C3	0.92743 (15)	−0.1177 (2)	−0.3050 (4)	0.0548 (8)
C2	0.8559 (2)	−0.0669 (2)	−0.1117 (5)	0.0669 (9)
C4	0.8611 (2)	−0.2041 (2)	−0.1057 (8)	0.0997 (14)
C1	3/4	−0.10848 (7)	3/8	0.0772 (4)
O1†	0.8299 (2)	−0.1163 (3)	0.3293 (8)	0.105 (2)
O2†	0.7447 (2)	−0.0404 (2)	0.4333 (8)	0.145 (3)
O3†	0.7161 (3)	−0.1317 (4)	0.2318 (7)	0.188 (4)
O4†	0.7480 (4)	−0.1570 (3)	0.5207 (6)	0.126 (2)

† Site-occupancy factor of 0.50.

Table 2. *Selected geometric parameters ($\overset{\circ}{A}$, °)*

Zn—N1	1.991 (2)	N2—C2	1.376 (4)
N1—C3	1.311 (4)	N2—C4	1.483 (5)
N1—C1	1.352 (4)	C1—C2	1.332 (5)
N2—C3	1.333 (4)		
N1^i—Zn—N1^{ii}	112.80 (8)	C3—N2—C4	126.3 (3)
N1^i—Zn—N1	103.00 (14)	C2—N2—C4	126.8 (3)
C3—N1—C1	106.3 (3)	C2—C1—N1	110.1 (3)
C3—N1—Zn	125.8 (2)	N1—C3—N2	110.7 (3)
C1—N1—Zn	127.4 (2)	C1—C2—N2	106.0 (3)
C3—N2—C2	106.9 (3)		

Symmetry codes: (i) $2 - x, -y, z$; (ii) $1 + y, 1 - x, -1 - z$.

The O atoms of the twofold disordered perchlorate anion were subjected to geometrical restraints with site-occupancy factors of 0.50. H atoms were placed at calculated positions riding on their carrier atoms.

Data collection: *SDP* (Frenz, 1978). Cell refinement: *SDP*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93.

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A Methoxycarbonyl-Substituted Cyclopentadienyl–Dicarbonyl–Trimethylphosphite–Molybdenum Complex Dimer, [Mo(η^5-MeO2C2Cp){P(OMe)3}(CO)2]2

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Abstract

The title compound, bis[di(carbonyl-C)(η^5-methoxycarbonylcyclopentadienyl)(trimethylphosphite-P)molybdenum](*Mo—Mo*), $[Mo(\eta\text{-}C_7H_7O_2)(C_3H_9PO_3)(CO)_2]_2$, belongs to a type of dinuclear molybdenum complex with an Mo—Mo single-bond length of 3.230 (4) Å. The molecule has C_i symmetry, with two asymmetric units which are connected through the Mo—Mo bond.

Comment

The chemistry of molybdenum–cyclopentadienyl–carbonyl complexes with metal–metal multiple bonds is of interest due to their rich reactivities. It has been found that the unsubstituted and methyl-substituted cyclopentadienyl–dicarbonylmolybdenum complexes $[C_5R_5\text{-}(CO)_2Mo]_2$ (R = H or Me) differ markedly in their behaviour when reacted with trimethylphosphite, $P(OMe)_3$ (Curtis & Klingler, 1978; Riess, Klement & Wachter, 1985). We report here the crystal structure of the title compound, (I), which is the product of the reaction of methoxycarbonyl-substituted cyclopentadienyl–dicarbonylmolybdenum dimer and trimethylphosphite.

