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Synthesis and Solid State Structure of Bis(μ-acetate)bis(p-methylbenzyl)bis-(trimethylphosphine)-dimolybdenum (Mo≣Mo), $Mo_2(O_2CCH_3)_2$-$(CH_2Ph$-p-$Me)_2(PMe_3)_2$

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Abstract

The reaction of $Mo_2(OAc)_4$ [OAc≡O_2CCH_3] with 2 equivalents of $Mg(CH_2Ph$-p-$Me)_2$ (CH_2Ph-p-Me = p-methylbenzyl) in the presence of PMe_3 has led to the isolation of the acetate bridged dimer $Mo_2(OAc)_2(CH_2Ph$-p-$Me)_2(PMe_3)_2$ as deep pink crystals which have been studied by X-ray diffraction methods. Crystal data for $Mo_2P_2O_4C_{26}H_{42}$, M_r = 672.45, $P\bar{1}$, $a = 9.476(6)$, $b = 11.828(3)$, $c = 15.202(3)$ Å; $\alpha = 96.89(2)$, $\beta = 97.27(4)$, $\gamma = 111.18(4)°$, $V = 1550(2)$ Å^3, $Z = 2$, $D_x = 1.440$ g cm^{-3}, Mo Kα, $\lambda = 0.71703$ Å, $\mu = 9.17$ cm^{-1}, $F(000) = 688.0$, $T = 24.0$ °C, $R = 0.060$ for 4043 unique observation reflections. The unit cell contains two independent but essentially identical molecules. The structures consist of two molybdenum atoms bridged by two acetate molecules with a terminally bound benzyl and phosphine ligand at each metal center. The coordination geometry at each metal is approximately tbp, with a M–M distance consistent with a bond order of four.

Introduction

There are few examples in the literature of binuclear complexes containing benzyl ligands. As part of our ongoing studies of the early transition metal chemistry of compounds containing benzyl and related ligands, we have isolated a dinuclear benzyl molybdenum complex containing a formal molybdenum–molybdenum quadruple bond and we wish to report here its synthesis and structure.

Results and Discussion

While investigating the reactivity of the benzylating agent $Mg(CH_2Ph$-p-$CH_3)_2(Et_2O)_2$ towards dinuclear molybdenum systems, the complex $Mo_2(OAc)_2(CH_2Ph$-p-$CH_3)_2(PMe_3)_2$ (1) was isolated. Reaction of $Mo_2(OAc)_4$ with the dialkyl magnesium salt in diethylether solvent in the presence of trimethylphosphine afforded the product as pink crystals from hexane. A structural study confirmed a binuclear molybdenum system, with bridging acetate groups and terminally bound benzyls and phosphines.

The molecular structure of 1 is shown in Fig. 1. The crystallographic data is collected in Table I while

TABLE I. X-ray Diffraction Data

Formula	$Mo_2P_2O_4C_{26}H_{42}$
Formula weight	672.45
Space group	$P\bar{1}$
a (Å)	9.476(6)
b (Å)	11.828(3)
c (Å)	15.202(3)
α (°)	96.89(2)
β (°)	97.27(4)
γ (°)	111.18(4)
V (Å^3)	1550.0(2)
Z	2
D_c (g/cm^3)	1.440
Crystal size (mm)	0.40 × 0.17 × 0.09
Crystal color	pink
Radiation	Mo Kα (λ = 0.71073 Å)
Linear absorption coefficient (cm^{-1})	9.17
T (°C)	24.0
Diffractometer	Enraf-Nonius CAD4
Scan method	θ–2θ
h,k,l limits	−10 to 10; −12 to 12; 0 to 16
2σ range (°)	4.00–45.00
Scan width (°)	0.75 + 0.35 tan (θ)
Take-off angle (°)	5.00
Programs used	Enraf-Nonius SDP
F(000)	688.0
Unique data	4043
Data with $I > 3.0\sigma(I)$	2576
Number of variables	307
Largest shift/e.s.d. in final cycle	0.03
R	0.060
R_w	0.072
Goodness of fit	1.607

