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Reactions of a novel quadruply chelated molybdenum–silyl complex with β-dicarbonyl compounds

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Abstract

The novel molybdenum–silyl complex $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)–C_6H_4\text{-}o]_2(Ar)Si\text{-}P,P,P,P,Si\}]$ (**1**) reacted with 2,4-pentanedione to give eight-coordinate dihydrido complex **2** (**a**, Ar = Ph; **b**, Ar = *o*-tolyl) with a chelated 2,4-pentanedionato ligand as a result of repelling one of four Mo–P bonds in **1**. On the other hand, the reaction between **1** and dialkyl malonates gave an η^1-*O*-enolato type complex in which the quadruply chelated P–P–Si–P–P framework was found to be kept intact. The structure of **2a** was confirmed by X-ray crystallographic structure analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Hydrido complexes; β-dicarbonyl compounds; Molybdenum–silicon bonds; Quinquidentate ligands; Silyl ligand

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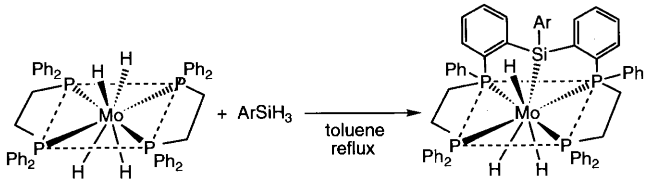
1. Introduction

β-Dicarbonyl compounds such as 2,4-pentanedione (acetylacetone) and dialkyl malonates and their deprotonated anions have been known to show versatile modes of coordination to the transition metal center [1]. These include their coordination to the metal in a bidentate (*O,O′*-) and an unidentate (*O*- or central *C*-) fashion as well as that incorporating a C–C double bond. Some β-dicarbonyl complexes of molybdenum have hitherto been reported, e.g. $[MoH\{CH(COCH_3)_2\text{-}O,O'\}(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [2], $[Mo(NNC_6H_4R\text{-}p)_2\{CH(COCH_3)_2\text{-}O,O'\}_2]$ [3], and $[MH\{CH(COOR)_2\text{-}O,O'\}(dppe)_2]$ [4], all of which possess a bidentate chelate mode of coordination.

Recently we have reported the unexpected formation of novel molybdenum–silyl complexes, $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)–C_6H_4\text{-}o]_2(Ar)Si\text{-}P,P,P,P,Si\}]$ (**1**) (Ar = phenyl, *o*-tolyl, and *p*-tolyl), with a quinquidentate ligand composed of a P–P–Si–P–P framework, which are obtained by the reaction of $[MoH_4(dppe)_2]$ with the corresponding primary silanes, SiH_3Ar, in refluxing toluene (Eq. (1)) [5,6].



Ar = Ph (**a**), *o*-tolyl (**b**), *p*-tolyl (**c**) **1**

(1)

The formation of complexes **1** is itself very novel because activation of not only an Si–H bond but also two C–H bonds of the ortho positions of the phenyl groups in the dppe ligand took place concurrently. In addition, complexes **1** have been found to be interesting in view of their reactivity since they have an almost open coordination site at the axial position opposite to the Si atom, which has been known to have a strong *trans*-effect. In fact, we have shown that complexes **1** react with a further mole of $PhSiH_3$ or gaseous dioxygen to give a disilyl complex or a peroxo type η^2-O_2 complex, respectively, in which a quinquidentate P–P–Si–P–P framework is found to be kept intact (Scheme 1) [5,6].

As a continuation of this line of investigation, the reactions of the trihydrido complex **1** with β-dicarbonyl compounds were examined. Thus, one of four phosphorus atoms originally bonded to the central metal as a member of the quinquidentate ligand has been cleaved

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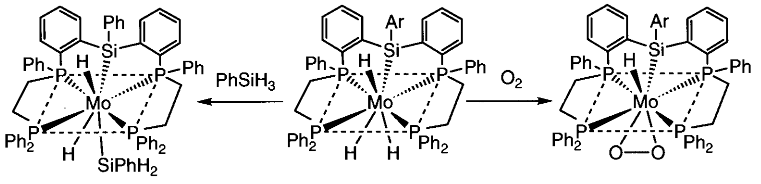


