Synthesis and Structural Characterization of the New Dioxygen Complexes of Molybdenum(IV)

Da-Yang Zhou, Li-Bin Zhang, Makoto Minato, Takashi Ito,* and Kohtaro Osakada†
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240
†*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226*

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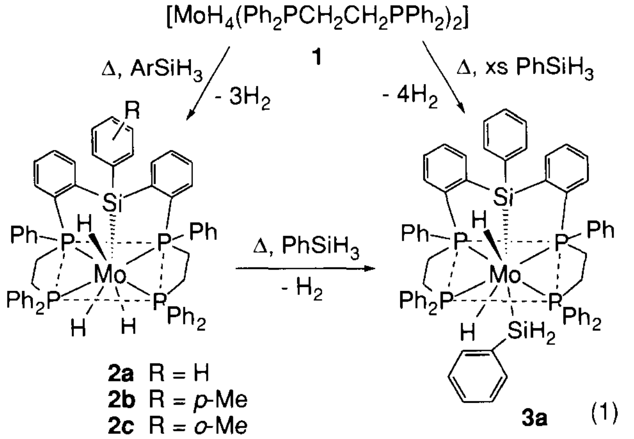
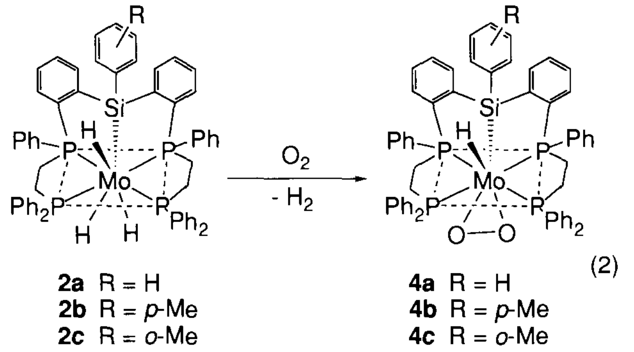
The molybdenum trihydrido complexes, $[\mathrm{MoH_3\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}\mathit{o}]_2(Ar)Si\text{-}\mathit{P,P,P,P,Si}\}}]$, which were readily formed by the thermal reaction of $[\mathrm{MoH_4(Ph_2PCH_2CH_2PPh_2)_2}]$ with arylsilanes, reacted with molecular dioxygen to give the unprecedented molybdenum(IV) peroxo type $\eta^2\text{-}\mathrm{O_2}$ complexes, $[\mathrm{MoH\{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}\mathit{o}]_2(Ar)Si\text{-}\mathit{P,P,P,P,Si})\}(\eta^2\text{-}O_2)}]$, the structure of which were studied spectroscopically as well as X-ray crystallographically.

Much attention has been focused recently on the interaction of dioxygen with transition metal complexes with special reference to the activation of the former on an active center of the monooxygenase such as cytochrome P450 and fairly a lot of dioxygen coordinated transition metal complexes have been reported.[1,2] Although a certain number of peroxo type dioxygen complexes of group 6 transition metals has so far been reported, most of them are prepared using $\mathrm{H_2O_2}$ as a source of peroxo ligand and all possess central metals in an extremely high oxidation number such as 6.[3] Here we report the synthesis and the structural characterization of the molybdenum(IV)-dioxygen complex which possesses a peroxo type $\eta^2\text{-}\mathrm{O_2}$ ligand as well as a novel quinquedentate ligand bonded to the metal via four phosphorus atoms and a silicon atom. This is, to our knowledge, the first example of the structurally characterized mononuclear peroxo complex of the Mo(IV) oxidation state formed directly from dioxygen under very mild conditions.

Recently we found that the reaction of $[\mathrm{MoH_4(dppe)_2}]$ (**1**, dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) with phenylsilane in refluxing toluene for 2 h gives a novel trihydrido complex [MoH$_3$(P~P~Si~P~P)] (**2a**, P~P~Si~P~P stands for $\{\mathrm{[Ph_2PCH_2CH_2P(Ph)C_6H_4\text{-}\mathit{o}]_2(Ph)Si\text{-}\mathit{P,P,P,P,Si}}\}$) which possesses an unusual doubly chelated quinquedentate ligand (eq 1).[4] Subsequently, the analogous complexes **2b**[5] and **2c**[6] have been prepared by the similar reactions employing *p*- and *o*-tolylsilanes in the place of phenylsilane. The novel framework of the quinquedentate ligand was confirmed by the X-ray crystallographic analysis of the disilyl complex **3a** which was derived from **2a** by its treatment with another mole of phenylsilane (eq 1).[4] Isolation of the disilyl type complex corresponding to **3a** was unsuccessful in the case of **2b** due to the highly unstable nature of the product. On the contrary, **2c** was found to be inert to such a reaction. The chemical properties of complexes **2** and **3** were thus found to be very sensitive to the subtle change of the arylsilanes.