(I)
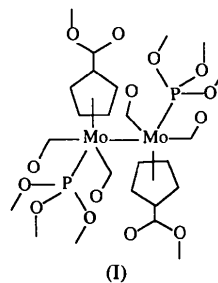
An *ORTEP*II (Johnson, 1976) diagram of the structure of the title compound is shown in Fig. 1. The structure consists of two asymmetric units, with each asymmetric unit having the formula $(MeO_2CCp)[P(OMe)_3](CO)_2Mo$

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(where Cp is cyclopentadienyl), in which there is an Mo atom with 17 electrons coordinated by an MeO_2CCp moiety, two carbonyl groups and a $P(OMe)_3$ ligand. The Mo—Mo bond length of 3.230 (4) Å is within the range of Mo—Mo single-bond lengths observed in compounds such as $Cp_2Mo_2(CO)_4$ (Wilson & Shoemaker, 1957; Adams, Collins & Cotton, 1974), $HCp_2Mo(C_5H_4)MoCp$ (Green, Poveda, Bashkin & Prout, 1982) and $Cp_2Mo_2(CO)_4CNPh$ (Adams, Katahira & Yang, 1982). The C—C bond lengths in the cyclopentadiene ring range from 1.40 (2) to 1.44 (2) Å, which are close to those in $Cp_2Mo_2(CO)_4$, which range from 1.370 to 1.442 Å (Wilson & Shoemaker, 1957). The Mo—P bond length of 2.345 (5) Å is shorter than that found in $(C_5Me_5)_2Mo_2(CO)_3$–phoran of 2.386 (2) Å (Riess, Klement & Wachter, 1985). As the Mo—C(11*) and Mo—C(12*) distances (where * denotes symmetry-generated atoms) are 3.16 (2) and 3.15 (1) Å, respectively, there is no bridging carbonyl in this compound. The dihedral angle between the cyclopentadienyl ring plane and the plane formed by atoms O(4), O(5), C(4) and C(5) in the asymmetric unit is 19 (1)°.
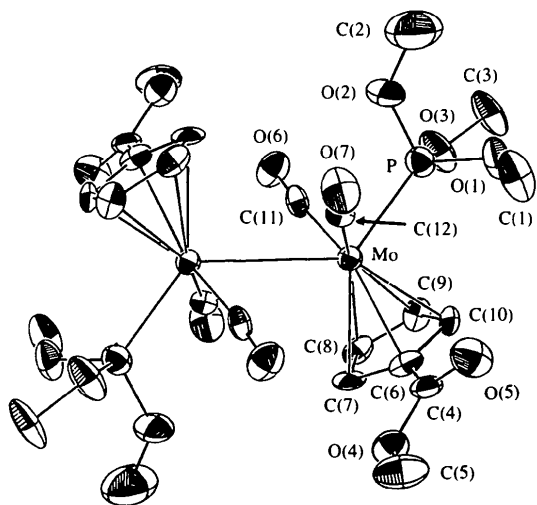

Fig. 1. The structure of (I) shown with 50% probability displacement ellipsoids.

Experimental

The synthesis of (I) was carried out by reaction of $[Mo(\eta^5\text{-}MeO_2C_2Cp)(CO)_2]_2$ and trimethylphosphite (molar ratio 1:5) in toluene solution under nitrogen for 12 h at room temperature. Recrystallization was from methylene chloride/petroleum solution. Crystals suitable for X-ray analysis were grown by evaporation of a methylene chloride/n-hexane solution.

Crystal data

$[Mo_2(C_7H_7O_2)_2(C_3H_9PO_3)_2$ $(CO)_4]$	Mo $K\alpha$ radiation
$M_r = 798.34$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
	$\theta = 6\text{-}15°$

$a = 10.387\,(7)$ Å
$b = 10.63\,(1)$ Å
$c = 8.016\,(8)$ Å
$\alpha = 111.76\,(8)°$
$\beta = 103.34\,(7)°$
$\gamma = 104.20\,(7)°$
$V = 744\,(3)$ Å^3
$Z = 1$
$D_x = 1.78$ Mg m^{-3}
D_m not measured

