

Table 3. Bond lengths (Å) and bond angles (°) for hydrogen bonds with *e.s.d.*'s in parentheses

OW—HW···O	OW—		OW···O	OW—
	HW	HW···O		
OW(5)—HW(5A)···O(5)	1.05 (5)	1.86 (5)	2.772 (6)	143 (4)
OW(2) <sup>y</sup> —HW(2B) <sup>y</sup> ···O(9)	1.04 (5)	1.81 (4)	2.763 (5)	149 (5)
OW(4) <sup>x</sup> —HW(4B) <sup>x</sup> ···O(13)	1.04 (5)	1.70 (6)	2.682 (6)	154 (4)

$x, \frac{1}{2} - y, -z$ ] the greatest deviations are for C(16)  $-0.236$  (5) Å and O(17)  $-0.256$  (3) Å.

It is noteworthy that the carboxylate groups are symmetric, with the angles  $\varphi_1 = \varphi_2$  ( $\varphi = \text{C—C—O}$ ) and the distance  $r_1 = r_2$  ( $r = \text{C—O}$  Å) (Table 2). The average C—C—O angle is  $117.5$  (7)°, while the average C—O bond distance is  $1.250$  (7) Å. The configurations of the carboxylate groups have not been greatly influenced by the perturbations produced by the different M—O bonds. Following the standard notation described by Porai-Koshits (1980) for the bridging carboxylates, four different structural functions have been distinguished. The classification for the different carboxylates is: 1-*a* for C(8), *s*-3-*sa* for C(4), *a*-2-*s* C(12), and for the last one C(16) *a*-4<sub>3</sub>-*s*.

Some water molecules are involved in hydrogen bonds with the O atoms from carboxylate groups, providing intermolecular links. The water molecule not involved in a metal bond is linked to one O atom from a carboxylate group, O(5)···OW(5)  $2.772$  (6) Å (Table 3). None of the O atoms with three links form hydrogen bonds.

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## Dicarbonyl( $\eta^5$ -cyclopentadienyl)(triphenylphosphite)[(triphenylphosphonio)methanide]-molybdenum *p*-Toluenesulfonate

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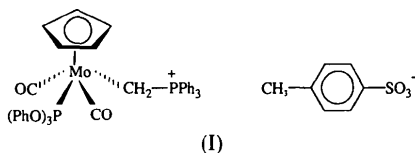
**Abstract.** [Mo(C<sub>5</sub>H<sub>5</sub>)(C<sub>19</sub>H<sub>17</sub>P)(C<sub>18</sub>H<sub>15</sub>O<sub>3</sub>P)(CO)<sub>2</sub>]-[C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S]·2.6H<sub>2</sub>O,  $M_r = 1018.89$ , triclinic,  $P\bar{1}$ ,  $a = 14.370$  (3),  $b = 14.990$  (3),  $c = 13.324$  (3) Å,  $\alpha = 110.30$  (2),  $\beta = 94.91$  (2),  $\gamma = 110.38$  (2)°,  $V = 2453.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) =$

$0.7093$  Å, graphite monochromator,  $\mu = 4.2$  cm<sup>-1</sup>,  $F(000) = 1062$ ,  $T = 296$  K,  $R = 0.028$ ,  $wR = 0.032$  for 7770 observed reflections with  $I > 3\sigma(I)$ . The coordination environment about the Mo atom consists of a cyclopentadienyl ring, two carbonyls, a triphenylphosphite and a C-bound methylene (a triphenylphosphine unit is bound to the methylene C

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atom). The geometry about the Mo atom is best described as having a piano-stool arrangement with the cyclopentadienyl ligand assuming the apical position. The two carbonyls, which are *trans* to each other, occupy two basal positions while the other two basal positions are occupied by triphenylphosphite and methylene phosphorane ligands. The angle at the methylene C atom (Mo—C—P) is 126.4 (1)° owing to steric interactions.

**Introduction.** The diversity of bonding modes which are possible for transition-metal ylide complexes has created interest in these compounds as possible intermediates in catalytic processes (Kaska, 1983; Schmidbaur, 1983). Several traditional strategies for the synthesis of compounds containing phosphorus ylide ligands have been reported, ranging from direct reactions between phosphorus ylides and transition-metal complexes to nucleophilic substitutions on halomethyl complexes by alkyl or aryl phosphines (Hoover & Stryker, 1988). Cyclopentadienyl- or pentamethylcyclopentadienyl-substituted Mo complexes bearing methylene phosphorane ligands have been particularly difficult to prepare by these techniques (Pelling, Botha & Moss, 1983; Moss, Niven & Stretch, 1986). We have prepared the title compound (I) by a modification of a method reported recently (Guerchais, Astruc, Nunn & Cowley, 1990); its structure is reported herein.