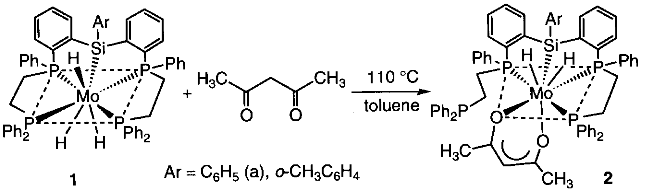
Scheme 1.

to give a dihydrido(2,4-pentanedionato-*O,O′*) complex in the reaction of **1** with 2,4-pentanedione, whereas the reaction of **1** with dialkyl malonates afforded a unidentately coordinated dihydrido(malonato-*O*) complex with the P–P–Si–P–P quinquidentate ligand kept intact. In this contribution, we report these reactions and the spectral and structural characterization of the resulting complexes.

2. Results and discussion

2.1. Reaction of $[MoH_3\{[Ph_2PCH_2CH_2P(Ph)-C_6H_4\text{-}o]_2(Ar)Si\text{-}P,P,P,P,Si\}]$ (**1**) with 2,4-pentanedione

Trihydrido complexes **1** in toluene were allowed to react with excess amount of 2,4-pentanedione under reflux to give red crystalline complexes which were assigned to $[MoH_2(2,4\text{-pentanedionato-}O,O')\{[Ph_2PCH_2CH_2P(Ph)-C_6H_4\text{-}o]_2(Ar)Si\text{-}P,P,P,Si\}]$ (**2**, Ar = C_6H_5 (**a**) and *o*-$CH_3-C_6H_4$ (**b**)) on the basis of IR, ^1H and $^{31}P\{^1H\}$-NMR, and X-ray crystallographic analyses (vide infra) in yields of 54% (**2a**) and 51% (**2b**) (Eq. (2)). The resultant complexes **2a** and **2b** were stable in air to some extent in the solid state but deteriorated quickly in solution. They are soluble in benzene, toluene and THF and are hardly soluble in hexane or diethyl ether.



(2)

Complex **2a** shows IR absorption at 1582 and 1513 cm^{-1} assignable to C=O and C=C stretching bands, suggesting that the 2,4-pentanedionato ligand coordinates to the metal through both of its oxygen atoms [7]. The Mo–H stretching band was observed at 1816 cm^{-1}, which is at a higher frequency than that of **1** (1714 cm^{-1}). Similar results were obtained for complex **2b** (see Section 3).

The ^1H-NMR spectrum of complex **2a** in C_6D_6 exhibits three singlets at δ 1.78, 1.88, and 5.05 in an integration ratio of 3:3:1 assignable to two independent methyl groups and one methine proton, respectively, of the 2,4-pentanedionato ligand. In addition, there are multiplet signals of equal intensity in a high field region assignable to hydrido ligands as well as those assignable to a phosphorus ligand. The multiplet signals were analyzed by computer simulation using gNMR [8] to show that they consist of two resonances centered at δ -2.69 and at δ -3.25 each in an integration ratio of 1:1 (Fig. 1). It is shown that the δ -2.69 resonance is a doublet of quartets ($J = 21.6$ and 6.1 Hz) and the δ -3.25 resonance is a doublet of triplets of doublets ($J = 105.8$, 17.8, and 6.1 Hz). These results suggest that each hydrido ligand couples to another hydride as well as to three coordinated phosphorus nuclei.

Dynamic ^1H-NMR measurement in toluene-d_8 in the range from -40 to 90°C did not cause any significant spectrum change except a slight upfield shift of the lower signal at the elevated temperature. The results indicate the absence of the exchange process between two hydrido ligands in this temperature region. The $^{31}P\{^1H\}$-NMR spectrum of **2a** in C_6D_6 at room temperature shows signals at δ 102.7 (m), 70.4 (m), and -5.4 (m) with the integration ratio 1:2:1. The resonance at δ -5.4 is particularly diagnostic of the presence of an uncoordinated phosphorus nucleus since the phosphorus atoms in a free dppe ligand are known to resonate at δ -6.9 under the same conditions. The unidentately coordinated dppm ligand, $Ph_2PCH_2PPh_2$, in the cationic platinum complex $[PtCH_3(Ph_2PCH_2PPh_2\text{-}P,P')(Ph_2PCH_2PPh_2\text{-}P)]PF_6$ prepared by Fallis et al. has been shown to exhibit its ^{31}P-NMR resonance at δ 15.7 and -28.5 ppm [9]. Similar NMR spectra were observed for complex **2b** (see Section 3).

