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Reactions of Alkyl malonates with Molybdenum and Tungsten Complexes. Syntheses and Structure of Hydrido-Malonato Complexes

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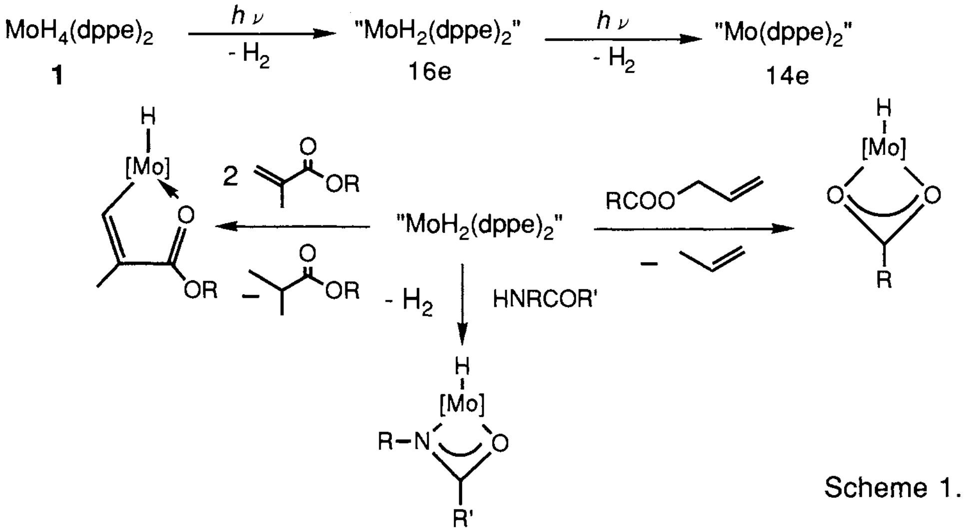
Molybdenum and tungsten hydrido-malonato complexes have been prepared by the photochemical or thermal reactions of $[MoH_4(dppe)_2]$ or *trans*-$[W(N_2)_2(dppe)_2]$ with an excess of alkyl malonates. The structure of the complex is reported, and a possible mechanism is proposed for the reaction.

Molybdenum polyhydride, $[MoH_4(PR_3)_4]$¹⁾ has been proved to be very useful as starting materials in the syntheses of coordination compounds of molybdenum. The photoreaction of tetrahydride $[MoH_4(dppe)_2]$ (**1**) (dppe = $Ph_2PCH_2CH_2PPh_2$) has been known to give the coordinatively unsaturated 16e and 14e species stepwise.²⁾ Seven coordinate complexes of the type $[MoHX(dppe)_2]$ (X = amido, carboxylato, β-carboalkoxyalkenyl) have recently been prepared and have been shown to exhibit some interesting chemistry.³⁻⁶⁾



Scheme 1.

Here we report the reaction of $[MoH_4(dppe)_2]$ (**1**) with alkyl malonates, $CH_2(COOR)_2$. Analogous reaction of the tungsten complexes is also described. It is well known that the β-ketoenolate ions form very stable chelate complexes with most metal ions and much work has been done on the chemistry of acetylacetonato (acac) complexes.⁷⁾ On the other hand, alkyl malonates, which also possess active methylene protons, have less been used as ligands in transition-metal chemistry, despite malonate compounds have played a significant role in various organic reactions catalyzed by transition metals.[8)]

The photochemical or thermal reactions of **1** with alkyl malonates gave the hydrido-malonato complexes **4**.

$$\mathbf{1,2}\text{ or }\mathbf{3} + CH_2(COOR)_2 \xrightarrow{h\nu \text{ or } \triangle} [MH\{CH(COOR)_2\text{-}O,O'\}(dppe)_2]$$

$$M = Mo\ (\mathbf{4}),\ W\ (\mathbf{5});\quad R = Me\ (\mathbf{a}),\ Et\ (\mathbf{b}),\ i\text{-}Pr\ (\mathbf{c})$$

Table 1. Preparation of Complexes **4** (M = Mo) and **5** (M = W)