**Experimental.** Under nitrogen, CpMo(CO)<sub>2</sub>P(OPh)<sub>3</sub>-CH<sub>2</sub>OCH<sub>3</sub> (0.050 g, 0.09 mmol) and triphenylphosphine (0.023 g, 0.09 mmol) were dissolved in 5 mL CH<sub>2</sub>Cl<sub>2</sub> and the resulting solution was cooled to 273 K. While stirring, *p*-toluenesulfonic acid monohydrate (0.017 g, 0.09 mmol) was added; after 20 min, the solution was dried with MgSO<sub>4</sub>, filtered and the filtrate evaporated to dryness on a rotary evaporator. The residue was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> (2–3 mL) and diluted with pentane to the cloud point. Overnight cooling at 273 K gave yellow crystals which were collected by filtration.

X-ray diffraction data were obtained with an Enraf-Nonius CAD-4H diffractometer, Mo *K* $\alpha$  radiation, incident-beam graphite monochromator, from a yellow fragment (cut) crystal having approximate dimensions of 0.40 × 0.42 × 0.48 mm mounted on a glass fiber in a random orientation. The cell dimensions were taken from a least-squares refinement of the setting angles of 25 reflections

whose  $\theta$  angles ranged from 18 to 20°. Data were collected using the  $\omega/2\theta$  scan technique to a maximum  $2\theta$  of 50° over the range  $\pm 17$ ,  $17$ ,  $\pm 15$  for *h, k, l*. Three standard reflections (468, 3,10,0, 38 $\bar{1}$ ) were measured every 60 min of exposure time as a check on crystal stability and showed no variation (0.1%). A total of 9325 reflections were collected of which 8609 were unique; 7770 reflections were considered observed with  $I > 3\sigma(I)$  where  $\sigma(I)$  was determined from counting statistics (839 unobserved).  $R_{\text{int}}(F) = 0.008$  for 654 reflections. The structure was solved by Patterson technique (Mo atom) and subsequent least-squares and difference Fourier cycles; H atoms were included in calculated positions (C—H = 0.97 Å) with isotropic thermal parameters set to 1.2 times the value of  $B_{\text{eq}}$  of the bonded atom, H<sub>2</sub>O H atoms were included in positions from  $\Delta F$  maps; H-atom parameters were not refined. Data were corrected for Lorentz and polarization factors as well as absorption ( $\psi$  scans) with minimum and maximum corrections of 0.964 and 0.999. An isotropic extinction parameter refined to a value of  $2(1) \times 10^{-8}$ . The structure was refined in full-matrix least squares where the function minimized was  $\sum w(|F_o| - |F_c|)^2$ ;  $w = [\sigma(F)^2 + (0.008F)^2 + 0.8]^{-1}$  (Killean & Lawrence, 1969). Atomic scattering factors used were those of Cromer & Waber (1974) and were corrected for anomalous-dispersion effects (Cromer, 1974). The model converged (maximum  $\Delta/\sigma = 0.03$ ) for 7770 reflections and 597 variables with  $R = 0.028$ ,  $wR = 0.032$ ,  $S = 1.01$  and highest and lowest peaks on a difference Fourier map of 0.65 (4) and -0.36 (4) e Å<sup>-3</sup>. All calculations were performed on a VAX 11/750 computer using SDP/VAX (Frenz, 1978). Final positional and isotropic equivalent thermal parameters for non-H atoms are given in Table 1.\*

**Discussion.** Fig. 1 gives a view of the cation with the atomic numbering scheme. Selected bond lengths and angles are given in Table 2.

The structure consists of discrete cations and anions. Three water molecules of solvation were identified with one O atom, O(12), having only partial occupancy [0.63 (1)]. Hydrogen bonding is observed between the water molecules and with the sulfonate anion. A complete list of hydrogen-bond interactions may be found in the supplementary material.