2.2. The structure of $[MoH_2(2,4\text{-pentanedionato-}O,O')\{[Ph_2PCH_2CH_2P(Ph)-C_6H_4\text{-}o]_2(Ph)Si\text{-}P,P,P,Si\}]$ (**2a**)

Red crystals of complex **2a** suitable for single crystal X-ray analysis were obtained from toluene–hexane. The molecular structure of **2a** is illustrated in Fig. 2 and the selected bond lengths and bond angles are summarized in Table 1. The positions of the hydrido ligands could not be determined. These structural data are consistent with the spectroscopic data for **2a** shown above.

As suggested by the IR and the $^{31}P\{^1H\}$-NMR spectra, X-ray analysis shows the existence of both chelating and monodentate dppe moieties together with the

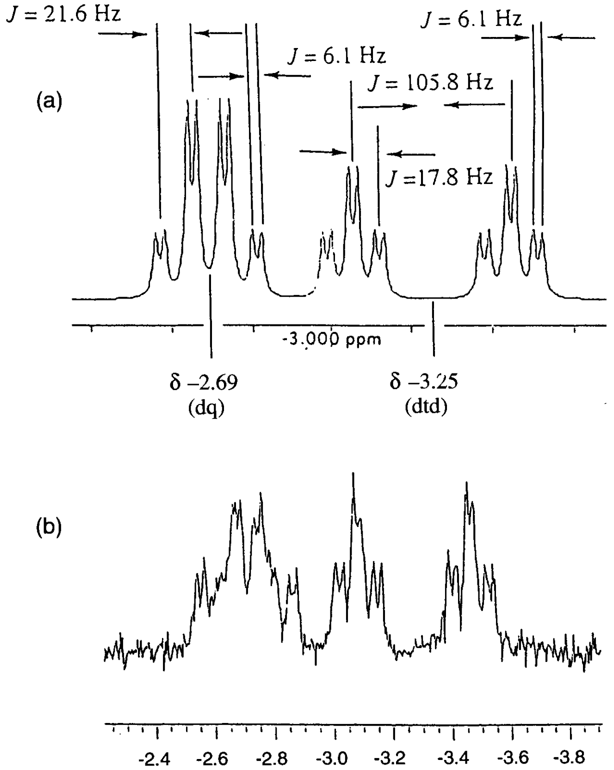


Fig. 1. Computer simulated (a) and observed (b) ^{1}H-NMR signals at the high field region of the spectrum of complex **2a**.

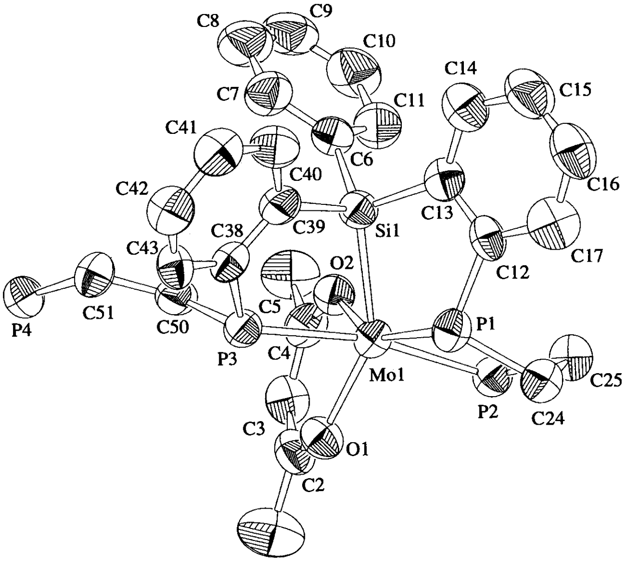


Fig. 2. An ORTEP drawing of complex **2a** showing the numbering system. Thermal ellipsoids are drawn at the 50% probability level. Only the core unit of complex **2a** is shown for clarity. All hydrogen atoms are omitted.