$\mu = 0.99$ mm^{-1}
$T = 293$ K
Cubic
$0.10 \times 0.10 \times 0.10$ mm
Red

Data collection

Rigaku AFC-5R diffractometer	1183 observed reflections $[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.016$
Absorption correction:	$\theta_{max} = 23°$
empirical via ψ scans	$h = 0 \rightarrow 11$
(North, Phillips &	$k = -11 \rightarrow 11$
Mathews, 1968)	$l = -8 \rightarrow 8$
$T_{min} = 0.75$, $T_{max} = 1.0$	3 standard reflections
2231 measured reflections	monitored every 250
2075 independent reflections	reflections
	intensity decay: 2.7%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.050$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
$wR = 0.054$	$\Delta\rho_{min} = -0.60$ e Å^{-3}
$S = 1.13$	Extinction correction: none
1183 reflections	Atomic scattering factors
190 parameters	from $International$ $Tables$
H atoms not refined	for X-ray $Crystallography$
$w = 1/[\sigma^2(F)]$	(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo	0.1210 (1)	1.0035 (1)	0.1712 (1)	0.0243 (4)
P	0.1965 (4)	0.8130 (3)	0.1716 (5)	0.038 (2)
O(1)	0.360 (1)	0.836 (1)	0.233 (1)	0.051 (5)
O(2)	0.125 (1)	0.672 (1)	-0.031 (1)	0.067 (5)
O(3)	0.158 (1)	0.760 (1)	0.321 (1)	0.058 (8)
O(4)	0.3808 (9)	1.4284 (9)	0.280 (1)	0.042 (4)
O(5)	0.493 (1)	1.270 (1)	0.254 (1)	0.056 (5)
O(6)	-0.158 (1)	0.757 (1)	0.082 (1)	0.049 (6)
O(7)	0.209 (1)	0.923 (1)	-0.188 (1)	0.057 (5)
C(1)	0.458 (2)	0.906 (2)	0.163 (2)	0.061 (8)
C(2)	0.169 (2)	0.561 (2)	-0.111 (3)	0.12 (1)
C(3)	0.217 (2)	0.676 (2)	0.395 (2)	0.070 (8)
C(4)	0.401 (2)	1.311 (1)	0.290 (2)	0.035 (6)
C(5)	0.467 (2)	1.489 (1)	0.192 (2)	0.063 (7)
C(6)	0.296 (1)	1.243 (1)	0.360 (2)	0.036 (5)
C(7)	0.165 (2)	1.256 (1)	0.365 (2)	0.034 (5)
C(8)	0.110 (1)	1.177 (1)	0.456 (2)	0.034 (5)
C(9)	0.204 (1)	1.111 (1)	0.504 (2)	0.036 (6)
C(10)	0.320 (1)	1.151 (1)	0.448 (2)	0.037 (6)
C(11)	-0.056 (1)	0.850 (1)	0.101 (2)	0.036 (6)
C(12)	0.168 (1)	0.947 (1)	-0.063 (2)	0.040 (6)

Table 2. *Selected geometric parameters (Å, °)*

Mo—Mo^i	3.230 (4)	O(1)—C(1)	1.45 (2)
Mo—P	2.345 (5)	O(2)—C(2)	1.36 (2)
Mo—C(6)	2.383 (9)	O(3)—C(3)	1.42 (3)
Mo—C(7)	2.41 (1)	O(4)—C(4)	1.34 (2)
Mo—C(8)	2.39 (1)	O(4)—C(5)	1.44 (2)