\* A stereoview of the cell contents, lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54724 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0008]

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)
$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + \dots ab(\cos\gamma)\beta_{12} + \dots]$$

	x	y	z	B <sub>eq</sub>
Mo	0.32214 (1)	0.35119 (1)	0.21778 (1)	2.426 (4)
S	-0.02448 (5)	0.27289 (4)	0.46090 (5)	3.74 (1)
P(1)	0.44858 (4)	0.30106 (4)	0.13706 (4)	2.95 (1)
P(2)	0.07423 (4)	0.27489 (4)	0.03802 (4)	2.68 (1)
O(1)	0.3427 (1)	0.4545 (1)	0.0499 (1)	4.59 (4)
O(2)	0.2127 (1)	0.1087 (1)	0.1046 (2)	4.94 (5)
O(3)	0.5675 (1)	0.3768 (1)	0.1741 (1)	4.12 (4)
O(4)	0.4202 (1)	0.2622 (1)	0.0071 (1)	3.74 (4)
O(5)	0.4645 (1)	0.2012 (1)	0.1429 (1)	3.85 (4)
O(6)	0.0498 (1)	0.2523 (1)	0.4016 (2)	5.36 (5)
O(7)	0.0204 (2)	0.3671 (1)	0.5613 (2)	5.62 (5)
O(8)	-0.1114 (1)	0.2679 (1)	0.3927 (2)	5.34 (5)
O(10)	0.8420 (2)	0.4461 (2)	0.4353 (2)	8.73 (8)
O(11)	0.8811 (2)	0.4597 (2)	0.6528 (2)	10.90 (9)
O(12)	0.2292 (4)	0.7275 (5)	0.3229 (4)	10.5 (2)
C(1)	0.3312 (2)	0.4113 (2)	0.1075 (2)	3.02 (5)
C(2)	0.2534 (2)	0.1979 (2)	0.1415 (2)	3.13 (5)
C(3)	0.4451 (2)	0.4181 (2)	0.3801 (2)	4.03 (6)
C(4)	0.3525 (2)	0.3607 (2)	0.3989 (2)	4.27 (6)
C(5)	0.2847 (2)	0.4075 (2)	0.3908 (2)	4.05 (6)
C(6)	0.3361 (2)	0.4955 (2)	0.3685 (2)	3.97 (6)
C(7)	0.4352 (2)	0.5023 (2)	0.3635 (2)	3.89 (6)
C(8)	0.6130 (2)	0.4854 (2)	0.2201 (2)	3.24 (5)
C(9)	0.6873 (2)	0.5324 (2)	0.3164 (2)	3.72 (5)
C(10)	0.7363 (2)	0.6392 (2)	0.3635 (2)	4.20 (6)
C(11)	0.7109 (2)	0.6979 (2)	0.3154 (2)	4.75 (7)
C(12)	0.6374 (2)	0.6489 (2)	0.2179 (2)	4.96 (6)
C(13)	0.5880 (2)	0.5420 (2)	0.1691 (2)	4.08 (6)
C(14)	0.4682 (2)	0.2148 (2)	-0.0699 (2)	3.57 (5)
C(15)	0.5444 (2)	0.2762 (2)	-0.1019 (2)	4.86 (7)
C(16)	0.5800 (2)	0.2279 (3)	-0.1898 (3)	6.60 (9)
C(17)	0.5397 (2)	0.1221 (3)	-0.2421 (3)	7.16 (9)
C(18)	0.4661 (2)	0.0619 (2)	-0.2065 (3)	6.71 (9)
C(19)	0.4287 (2)	0.1085 (2)	-0.1188 (2)	5.12 (7)
C(20)	0.4975 (2)	0.1983 (2)	0.2436 (2)	3.62 (5)
C(21)	0.4271 (2)	0.1436 (2)	0.2857 (2)	5.23 (7)
C(22)	0.4596 (2)	0.1399 (2)	0.3853 (3)	6.72 (8)
C(23)	0.5608 (3)	0.1897 (2)	0.4385 (3)	6.70 (9)
C(24)	0.6306 (2)	0.2417 (2)	0.3941 (3)	6.15 (8)
C(25)	0.6002 (2)	0.2471 (2)	0.2955 (2)	4.72 (7)
C(26)	0.1484 (2)	0.3158 (1)	0.1715 (2)	2.87 (5)
C(27)	-0.0604 (2)	0.2287 (1)	0.0373 (2)	3.22 (5)
C(28)	-0.1310 (2)	0.1889 (2)	-0.0631 (2)	4.49 (6)
C(29)	-0.2343 (2)	0.1523 (2)	-0.0658 (3)	5.82 (8)
C(30)	-0.2674 (2)	0.1554 (2)	0.0282 (3)	6.27 (9)
C(31)	-0.1983 (2)	0.1952 (2)	0.1275 (3)	5.59 (7)
C(32)	-0.0943 (2)	0.2318 (2)	0.1315 (2)	4.06 (6)
C(33)	0.1018 (2)	0.3794 (1)	-0.0073 (2)	3.08 (5)
C(34)	0.1288 (2)	0.4798 (2)	0.0700 (2)	4.12 (6)
C(35)	0.1466 (2)	0.5600 (2)	0.0355 (2)	5.30 (7)
C(36)	0.1371 (2)	0.5407 (2)	-0.0740 (2)	5.57 (7)
C(37)	0.1085 (2)	0.4414 (2)	-0.1519 (2)	5.28 (7)
C(38)	0.0907 (2)	0.3600 (2)	-0.1182 (2)	4.24 (6)
C(39)	0.0895 (2)	0.1677 (1)	-0.0633 (2)	2.88 (5)
C(40)	0.1720 (2)	0.1844 (2)	-0.1122 (2)	3.39 (5)
C(41)	0.1866 (2)	0.1012 (2)	-0.1842 (2)	3.97 (6)
C(42)	0.1194 (2)	0.0006 (2)	-0.2067 (2)	4.46 (6)
C(43)	0.0371 (2)	-0.0162 (2)	-0.1596 (2)	4.26 (6)
C(44)	0.0211 (2)	0.0663 (2)	-0.0881 (2)	3.52 (5)
C(45)	-0.0728 (2)	0.1713 (2)	0.5066 (2)	3.52 (5)
C(46)	-0.0078 (2)	0.1581 (2)	0.5761 (2)	5.07 (7)
C(47)	-0.0429 (2)	0.0787 (2)	0.6109 (2)	5.36 (7)
C(48)	-0.1431 (2)	0.0102 (2)	0.5774 (2)	4.61 (6)
C(49)	-0.2082 (2)	0.0222 (2)	0.5048 (3)	5.77 (8)
C(50)	-0.1742 (2)	0.1026 (2)	0.4699 (2)	5.07 (7)
C(51)	-0.1797 (3)	-0.0773 (2)	0.6159 (3)	6.53 (8)