η^2-2,4-pentanedionato ligand. Thus one of the Si–C–C–P–Mo frameworks in the quadruply chelated quinquidentate ligand seems not to have survived the reaction. Such cleavage of one M–P bond has been found in the reaction of *trans*-[W(CO)(N_2)(dppe)$_2$] with secondary amines under CO_2 [10]. The complex **2a** may be regarded as having a distorted octahedral configuration with three P atoms and O2 in the pseudo-equatorial basal plane and the O1 and Si1 atoms in the apical sites. The sum of the angles O2–Mo1–P3, P3–Mo1–P1, P1–Mo1–P2, and P2–Mo1–O2 is 365.9° indicating slight deviation of each atom from the equatorial plane. The Mo1–Si1 distance of 2.520(3) Å is comparable to the above-mentioned η^2-O_2 complex (2.515(2) Å) [6]. The bond lengths of three Si–C bonds, Si1–C6 (1.88(1) Å), Si1–C13 (1.89(1) Å), and Si1–C39 (1.91(2) Å), are all very similar to those found for the disilyl type complex [MoH$_2$(SiH$_2$Ph){[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] [5]. A resemblance of these values to that found for [Fe{Si(C$_6$H$_5$){2-(MeNCH$_2$)-C$_6$H$_4$}}(CO)$_4$] suggests these bonds between Si and C are all single bonds [11].

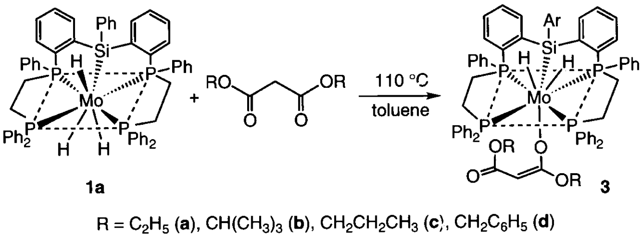
An average Mo–O distance of 2.160 Å is shorter than that found for the molybdenum–malonato bond (Mo–O = 2.225 Å) in [MoH{[CH(COOCH(CH$_3$)$_2$)$_2$}-*O,O′*}(dppe)$_2$] [4]. The O1–Mo1–O2 bond angle of 80.8(3)° is much smaller than that found in the 2,4-pentanedionato-molybdenum complex [Mo(NNC$_6$H$_4$-OCH$_3$-*p*)(2,4-pentanedionato)$_2$] (84.8(4)°) [12], suggesting the presence of a steric congestion in **2a** induced by the bulky terdentate chelating ligand. The bond length between Mo1 and O1 (2.154(8) Å) which is *trans* to Si is slightly shorter than that between Mo1 and O2 (2.166(9) Å) which resides *trans* to the P atom.

Table 1
Selected bond distances (Å) and bond angles (°)

