with Mo=Si bond may result in the formation of the intermediate **11** through the intermediate **D**. The alternative path incorporating oxidative addition of ortho C–H bonds of dppe, reductive elimination of Mo–C and Mo–Si bonds, and oxidative addition of Si–H bond (the path involving **E** through **G** in Scheme 11) without intervention of silylene intermediate, however, cannot be ruled out.[44]

Several reactions incorporating trihydrido complex **11** were examined and it was found that two of three hydrido ligands in **11** are readily displaced with various substrates such as dioxygen, caboxylic acid, alkyl iodide, and β-diketones to give the corresponding complexes.

The trihydrido complex **11** was found to undertake versatile reactions, mostly maintaining the unique quinquidentate ligand intact, as is summarized in Scheme 12. As described above, **11a** reacts with further mole of phenylsilane to give



Scheme 11. Possible reaction path from **1** to **10** and **11**.



Scheme 12. Some reactions of trihydrido complex **11a**.

10. Solutions of complexes **11** in THF were found to be very susceptible to air and changed their color from yellow to greenish in the presence of even trace amounts of the contaminated air. When dioxygen was bubbled through a THF solution of **11a** at room temperature, a yellow solution immediately turned green. The work up of the solution afforded green crystals which were analyzed as [MoH(P~P~Si~P~P)(η^2-O_2)] (**13**) on the basis of spectral and X-ray structural analyses (Table 2). The analogous dioxygen complexes corresponding to **13** were obtained similarly for tolyl derivatives **11b** and **11c**. Evolution of a significant amount of H_2 was detected by GLC when the reaction of **2** with O_2 was conducted in a sealed system.

Carboxylic acids such as formic, acetic, and benzoic acids reacted with **11a** to give corresponding carboxylato complexes **14** where the carboxylato ligand coordinates to the metal in a unidentate mode through one oxygen atom as is evidenced spectroscopically as well as by the single crystal X-ray analysis (Table 2).[46] If one takes into account that most of the related carboxylatomolybdenum complexes so far reported possess the bidentate type carboxylato ligand,[12,14,19] the firm double chelate framework consisting of Si, four phenyl carbons and two P atoms in **14** seem to have hindered the coordination of the second oxygen atom of the carboxylato ligand. The corresponding carboxylato-κO complexes were obtained similarly by the reaction of carboxylic acids with the trihydrido complex derived from *o*-tolylsilane **11b**.

Heating the THF solution of **11a** or **11b** at 70 °C in the presence of twice as many moles of CH_3I, the reddish orange iodo complex **15** was obtained accompanied by evolution of methane (Scheme 12). The similarity between **14** and **15** in the pattern and the chemical shift of the ^{1}H NMR signal assignable to the hydrido ligand strongly suggests that the latter has a similar molecular arrangement to the former, the structure of which was confirmed by X-ray structure analysis.

The reaction of **11a** with malonates in refluxing toluene afforded malonato complex **16** shown in Scheme 12, which has a unique unidentate malonato ligand bonded via one enolic oxygen atom to the metal, with the quinquedentate P~P~Si~P~P framework being kept intact.[47] The highly stable nature of the framework seems to have hindered the chelation of the malonato ligand.

In contrast, when 2,4-pentandione (acetylacetone) was allowed to react with **11a** under the similar conditions, chelated 2,4-pentandionato complex **17** was obtained in which one of four phosphorus atoms of the framework is dissociated.[47] This result of the unique reaction was confirmed by the X-ray structure analysis of the complex **17** (Table 2). Although the rational explanation of these results obtained for two types of β-dicarbonyl compounds, malonate and 2,4-pentanedione, is not straightforward at present, the difference in the steric congestion between two dicarbonyl compounds seems to be responsible for these results.

Selected bond lengths and angles of some complexes prepared in the present study are summarized in Table 1 for complexes **3**, **4**, **6a**, **6b**, **7a**, and **8a**, and in Table 2 for silyl complexes **10**, **12**, **13**, **14**, and **17**. The close resemblance of the structural data for the quinquedentate P~P~Si~P~P ligand between complexes **10**, **13**, **14**, and even the terdentate P~P~Si ligand strongly suggests that such a unique reaction as a simultaneous activation of a Si–H and two C–H bonds may occur due, at least partially, to the template effect; ortho carbons of one of two phenyl groups attached to one phosphorus may be placed in the bonding distance with Si caused by steric congestion.

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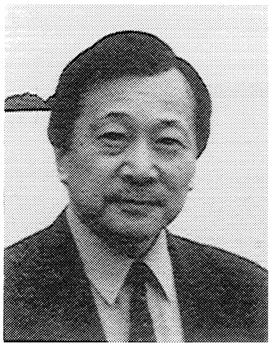

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