Table 2. Selected bond lengths (Å) and angles (°)

Mo—P(1)	2.3972 (7)	P(1)—O(4)	1.588 (2)
Mo—C(1)	1.965 (3)	O(4)—C(14)	1.410 (3)
Mo—C(2)	1.979 (2)	P(1)—O(5)	1.618 (2)
Mo—C(3)	2.327 (2)	O(5)—C(20)	1.405 (3)
Mo—C(4)	2.361 (3)	C(3)—C(4)	1.408 (4)
Mo—C(5)	2.344 (2)	C(4)—C(5)	1.402 (5)
Mo—C(6)	2.318 (2)	C(5)—C(6)	1.416 (4)
Mo—C(7)	2.321 (2)	C(6)—C(7)	1.401 (4)
Mo—C(26)	2.341 (2)	C(7)—C(3)	1.406 (4)
C(1)—O(1)	1.153 (3)	C(26)—P(2)	1.772 (3)
C(2)—O(2)	1.149 (2)	P(2)—O(7)	1.812 (2)
P(1)—O(3)	1.603 (1)	P(2)—C(33)	1.800 (3)
O(3)—C(8)	1.397 (2)	P(2)—C(39)	1.801 (2)
P(1)—Mo—C(1)	80.24 (7)	P(1)—O(3)—C(8)	128.8 (2)
P(1)—Mo—C(2)	75.81 (7)	P(1)—O(4)—C(14)	128.1 (2)
P(1)—Mo—C(26)	139.75 (5)	P(1)—O(5)—C(20)	121.7 (1)
C(1)—Mo—C(2)	108.91 (9)	Mo—C(26)—P(2)	126.04 (1)
C(1)—Mo—C(26)	83.46 (9)	C(26)—P(2)—C(27)	110.2 (2)
C(2)—Mo—C(26)	75.15 (8)	C(26)—P(2)—C(33)	112.12 (9)
Mo—C(1)—O(1)	174.1 (4)	C(26)—P(2)—C(39)	112.7 (1)
Mo—C(2)—O(2)	175.0 (2)	C(27)—P(2)—C(33)	106.6 (1)
Mo—P(1)—O(3)	122.82 (6)	C(27)—P(2)—C(39)	105.67 (9)
Mo—P(1)—O(4)	111.35 (7)	C(33)—P(2)—C(39)	109.1 (2)
Mo—P(1)—O(5)	119.93 (7)	C(3)—C(4)—C(5)	108.2 (3)
O(3)—P(1)—O(4)	104.84 (9)	C(4)—C(5)—C(6)	107.9 (2)
O(3)—P(1)—O(5)	95.91 (9)	C(5)—C(6)—C(7)	107.8 (3)
O(4)—P(1)—O(5)	98.25 (9)	C(6)—C(7)—C(3)	108.4 (2)
		C(7)—C(3)—C(4)	107.8 (3)