Mo(1)–P(1)	2.359(4)	Si(1)–C(13)	1.89(1)
Mo(1)–P(2)	2.454(4)	Si(1)–C(39)	1.91(2)
Mo(1)–P(3)	2.470(4)	O(1)–C(2)	1.28(2)
Mo(1)–Si(1)	2.520(3)	O(2)–C(4)	1.27(2)
Mo(1)–O(1)	2.154(8)	C(1)–C(2)	1.50(2)
Mo(1)–O(2)	2.166(9)	C(2)–C(3)	1.39(2)
P(1)–C(12)	1.85(1)	C(3)–C(4)	1.39(2)
P(1)–C(24)	1.84(1)	C(4)–C(5)	1.50(2)
P(2)–C(25)	1.86(1)	C(12)–C(13)	1.41(2)
P(3)–C(38)	1.83(1)	C(24)–C(25)	1.55(2)
P(3)–C(50)	1.81(1)	C(38)–C(39)	1.37(2)
P(4)–C(51)	1.82(1)	C(50)–C(51)	1.55(2)
Si(1)–C(6)	1.88(1)		
P(1)–Mo(1)–P(2)	80.6(1)	C(6)–Si(1)–C(39)	104.4(6)
P(1)–Mo(1)–P(3)	104.9(1)	C(13)–Si(1)–C(39)	102.7(6)
P(1)–Mo(1)–O(2)	149.9(2)	Mo(1)–O(1)–C(2)	131.5(7)
P(2)–Mo(1)–P(3)	167.3(1)	Mo(1)–O(2)–C(4)	132.1(7)
P(2)–Mo(1)–O(2)	90.8(3)	O(1)–C(2)–C(1)	116(1)
P(3)–Mo(1)–O(2)	89.6(3)	O(1)–C(2)–C(3)	125(1)
Si(1)–Mo(1)–O(1)	149.1(3)	C(1)–C(2)–C(3)	119(1)
O(1)–Mo(1)–O(2)	80.8(3)	C(2)–C(3)–C(4)	125(1)
Mo(1)–Si(1)–C(6)	117.4(4)	O(2)–C(4)–C(3)	124(1)
Mo(1)–Si(1)–C(13)	111.3(5)	O(2)–C(4)–C(5)	115(1)
Mo(1)–Si(1)–C(39)	110.2(4)	C(3)–C(4)–C(5)	121(1)
C(6)–Si(1)–C(13)	109.6(6)		

2.3. Reaction of [MoH_3{[$Ph_2PCH_2CH_2P(Ph)$–C_6H_4-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**1a**) with dialkyl malonates

When the trihydrido complex **1a** in toluene was allowed to react with excess amount of dialkyl malonates $CH_2(COOR)_2$ (R = Et, *i*-Pr, *n*-Pr, CH_2Ph) under reflux, the color of the solution changed from green to deep brown, from which a yellow powdery product was obtained on working up. These products were spectroscopically analyzed as having the general formula [MoH_2{$CH(COOR)_2$-*O*}{[$Ph_2PCH_2CH_2P(Ph)$–C_6H_4-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**3**, R = C_2H_5 (**a**), $CH(CH_3)_2$ (**b**), $CH_2CH_2CH_3$ (**c**), and $CH_2C_6H_5$ (**d**)) (vide infra) and their yields were around 50% (Eq. (3)). The resultant complexes **3** were stable in air to some extent in the solid state but deteriorated quickly in solution. They are soluble in benzene, toluene and THF and are hardly soluble in hexane or diethyl ether.



(3)

In addition to the Mo–H stretching band at 1708–1736 cm^{-1}, IR spectra of complexes **3** show the ketonic carbonyl stretching band at around 1650 cm^{-1}, suggesting the malonato ligand in **3** coordinates to the metal through one of its oxygen atoms [13]. The $^{31}P\{^1H\}$-NMR spectrum of **3a** in C_6D_6 at room temperature exhibited four peaks of resonance at δ 104.1 (dd, 61.0 and 12.2 Hz), 86.3 (dd, 146.0 and 12.2 Hz), 57.3 (dd, 61.0 and 18.3 Hz), and 48.8 (dd, 146.0 and 18.3 Hz), integrating in the ratio of 1:1:1:1 and these chemical shifts are diagnostic of the coordinated P atoms. The ^1H-NMR spectrum of complex **3a** in C_6D_6 at room temperature showed two doublet of triplets signals with equal intensity attributable to Mo–*H* at δ −2.43 and −2.65. The signal of the α-methine proton of an unidentately bonded malonato ligand was observed as a singlet at δ 4.48. Complexes **3b**, **3c**, and **3d** exhibited similar NMR behavior to **3a**. Variable temperature ^1H-NMR measurement of **3a** showed that methyl and methylene protons of an ethoxide group which appeared as a triplet and a multiplet, respectively, at 80°C, each split into two sets of signals at −50°C.

These results indicate that the coordination mode of the malonato ligand in **3** is different from that of the 2,4-pentanedionato ligand in **2**. Similar behavior has been observed by Komiya et al. for the reaction of a ruthenium(0) complex with dimethyl malonate or 2,4-pentanedione [13]. In the case of complex **2**, the highly oxophilic nature of Mo(IV) might have favored the coordination of oxygen to the originally attached phosphorus atom. Taking into account that esters generally have a much smaller enolic content than ketones in solution, it may be conceivable that the difference in reactivity between 2,4-pentanedione and dialkyl malonate might be attributable to the steric factor, methyl groups in 2,4-pentanedione being less bulky than alkoxy groups in malonates.