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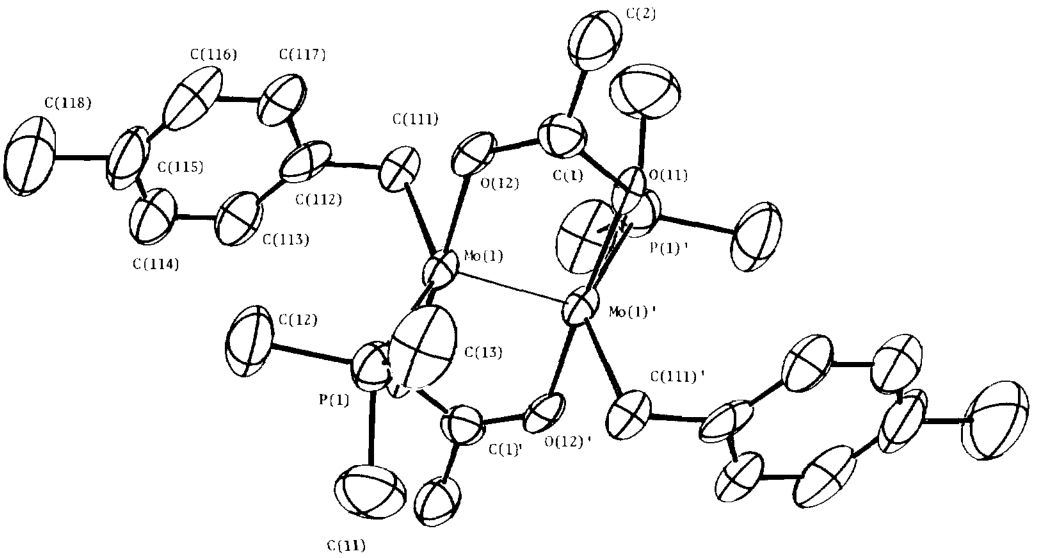

Fig. 1. ORTEP drawing of 1 with hydrogen atoms omitted.

TABLE II. Fractional Atomic Coordinates and Isotropic Thermal Parameters[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Molecule 1				
Mo1	0.3933(1)	0.42729(9)	0.97325(6)	3.00(2)
P1	0.4709(3)	0.2316(3)	0.9205(2)	4.05(8)
O11	0.3994(7)	0.4721(7)	0.8431(5)	3.7(2)
O12	0.3773(7)	0.3733(7)	1.0993(5)	3.8(2)
C11	0.578(2)	0.263(1)	0.832(1)	7.4(4)
C12	0.300(2)	0.116(1)	0.874(1)	7.2(5)
C13	0.571(2)	0.199(1)	1.003(1)	7.6(5)
C1	0.516(1)	0.566(1)	0.8341(7)	3.5(3)
C2	0.533(1)	0.592(1)	0.7423(8)	4.7(3)
C111	0.184(1)	0.469(1)	0.9324(8)	4.0(3)
C112	0.071(1)	0.344(1)	0.9444(8)	4.1(3)
C113	0.016(1)	0.303(1)	0.8333(7)	4.8(3)
C114	−0.079(1)	0.181(1)	0.818(1)	5.8(4)
C115	−0.120(1)	0.098(1)	0.872(1)	6.2(4)
C116	−0.066(1)	0.135(1)	0.963(1)	6.5(4)
C117	0.028(1)	0.254(1)	0.9990(9)	5.8(4)
C118	−0.219(2)	−0.037(2)	0.835(1)	10.5(7)
Molecule 2				
Mo2	0.8881(1)	0.43183(9)	0.48984(6)	3.09(2)
P2	0.1406(3)	0.7040(3)	0.6591(2)	3.81(8)
O21	0.9701(7)	0.3161(6)	0.5578(3)	3.6(2)
O22	0.7959(7)	0.5382(7)	0.4185(5)	3.7(2)
C21	0.331(1)	0.827(1)	0.686(1)	5.5(4)
C22	0.133(2)	0.640(1)	0.7593(9)	6.4(4)
C23	0.019(2)	0.790(1)	0.668(1)	7.3(5)
C3	1.111(1)	0.354(1)	0.5888(7)	3.8(3)
C4	1.175(1)	0.277(1)	0.6373(8)	4.6(3)
C211	0.760(1)	0.459(1)	0.5979(7)	4.2(3)
C212	0.620(1)	0.346(1)	0.5632(7)	3.4(3)
C213	0.513(1)	0.341(1)	0.4904(8)	4.1(3)
C214	0.384(1)	0.232(1)	0.4331(8)	4.6(3)
C215	0.364(1)	0.126(1)	0.4892(9)	4.6(3)
C216	0.470(1)	0.131(1)	0.5577(9)	4.9(3)
C217	0.602(1)	0.237(1)	0.5946(8)	4.3(3)
C218	0.224(2)	0.011(1)	0.453(1)	7.1(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table II lists the final atomic positions and isotropic thermal parameters. Some selected bond distances and angles are given in Table III and Table IV. There are two independent molecules in the unit cell, each of which contains a crystallographically imposed inversion center. The short Mo–Mo distances of 2.108(2) and 2.107(1) Å are consistent with a quadruple bond, and are well within the expected range reported for other $Mo\equiv Mo$ systems (2.065(1)–2.183(2) Å) [1, 2]. The molecule is isostructural with the previously reported complex, $Mo_2(OAc)_2(CH_2SiMe_3)_2(PMe_3)_2$, which was obtained by similar methods [3]. Hursthouse and co-workers structurally characterized the molecule and also observed a metal–metal distance of 2.0984(5) Å, consistent with a bond order of four, as well as a crystallographic inversion center [4].