Mo—C(9)	2.32 (1)	O(5)—C(4)	1.19 (2)
Mo—C(10)	2.32 (1)	O(6)—C(11)	1.19 (1)
Mo—C(11)	1.93 (1)	O(7)—C(12)	1.15 (2)
Mo—C(11^i)	3.16 (2)	C(4)—C(6)	1.49 (2)
Mo—C(12)	1.96 (2)	C(6)—C(7)	1.41 (2)
Mo—C(12^i)	3.15 (1)	C(6)—C(10)	1.44 (2)
P—O(1)	1.58 (1)	C(7)—C(8)	1.41 (2)
P—O(2)	1.590 (8)	C(8)—C(9)	1.40 (2)
P—O(3)	1.59 (1)	C(9)—C(10)	1.40 (2)
P—Mo—C(6)	116.0 (3)	C(9)—Mo—C(11)	102.9 (6)
P—Mo—C(7)	142.5 (4)	C(9)—Mo—C(12)	147.2 (4)
P—Mo—C(8)	121.5 (4)	C(10)—Mo—C(11)	135.5 (6)
P—Mo—C(9)	89.0 (3)	C(10)—Mo—C(12)	112.6 (5)
P—Mo—C(10)	85.4 (3)	C(11)—Mo—C(12)	104.2 (5)
P—Mo—C(11)	78.0 (4)	O(1)—P—O(2)	104.2 (5)
P—Mo—C(12)	79.0 (4)	O(1)—P—O(3)	99.1 (6)
C(6)—Mo—C(7)	34.2 (6)	O(2)—P—O(3)	105.4 (5)
C(6)—Mo—C(8)	57.3 (4)	P—O(1)—C(1)	124 (1)
C(6)—Mo—C(9)	58.5 (5)	P—O(2)—C(2)	131 (1)
C(6)—Mo—C(10)	35.6 (5)	P—O(3)—C(3)	127 (1)
C(6)—Mo—C(11)	154.3 (5)	C(4)—O(4)—C(5)	113 (1)
C(6)—Mo—C(12)	99.8 (5)	O(4)—C(4)—O(5)	125 (2)
C(7)—Mo—C(8)	34.0 (6)	O(4)—C(4)—C(6)	110 (2)
C(7)—Mo—C(9)	57.4 (5)	O(5)—C(4)—C(6)	125 (1)
C(7)—Mo—C(10)	57.8 (5)	C(4)—C(6)—C(7)	131 (1)
C(7)—Mo—C(11)	122.2 (6)	C(4)—C(6)—C(10)	122 (1)
C(7)—Mo—C(12)	119.4 (6)	C(7)—C(6)—C(10)	107 (1)
C(8)—Mo—C(9)	34.5 (4)	C(6)—C(7)—C(8)	109 (1)
C(8)—Mo—C(10)	57.8 (4)	C(7)—C(8)—C(9)	108 (1)
C(8)—Mo—C(11)	97.2 (5)	C(8)—C(9)—C(10)	109 (1)
C(8)—Mo—C(12)	153.4 (5)	C(6)—C(10)—C(9)	108 (1)
C(9)—Mo—C(10)	35.3 (5)		

Symmetry code: (i) $-x, 2 - y, -z$.

The title structure was solved by a combination of Paterson and subsequent Fourier methods. The structure was refined by full-matrix least-squares techniques. All calculations were carried out on a VAX-11/785 computer. Anomalous dispersion was corrected for according to Cromer & Waber (1974).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *OR-TEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Tetraphenylporphyrinato)hafnium(IV) Diacetate Acetonitrile Solvate

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Abstract

The title metalloporphyrin bis(acetato-O,O')[5,10,-15,20-tetraphenyl-21H,23H-porphinato(2−)-N^{21},N^{22},-N^{23},N^{24}]hafnium acetonitrile solvate, $[Hf(C_2H_3O_2)_2(C_{44}H_{28}N_4)].CH_3CN$, crystallizes in space group $C2/c$ with $Z = 4$. The complex has twofold crystallographic symmetry. The two acetate ligands are coordinated in a mutually *cis* configuration and the geometry about the hafnium center approximates a square antiprism. The distance of the Hf atom from the porphyrin plane is 1.033 (5) Å. The average Hf—N and Hf—O bond distances are 2.26 (2) and 2.25 (3) Å, respectively. The bite angle of the diacetate ($C_{carbonyl}$—Hf—$C_{carbonyl}$) and average N—Hf—N($-x + 1$, y, $-z + \frac{3}{2}$) angles are 83.8 (4) and 125.7 (4)°, respectively.

Comment

The title compound, [(TPP)Hf(OAc)$_2$].CH$_3$CN (TPP is tetraphenylporphinato), was prepared according to the literature method of Huhmann, Corey, Rath & Campana (1996) and recrystallized from CH$_3$CN at 296 K as the CH$_3$CN solvate, with one molecule of CH$_3$CN per molecule of the metalloporphyrin. The solvent molecule exhibits large anisotropic displacement