3. Experimental

3.1. Materials and procedures

Most manipulations were carried out either under dry, oxygen-free argon or nitrogen or in vacuo with Schlenk-type flasks. Solvents were dried and purified in the usual manner, and stored under an atmosphere of argon. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer using KBr disks prepared under an inert atmosphere. ^1H and $^{31}P\{^1H\}$-NMR spectra were measured on a JNM-EX270 spectrometer. ^1H and ^{31}P chemical shifts were reported on the scale relative to the internal $SiMe_4$ and external PPh_3 references, respectively. GLC was recorded on a Shimadzu GC-3BT gas chromatograph using Molecular Sieves 5A column. [$MoH_4(dppe)_2$] was prepared according to the literature method [14]. The parent complexes **1** were prepared as reported elsewhere [5]. Presence of the Si atom in complexes **2** and **3** seems to have hindered their complete combustion, which prevented us from obtaining reasonable microanalytical results.

3.2. Preparation of [MoH_2(2,4-pentanedionato-*O,O′*)-{[$Ph_2PCH_2CH_2P(Ph)$–C_6H_4-*o*]$_2$(Ph)Si-*P,P,P,Si* }] (**2a**)

The mixture of [MoH_3{[$Ph_2PCH_2CH_2P(Ph)$–C_6H_4-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**1a**) (0.460 g, 0.460 mmol) and 2,4-pentanedione (0.59 ml, 55 mmol) in toluene (25 ml) was stirred at 110°C for 5 h. The solution changed from green to dark brown and evolution of H_2 by the reaction was observed by GLC. Hexane (15 ml) was added to the resulting solution and the mixture was kept in a fridge overnight to yield a yellow precipitate, which was filtered off. From the filtrate, volatile liquid was removed by evaporation in vacuo. The residual solid was washed with hexane and dried in vacuo. The brown powder thus obtained was recrystallized from toluene–hexane to give red crystals which are analyzed as [MoH_2(2,4-pentanedionato-*O,O′*){[$Ph_2PCH_2CH_2P$-(Ph)–C_6H_4-*o*]$_2$(Ph)Si-*P,P,P,Si* }] (**2a**) (0.277 g, 54%). Melting point (under Ar): 174–176°C. IR (KBr, cm^{-1}): 1816 m (ν_{Mo-H}), 1582 s ($\nu_{C=O}$), 1513 s ($\nu_{C=C}$). ^1H-NMR (C_6D_6): δ 5.05 (s, 1H, C*H*$(COCH_3)_2$), 1.88 (s, 3H, CH(COC*H*$_3$)$_2$), 1.78 (s, 3H, CH(COC*H*$_3$)$_2$), −2.96 (doublet of quartets, $^2J = 21.6$ and 6.1 Hz, 1H, Mo–*H*), −3.25 (dtd, $^2J = 105.8$, 17.8, and 6.1 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 102.7 (m), 70.4 (m), −5.4 (m).

Similarly, [MoH$_2$(2,4-pentanedionato-*O,O′*){[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(*o*-CH$_3$C$_6$H$_4$)Si-*P,P,P,Si* }] (**2b**) was obtained from **1b** (0.192 g, 0.289 mmol) and 2,4-pentanedione (0.24 ml, 23 mmol) in 51% yield (0.108 g). IR (KBr, cm^{-1}): 1817 m ($\nu_{\mathrm{Mo-H}}$), 1585 s ($\nu_{\mathrm{C=O}}$), 1513 s ($\nu_{\mathrm{C=C}}$). ^{1}H-NMR (C$_6$D$_6$): δ 5.11 (s, 1H, C*H*(COCH$_3$)$_2$), 1.57 (s, 3H, CH(COC*H*$_3$)$_2$), 1.50 (s, 3H, CH(COC*H*$_3$)$_2$), −2.42 (ddt, $^2J = 44.1$, 36.6 and 6.1 Hz, 1H, Mo–*H*), −2.63 (dtdd, $^2J = 106.2$, 14.5, 6.1, and 3.9 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 99.9 (m), 73.4 (m), 65.6 (m), −4.9 (m).