Solutions of complexes **2** in THF were found to be very susceptible to air and changed their color from yellow to greenish in the presence of even trace amount of contaminated air. When dioxygen was bubbled through a THF solution of **2a** at room temperature, a yellow solution immediately turned green and the work up of the solution after stirring for 2 h afforded green crystals which were analyzed as [MoH(P~P~Si~P~P)($\eta^2\text{-}\mathrm{O_2}$)] (**4a**)[7] on the basis of spectral and X-ray structural analyses (vide infra) (eq 2). The analogous dioxygen complexes corresponding to **4a** were obtained similarly for tolyl derivatives **2b** and **2c** in yields of 83% and 80%, respectively. Evolution of a significant amount of $\mathrm{H_2}$ was detected by GLC when the reaction of **2** with $\mathrm{O_2}$ was conducted in a sealed system.





X-ray crystallographic analysis of a green crystal of **4a** which was obtained by the recrystallization from hexane/THF solution was conducted and the resulting ORTEP drawing is shown in Figure 1.[8]

The structure of complex **4a** shows that the dioxygen ligand is coordinated to molybdenum atom in a side-on fashion. It contains a bond between silicon and the ortho carbons of the phenyl groups of the dppe ligand constructing a quinquedentate ligand: the whole features of which are virtually the same as in the case of **3a**. The O–O bond distance is 1.41(3) Å which is longer than the O–O bond distance of the free $\mathrm{O_2}$ (1.21 Å) and is within the range of the common peroxo type coordination of dioxygen (1.4—1.5 Å).[3,9] The bond length of Mo–O1 and Mo–O2 are 2.12(1) Å and 2.11(2) Å, respectively, which are significantly longer than the M–O bond lengths reported for, e.g., $[\mathrm{Cr(\eta^2\text{-}O_2)_4}]^{3-}$ (1.89 and 1.94 Å),[9] $[\mathrm{OsH(\eta^2\text{-}O_2)}\{$1,2-bis(dicyclohexyl-

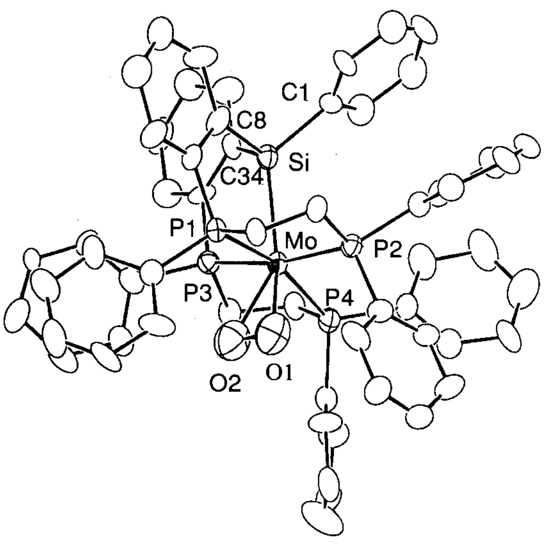
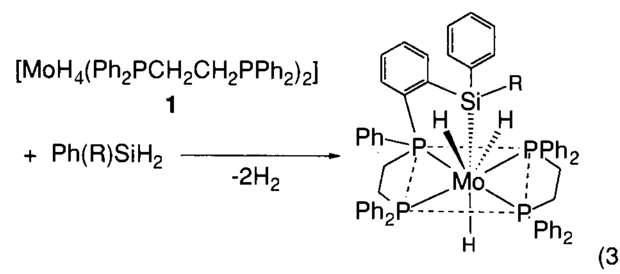


Figure 1. ORTEP drawing of the complex **4a**. Representative bond distances (Å) and angles (°): Mo–P1 2.434(5), Mo–P2 2.495(5), Mo–P3 2.422(5), Mo–P4 2.497(5), Mo–Si 2.554(5), Mo–O1 2.12(1), Mo–O2 2.11(2), Si–C1 1.93(2), Si–C8 1.91(2), Si–C34 1.85(2), O1–O2 1.41(3), P1–Mo–P2 80.9(2), P2–Mo–P4 102.6(2), P1–Mo–P3 99.2(2), P3–Mo–P4 80.0(2), O1–Mo–O2 38.9(7), Mo–Si–C1 124.2(5), Si–Mo–O1 151.6(5), Si–Mo-O2 144.9(5), P2–Mo–O1 74.2(5), P1–Mo–O2 83.9(5), Si–Mo–P1 76.4(2), Si–Mo–P2 92.3(2), Si–Mo–P3 77.4(2), Si–Mo–P4 116.9(1).