Complexes / mmol	$CH_2(COOR)_2$ R / mmol	Solvents / ml	Conditions	Products / Yield %[a)]
$MoH_4(dppe)_2$ (**1**) / 0.34	Me / 0.28	toluene / 17	110℃, 5 h	**4a** / 23
$MoH_4(dppe)_2$ (**1**) / 0.49	Et / 2.63	benzene / 49	20℃, 2 h, *h*ν [b)]	**4b** / 3.5
$MoH_4(dppe)_2$ (**1**) / 0.53	*i*-Pr / 2.62	benzene / 10	20℃, 5 h, *h*ν [b)]	**4c** / 35
$W(N_2)_2(dppe)_2$ (**3**) / 0.69	Me / 3.45	toluene / 50	65℃, 35 h	**5a** / 22
$WH_4(dppe)_2$ (**2**) / 0.85	Et / 4.25	benzene / 30	20℃, 6 h, *h*ν [b)]	**5b** / 2
$W(N_2)_2(dppe)_2$ (**3**) / 0.62	Et / 3.08	toluene / 50	65℃, 32 h	**5b** / 27
$W(N_2)_2(dppe)_2$ (**3**) / 0.92	*i*-Pr / 4.60	toluene / 50	65℃, 18 h	**5c** / 20

a) Isolated yields. b) Irradiation with 400-w high-pressure mercury-lamp through Pyrex filter.

In contrast to the molybdenum complex **1**, $[WH_4(dppe)_2]$ (**2**) was found to be inert and the analogous tungsten hydrido-malonato complexes were obtained in extremely low yield. However the reaction of *trans*-$[W(N_2)_2(dppe)_2]$ (**3**), which affords a coordinatively unsaturated reactive intermediate in a similar manner as **1**, with alkyl malonates led to the formation of the corresponding hydrido-malonato complexes in reasonable yields. In these reactions, carbonyl complexes $M(CO)_2(dppe)_2$ were formed as by-products. It seems likely that the molybdenum and tungsten complexes attack the ethoxy carbonyl groups in addition to the active methylene group.

Table 2. Spectroscopic Properties of Complexes **4** (M = Mo) and **5** (M = W)

	IR / cm^{-1} [a)]			^1H NMR / ppm[b)]		
Complex	ν (M-H)	ν (C=O)	ν (C=C)	δ (M-H)	*J* (H-Peq) Hz	*J* (H-Pax) Hz
4a	1800	1495	1600	-4.95 (tt)	89.1	18.9
4b	1800	1505	1605	-4.89 (tt)	90.3	18.3
4c	1800	1510	1605	-4.76 (tt)	90.9	18.3
5a	1870	1512	1620	-3.09 (tt)[c)]	86.0	14.0
5b	1860	1515	1613	-3.04 (tt)[c)]	86.4	13.1
5c	1860	1515	1609	-2.94 (tt)[c)]	87.1	14.3

a) KBr disc. b) 270 MHz in C_6D_6. c) Tungsten satellites were not observable due to low resolution.

Molybdenum complexes **4** were soluble in benzene or toluene, but not soluble in hexane, although tungsten complexes **5** were found to be soluble in hexane and pentane, and they were purified by recrystallization from these solvents. These complexes are stable to air to some extent in the solid state but are immediately decomposed in solution. The IR spectra of molybdenum complexes **4** showed characteristic bands at 1800 cm^{-1} assignable to ν (Mo-H) and they agreed closely with that of MoH(acac)(dppe)$_2$.9) W-H stretching bands of complexes **5** were observed at 1860 - 1870 cm^{-1}, which are higher frequency than that of the molybdenum complexes. IR bands originating from alkyl malonate ligands are listed in Table 2. The assignment of each band was made by comparison with that of the MoH(acac)(dppe)$_2$9). The ^{1}H-NMR spectra of complex **4** showed triplet of triplets at around -4.9 ppm, which can be assigned to hydridic Mo-H protons, suggesting the hydrido ligand and two of the four phosphorus atoms are in a pentagonal plane and the other phosphorus atoms occupy apical positions10). The hydridic W-H protons of complex **5** appeared at around -3.0 ppm, which are lower field than the molybdenum complexes, reflecting a difference in the nature of metals.