The coordination geometry about each metal center in 1 is best described as distorted square pyramidal, more akin to a trigonal/bipyramidal geometry. Considering this latter arrangement, the oxygens from the bridging carboxylate occupy the axial sites (O(11)–Mo(1)–O(12) = 176.9(2)°). The alkyl and

TABLE III. Selected Bond Distances for $Mo_2(OAc)_2(CH_2\text{-}Ph\text{-}p\text{-}CH_3)_2(PMe_3)_2$ (1)

Molecule 1		Molecule 2	
Mo(1)–Mo(1)′	2.108(2)	Mo(2)–Mo(2)′	2.107(1)
Mo(1)–P(1)	2.521(4)	Mo(2)–P(2)	2.537(3)
Mo(1)–C(111)	2.23(1)	Mo(2)–C(211)	2.23(1)
Mo(1)–O(11)	2.112(8)	Mo(2)–O(21)	2.109(8)
Mo(1)–O(12)	2.098(8)	Mo(2)–O(22)	2.099(8)
C(1)–O(11)	1.29(1)	C(3)–O(21)	1.25(1)
C(1)–O(12)	1.27(2)	C(3)–O(22)	1.30(1)
C(1)–C(2)	1.49(2)	C(3)–C(4)	1.48(2)

phosphine ligands are contained in a plane with the two metal atoms, with angles P(1)–Mo(1)–C(111) = 140.8(3)°, Mo(1)–Mo(1)–C(111) = 116.3(3)° and Mo(1)–Mo(1)–P(1) = 102.84(8)°. Similar angles were observed in the $Mo_2(OAc)_2(CH_2SiMe_3)_2(PMe_3)_2$ complex. The P–Mo–C angle of approximately 140° seems to reflect the steric demands of the bulky alkyl and phosphine ligands.