phosphino)ethane}$_2$]BPh$_4$ (2.045(8) and 2.037(8) Å),[10] and [CpW(O)(η^2-O$_2$)(CH$_2$SiMe$_3$)] (1.68(3) and 1.92(3) Å).[11] The hydrido ligand was not able to be located directly in the molecular structure, though its presence was evidenced by the ^{1}H NMR of **4a** in C_6D_6, where Mo–*H* signal was observed at δ 0.1 as a triplet of triplets assignable to an A_2K_2X spin system. The hydride is presumed to reside on the same side as the Si atom since there seems to be a plenty of room on the surface made of Si, P2, and P4.

The presence of the P~P~Si~P~P type of quinquedentate ligand in **4** seems to be crucial in stabilizing peroxo type dioxygen complex of Mo(IV) on the basis of the following two observations: (1) Treatment of the parent complex [MoH$_4$(dppe)$_2$] (**1**) with O_2 in solution only resulted in the deterioration of the complex. (2) The trihydrido complexes with a tridentate {[Ph$_2$P-CH$_2$CH$_2$P(Ph)C$_6$H$_4$-*o*](Ph)(R)Si-*P,P,P,P,Si*} (R = Me, Ph) ligand (complex **5a** and **5b** shown in eq 3), which were isolated from the reaction between **1** and the secondary silanes such as Ph_2SiH_2 or $PhMeSiH_2$ and structurally characterized by X-ray analysis,[12] did not give any dioxygen complex similar to **4** on their treatment with O_2 but led to the deterioration.



$$[\mathrm{MoH_4(Ph_2PCH_2CH_2PPh_2)_2}]\ \mathbf{1} + \mathrm{Ph(R)SiH_2} \xrightarrow[-2\mathrm{H_2}]{} \qquad (3)$$

5a R = Me
5b R = Ph

The coordination of the bulky quinquidentate ligand seems to be so robust that it prevents attack of the second molecule of dioxygen on the molybdenum(IV) metal center.

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5 Complex **2b**. Pale yellow-green powder. Yield 75%. ^{1}H NMR (C_4D_8O, 270 MHz): δ -4.2 – -5.1 (3H, m, Mo–*H*), 2.4 (3H, s, *p*-C*H*$_3$-C$_6$H$_4$); ^{31}P{^{1}H} NMR (C_4D_8O, 109.4 MHz): δ 83.6 (d, *J* = 58 Hz), 112.9 (d, *J* = 58 Hz); IR (KBr): ν(Mo–H) = 1705 cm^{-1}.

6 Complex **2c**. Pale yellow-green powder. Yield 85%. ^{1}H NMR (C_7D_8, 270 MHz): δ -3.9 – -4.6 (3H, m, Mo–*H*), 2.1 (3H, s, *p*-C*H*$_3$-C$_6$H$_4$); ^{31}P{^{1}H} NMR (C_4D_8O, 109.4 MHz): δ 76.9 (d, *J* = 61 Hz), 112.9 (d, *J* = 58 Hz); IR (KBr): ν(Mo–H) = 1708 cm^{-1}. Anal. Found: C, 67.24; H, 5.16%; Calcd for $C_{66}H_{68}O_4P_4MoSi$ (**4a**•2THF): C, 67.57; H, 5.84%.

7 Complex **4a**. Green crystals. Yield 85%. ^{1}H NMR (C_6D_6, 270 MHz): δ 0.1 (1H, tt, *J* = 15.9 and 34.8 Hz, Mo–*H*); ^{13}C NMR (C_4D_8O, 67.8 MHz): δ 29.5 (broad m, P*C*H$_2$CH$_2$P), 31.5 (broad m, PCH$_2$*C*H$_2$P); ^{31}P{^{1}H} NMR (C_4D_8O, 109.4 MHz, 80% H_3PO_4 reference): δ 105.3 (broad d, *J* = 61 Hz), 76.58 (broad d, *J* = 57 Hz); IR (KBr): ν(Mo–H) = 1705 cm^{-1}.

8 Crystals of **4a** are monoclinic, space group Cc (#9), with a = 26.760(4) Å, b = 12.108(4) Å, c = 19.926(7) Å, β = 116.03(2)°, V = 5801(2) Å^3, Z = 4, F(000) = 2444.00, μ = 4.05 cm^{-1}, D = 1.342 g/cm^3, Rigaku AFC5R, Mo-Kα (λ = 0.71069 Å), 5049 reflection with $Fo > 3\sigma(Fo)$, R = 0.068, and Rw = 0.058.

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12 Results of the X-ray structure analysis for **5b** will be reported elsewhere.