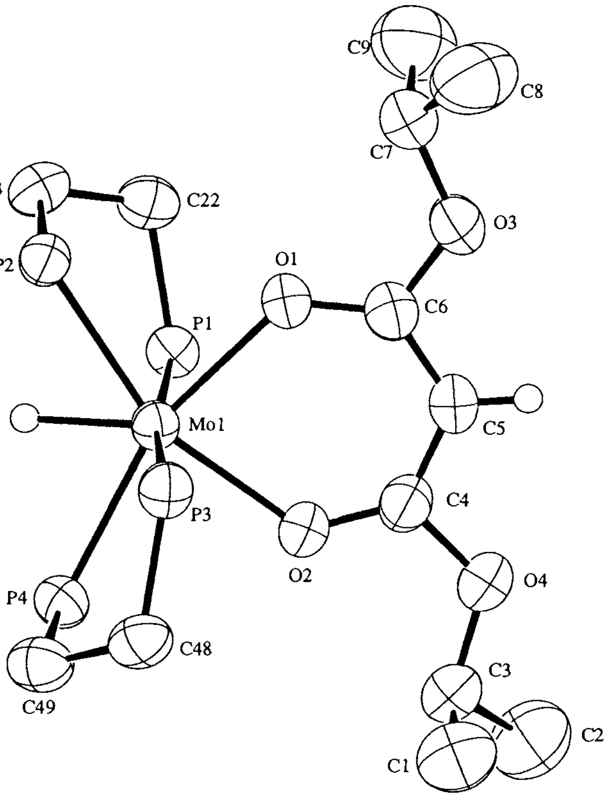
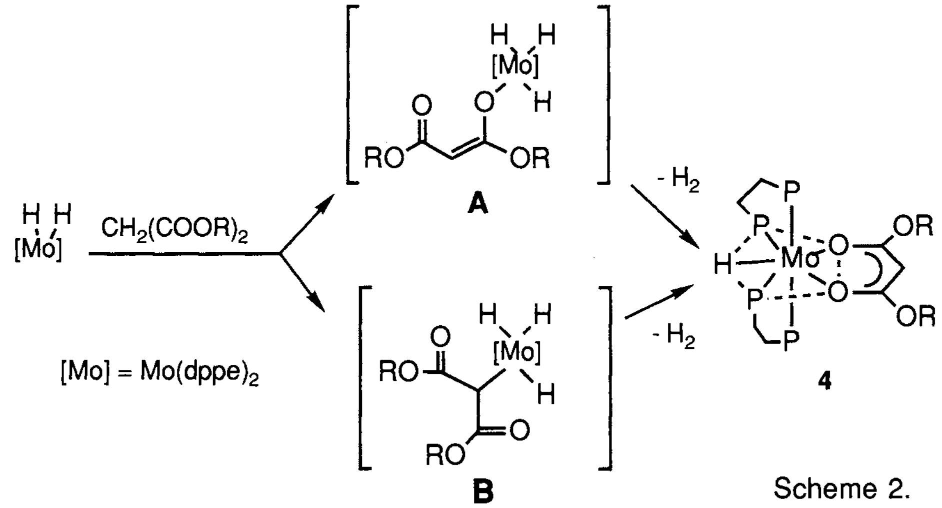


Fig. 1. Structure of **4c**.

The X-ray structure of complex **4c** (R = *i*-Pr) was confirmed by single crystal X-ray analysis11) and is found to be representative of this class of complex. An ORTEP plot of the structure is illustrated in Fig. 1. The structure of complex **4c** is best described as a distorted pentagonal-bipyramidal configuration with the hydride ligand bent slightly from the equatorial plane, which is formed by two phosphorus atoms and the oxygen atoms of the malonato ligand. The molybdenum-malonato bond length (Mo-O1 = 2.225(2) Å) is a little shorter than that found previously for molybdenum-carbonato bond (Mo-O = 2.271(2) Å) in [MoH(O_2COEt)(dppe)$_2$], reflecting less distortion of the six membered ring of the former than the four membered carbonato ligand.4) The O1-Mo-O2 bond angle of 81.29(9)° in **4c** is smaller than that found in acetylacetonato complex [Mo(NNC_6H_4OMe-*p*)(acac)$_2$] (84.8(4)°),12) suggesting that a steric crowding in **4c** induced by the bulky isopropyl groups.

The molybdenum-hydride distance is 1.64(3) Å and is also very similar to that of hydrido-carbonato molybdenum complex (1.69 Å). In the six-membered MoO_2C_3 ring, the C6-C5 distance 1.3865(5) Å is consistent with its being nearly a double bond.

Two possible mechanisms for formation of the complex are illustrated in Scheme 2. Pathway **A** requires the enolization of alkyl malonate. Pathway **B** involves direct C-H bond oxidative-addition to intermediary 16e MoH_2(dppe)$_2$. Since alkyl malonate is generally less enolic (the enol content of ethyl malonate is 7.7×10^{-3}%)13) as compared with acetylacetone (the enol content is 76.4%), pathway **B** appears to be more likely.



Scheme 2.

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10) The ^{13}C NMR spectrum of **4c** in C_6D_6 shows resonances at 171.8 ($\underline{C}$=O) and 66.9 ($\underline{C}$HC=O) ppm.
11) Crystal data for **4c**: $C_{61}H_{64}O_4P_4Mo$, Fw = 1081.01, monoclinic, space group P21/c, a = 21.385(3) Å, b = 10.806(4) Å, c = 23.987(5) Å, V = 5439(2) Å^3, Z = 4, Dc = 1.320 g cm^{-3}, R = 0.036, Rw = 0.046 for 6544 observed reflections.
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