The molecular geometry of the remaining ligands correspond to expected values. The $(MoO_2C)_2$ group is very nearly planar, and is perpendicular to the $(MoCP)_2$ plane. The Mo–O bond distances of 2.112(8) and 2.098(5) Å are comparable to those observed in other Mo_2 carboxylate systems [5]. Like the CH_2SiMe_3 analog, the Mo(1)–P(1) distance of 2.521(4) Å is somewhat elongated in comparison to other Mo–P bonds [5]. This is probably due to steric crowding effects within the complex. The Mo(1)–C(111) distance of 2.23(1) Å is virtually identical to the Mo–alkyl distance (2.231(2) Å) observed in the CH_2SiMe_3 complex. The reported Mo–C distance of other dimolybdenum benzyl systems is also comparable. Chisholm and co-workers found distances of 2.181(5)–2.22(1) Å in a number of Mo_2^{6+} benzyl species [7]. Similarly, in the complex $Mo_2(CH_2Ph)_6$, recently reported by our group, an Mo–C distance of 2.162(2) Å was observed [8].

The Mo–C–Ph angle of 96.4(8)° is rather acute. In the Mo≡Mo benzyl systems reported by Chisholm, bond angles ranging from 104.5(3)° to 114.4(11)° were observed. Further, in the binary homoleptic, $Mo_2(CH_2Ph)_6$, an angle of 98.9(1)° is seen. The benzyl ligands in these complexes can be considered to be purely σ-bound. Examples of compounds with π-bound ligands have shown more acute angles. In the complex $ThCp^*(CH_2Ph)_3$ reported by Marks, all three alkyl ligands were found to interact in a π-fashion with the metal, giving M–C–C angles of 86(1)°, 87(1)° and 91(1)° [9]. Andersen observed similar angles in the species $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$, which has two π-bound ligands (90(1)°, 88(1)°), and $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$ (83.0(4)°) which contains only one [10]. Other results from our group have shown equally acute angles in systems with π-bound benzyls. In the complexes $Zr(OAr')(CH_2Ph)_3$ and $Zr(OAr')(CH_2Ph\text{-}p\text{-}F)_3$ (OAr′ = 2,6-di-tert-butylphenoxide) one benzyl was found to interact with the metal center, giving a Zr–C–C angle of 84.3(3)° [11]. The angle observed in $Zr(CH_2Ph)_4$ is similarly collapsed, with an average angle for Zr–C–C of 92° [12]. Hence it would appear that the M–C–C angles in **1** are intermediate between those found for purely σ and π-bound benzyl ligands. An important characteristic of quadrupyl bonded M_2^{4+} (M = Mo, W) cores is the ability to undergo weak ligand coordination *trans* to the metal–metal bond. Hence, if the benzyl ligands in **1** were to try and donate further electron density to the metals this is the site where such interactions should occur. Indeed, the structure of **1** (Fig. 1) does show the phenyl ring of the CH_2Ph ligand is bending towards this position in the molecule. However, the Mo–C(ipso) distance of 2.81(1) Å is well outside the realm of any bonding interaction.

TABLE IV. Selected Bond Angles for $Mo_2(OAc)_2(CH_2Ph\text{-}p\text{-}CH_3)_2(PMe_3)_2$ (**1**)

Molecule 1		Molecule 2	
Mo(1)–Mo(1)′–O(11)	91.9(2)	Mo(2)–Mo(2)′–O(21)	91.3(2)
Mo(1)^1–Mo(1)–O(12)	91.3(2)	Mo(2)^1–Mo(2)–O(22)	91.6(2)
Mo(1)^1–Mo(1)–P(1)	102.84(8)	Mo(2)^1–Mo(2)–P(2)	104.77(8)
Mo(1)^1–Mo(1)–C(111)	116.3(3)	Mo(2)^1–Mo(2)–C(211)	112.7(2)
O(11)–Mo(1)–O(12)	176.9(2)	O(21)–Mo(2)–O(22)	176.8(2)
O(11)–Mo(1)–P(1)	88.1(2)	O(21)–Mo(2)–P(2)	89.5(2)
O(12)–Mo(1)–P(1)	90.5(3)	O(22)–Mo(2)–P(2)	88.6(2)
O(11)–Mo(1)–C(111)	91.8(4)	O(21)–Mo(2)–C(211)	91.9(4)
O(12)–Mo(1)–C(111)	87.5(4)	O(22)–Mo(2)–C(211)	88.2(4)
P(1)–Mo(1)–C(111)	140.8(3)	P(2)–Mo(2)–C(211)	142.4(2)
Mo(1)–C(111)–C(112)	96.4(8)	Mo(2)–C(211)–C(212)	96.4(7)