*3.3. Preparation of [MoH$_2${CH(COOEt)$_2$-O}{[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-o]$_2$(Ph)Si-P,P,P,P,Si }] (**3a**)*

The mixture of [MoH$_3${[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**1a**) (0.0899 g, 0.0899 mmol) and diethyl malonate (0.16 ml, 10.8 mmol) in toluene (8 ml) was stirred at 110°C for 5 h. The solution changed from green to dark brown and evolution of H$_2$ by the reaction was observed by GLC. Hexane (4 ml) was added to the resulting solution and the mixture was kept in a fridge overnight to yield a pale brown precipitate, which was filtered off. From the filtrate, volatile liquid was removed by evaporation in vacuo. The residual solid was washed with hexane and dried in vacuo. The yellow powder thus obtained was [MoH$_2${CH(COOEt)$_2$-*O*}{[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**3a**) (0.054 g, 55%). IR (KBr, cm^{-1}): 1734 m ($\nu_{\mathrm{Mo-H}}$), 1654 s ($\nu_{\mathrm{C=O}}$). ^{1}H-NMR (C$_6$D$_6$): δ 4.48 (s, 1H, C*H*(COOEt)$_2$), 4.19 (m, 2H, C*H*$_2$Me), 4.03 (m, 2H, C*H*$_2$Me), 1.20 (t, 3H, CH$_2$C*H*$_3$), −2.43 (dt, $^2J =$ 20.7 and 10.7 Hz, 1H, Mo–*H*), −2.65 (dt, $^2J = 20.7$ and 10.7 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 104.1 (dd, $^2J_{\mathrm{PP}} = 61$ and 12 Hz), 86.3 (dd, $^2J_{\mathrm{PP}} = 144$ and 12 Hz), 57.3 (dd, $^2J_{\mathrm{PP}} = 61$ and 20 Hz), 48.8 (dd, $^2J_{\mathrm{PP}} = 149$ and 17 Hz).

Similarly, [MoH$_2${CH(COOR)$_2$-*O*}{[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(Ph)Si-*P,P,P,P,Si* }] (**3b** (R = *i*-Pr); **3c** (R = *n*-Pr); **3d** (R = CH$_2$Ph)) was obtained from **1a** and the corresponding dialkyl malonates in yields of 41, 36, and 23%, respectively.

3b: IR (KBr, cm^{-1}): 1728 m ($\nu_{\mathrm{Mo-H}}$), 1649 s ($\nu_{\mathrm{C=O}}$). ^{1}H-NMR (C$_6$D$_6$): δ 4.82 (m, 2H, OC*H*), 4.21 (s, 1H, C*H*(COOPr^i)$_2$), 0.98 (d, $J = 6.1$ Hz, 6H, C*H*$_3$), 0.94 (d, $J = 6.1$ Hz, 6H, C*H*$_3$), −2.72 (dt, $^2J = 20.7$ and 11.0 Hz, 1H, Mo–*H*), −2.94 (dt, $^2J = 20.7$ and 11.0 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 103.7 (dd, $^2J_{\mathrm{PP}} = 60$ and 12 Hz), 85.7 (dd, $^2J_{\mathrm{PP}} = 150$ and 12 Hz), 57.3 (dd, $^2J_{\mathrm{PP}} = 62$ and 18 Hz), 48.7 (dd, $^2J_{\mathrm{PP}} = 149$ and 17 Hz).

3c: IR (KBr, cm^{-1}): 1708 m ($\nu_{\mathrm{Mo-H}}$), 1654 s ($\nu_{\mathrm{C=O}}$). ^{1}H-NMR (C$_6$D$_6$): δ 4.42 (s, 1H, C*H*(COOPr^n)$_2$), 3.95 (m, 4H, OC*H*$_2$), 1.60 (m, 4H, C*H*$_2$), 0.96 (m, 6H, C*H*$_3$), −2.06 (dt, $^2J_{\mathrm{HP}} = 20.7$ and 11.0 Hz, 1H, Mo–*H*), −2.27 (dt, $^2J_{\mathrm{HP}} = 20.7$ and 11.0 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 103.8 (dd, $^2J_{\mathrm{PP}} = 60$ and 12 Hz), 86.3 (dd, $^2J_{\mathrm{PP}} = 147$ and 12 Hz), 57.1 (dd, $^2J_{\mathrm{PP}} =$ 60 and 20 Hz), 48.9 (dd, $^2J_{\mathrm{PP}} = 148$ and 20 Hz).