Though not structurally characterized, the related benzyl complex $\mathrm{Mo_2(OAc)_2(CH_2Ph)_2(PMe_3)_2}$ was also isolated as a pink, crystalline product. From a spectroscopic comparison, we conclude that the two complexes are probably isostructural.

Experimental

Synthesis of Compounds

$\mathrm{Mo_2(OAc)_4}$ was prepared by previously reported methods. Reaction of a diethylether suspension of 0.5 g (1.2×10^{-3} mol) of $\mathrm{Mo_2(OAc)_4}$ with 1.1 g (2.9×10^{-3} mol) of $\mathrm{Mg(CH_2Ph\text{-}}p\mathrm{\text{-}CH_3)_2(Et_2O)_2}$ in the presence of excess $\mathrm{PMe_3}$ led to isolation of pink $\mathrm{Mo_2(OAc)_2(CH_2Ph\text{-}}p\mathrm{\text{-}CH_3)_2(PMe_3)_2}$. A saturated hexane solution was cooled to −15 °C to yield large pink crystals which were suitable for an X-ray diffraction study. Yield: 0.56 g, 70%. ^{1}H NMR (90 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 0.64 (d, $\mathrm{P}\mathit{Me}_3$); δ 2.05 (s, $\text{-}\mathit{CH}_2\mathrm{Ph\text{-}}p\text{-}\mathit{CH}_3$); δ 2.55 (s, $\mathrm{O_2CC}\mathit{H}_3$); δ 2.72 (s, $\mathit{CH}_2\text{-}\mathrm{Ph\text{-}}p\mathrm{\text{-}CH_3}$); δ 6.70–7.10 (m, $\mathrm{CH_2}\mathit{Ph}\text{-}\mathrm{p\text{-}CH_3}$).

The analogous $\mathrm{CH_2Ph}$ derivative was prepared in an identical fashion with 0.5 g $\mathrm{Mo_2(OAc)_4}$ and 0.6 g $\mathrm{Mg(CH_2Ph)_2}$ in the presence of excess $\mathrm{PMe_3}$. Yield: 0.60 g, 78%. *Anal.* Calc. for $\mathrm{Mo_2C_{24}H_{38}P_2O_4}$: C, 44.74; H, 5.94; P, 9.61. Found: C, 46.98; H, 6.16; P, 8.23%. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, 25 °C) δ 0.78 (d, $\mathrm{P}\mathit{Me}_3$); δ 2.58 (s, $\mathrm{O_2C}\mathit{CH}_3$); δ 2.66 (s, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$); δ 6.95–7.12 (m, $\mathrm{CH_2}\mathit{Ph}$). ^{13}C NMR (50 MHz, $\mathrm{C_6D_6}$, 28 °C) δ 23.59 ($\mathrm{O_2C}\mathit{C}\mathrm{H_3}$); δ 34.34 ($\mathrm{P}\mathit{Me}_3$), δ 64.29 ($\mathit{C}\mathrm{H_2Ph}$); δ 147.24 ($\mathrm{O_2}\mathit{C}\mathrm{CH_3}$); δ 1.20–130 (m, $\mathrm{CH_2}\mathit{Ph}$).

X-ray Diffraction Study

The X-ray diffraction data is given in Table I. A crystal ($0.40 \times 0.17 \times 0.09$ mm) was handled in degassed NUJOL and mounted in a capillary surrounded by epoxy resin. It was transferred to the goniostat of an Enraf-Nonius CAD4 diffractometer. The structure was solved by a combination of direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were located and refined isotropically.

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