3d: IR (KBr, cm^{-1}): 1736 m ($\nu_{\mathrm{Mo-H}}$), 1654 s ($\nu_{\mathrm{C=O}}$). ^{1}H-NMR (C$_6$D$_6$): δ 5.26 (m, 2H, C*H*$_2$Ph), 5.03 (m, 2H, C*H*$_2$Ph), 4.61 (s, 1H, C*H*(COOCH$_2$Ph)$_2$), −2.42 (dt, $^2J_{\mathrm{HP}} = 20.7$ and 10.9 Hz, 1H, Mo–*H*), −2.63 (dt, $^2J_{\mathrm{HP}} = 20.7$ and 10.9 Hz, 1H, Mo–*H*). ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ 103.8 (dd, $^2J_{\mathrm{PP}} = 61$ and 12 Hz), 87.7 (dd, $^2J_{\mathrm{PP}} = 144$ and 12 Hz), 57.1 (dd, $^2J_{\mathrm{PP}} = 61$ and 20 Hz), 48.7 (dd, $^2J_{\mathrm{PP}} = 148$ and 17 Hz).

*3.4. X-ray crystal structure analysis of [MoH$_2$(2,4-pentanedionato-O,O′){[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-o]$_2$-(Ph)Si-P,P,P,Si }](toluene) (**2a**·toluene)*

A single crystal of [MoH$_2$(2,4-pentanedionato-*O,O′*){[Ph$_2$PCH$_2$CH$_2$P(Ph)–C$_6$H$_4$-*o*]$_2$(Ph)Si-*P,P,P,Si* }]-(toluene) (**2a**·toluene) was grown from a toluene–hexane solution in a fridge, and was mounted on a Rigaku AFC-7R diffractometer, and irradiated with graphite monochromated Cu–K$_\alpha$ radiation ($\lambda = 1.54178$ Å). The data were collected at temperature of 23°C using the ω–2θ scan technique to a maximum 2θ value of 120.3°. The structure was solved by heavy-atom Patterson methods (PATTY) [15] and expanded using Fourier techniques (DIRDIF94) [16]. The positions of all hydrogen atoms were calculated by assuming idealized geometry. Several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final R and R_{w} values of 0.067 and 0.059, respectively. All calculations were performed using the TEXSAN [17] crystallographic software package of Molecular Structure Corporation. Crystallographic data are summarized in Table 2.

4. Supplementary material

Complete lists of bond lengths and angles, hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Center CCDC no. 141568. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 2
Crystal data and structure refinement for **2a**·toluene

Empirical formula	$C_{70}H_{68}MoO_2P_4Si$
Formula weight	1189.23
Crystal habit, color	Prismatic, red
Crystal size (mm)	$0.60 \times 0.30 \times 0.30$
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Lattice parameters	
a (Å)	21.550(7)
b (Å)	12.177(5)
c (Å)	24.427(7)
β (°)	108.60(2)
Volume (Å^3)	6075(3)
Z	4
Density (calculated) (g cm^{-3})	1.300
F(000)	2480.00
μ(Cu–K$_\alpha$) (cm^{-1})	32.91
Diffractometer	Rigaku AFC7R
Wavelength (Å)	Cu–K$_\alpha$, $\lambda = 1.54178$
Temperature (°C)	23
$2\theta_{max}$ (°)	120.3
Reflections collected	9829
Independent reflections	9543 ($R_{int} = 0.056$)
Reflections observed ($I > 3.00\sigma(I)$)	4316
Refinement method	Full-matrix least-squares on *F*
Residuals	$R = 0.067$, $R_w = 0.059$
Goodness-of-fit on *F*	2.62
Final difference map (e Å^{-3})	1.61(max), −0.99(min)

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