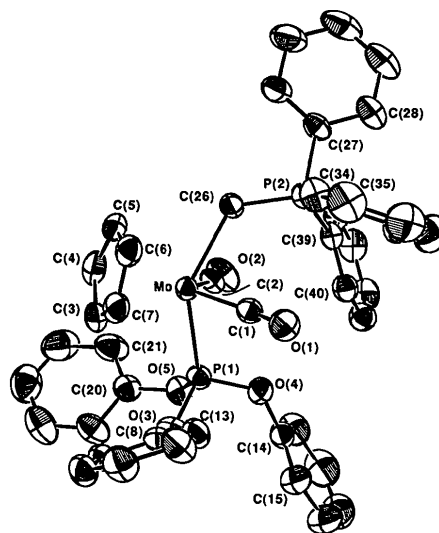


Fig. 1. ORTEP (Johnson, 1965) plot of the title compound (cation only) showing the atomic numbering system. The thermal ellipsoids are drawn at the 50% probability level.

The cation is an Mo complex having a piano-stool arrangement of ligands with the cyclopentadienyl (Cp) in the apical position. The four basal positions are occupied by two carbonyl ligands in a *trans* orientation, a triphenylphosphite and a C-bound methylene phosphorane ligand. The carbonyls, Cp ring, phosphine unit on the methylene and phenyl rings of the phosphite show no unusual structural features. Bonding to the Mo center is slightly dis-

torted as a result of steric crowding of the ligands (see below). The anion exhibits typical bonding parameters.

The closest analog of the title compound for which the structure has been determined is [Cp\*W(CO)<sub>3</sub>-(CH<sub>2</sub>PPh<sub>3</sub>)<sup>+</sup>·I<sup>-</sup>] (Cp\* = pentamethylcyclopentadienyl) (Moss, Niven & Stretch, 1986), but there are significant structural differences between the two compounds caused by differing steric demands of the ligands. In particular, the W—C—P angle involving the methylene C atom is 119.0 (1)° in the W complex but is expanded further to 126.4 (1)° in the Mo

complex. This is comparable to the seven-coordinate, and sterically crowded,  $[\text{W}(\text{CH}_2\text{PMe}_3)(\text{CO})_2\text{Cl}(\text{PMe}_3)_3]^+\cdot\text{CF}_3\text{SO}_3^-$  (Churchill & Wasserman, 1982) which shows  $126.4(4)^\circ$  for the analogous W—C—P bond angle. In contrast,  $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{CH}_2\text{PPh}_3)]^+\cdot\text{BF}_4^-$  (Guerchais, Astruc, Nunn & Cowley, 1990), a sterically less demanding complex, has an Fe—C—P angle of only  $118.1(7)^\circ$ . The steric crowding is also manifested in distortions of the bonding of ligands about the metal. The Cp ring is tilted with respect to the Mo center having Mo—C distances ranging from 2.318 (2) to 2.327 (2) Å for C(6), C(7), C(3) to 2.364 (2) and 2.344 (2) Å for C(4) and C(5), respectively. Further, the Mo—P(1)—O angles of the phosphite ligand are found to vary from  $111.35(7)$  to  $122.82(6)^\circ$  and the O—P(1)—O angles range from  $95.91(9)$  to  $104.84(9)^\circ$ .

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## Structure of Bis(4-nitro-1,2-catecholato)oxotechnetium(V)

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**Abstract.** Tetra-*n*-butylammonium bis(4-nitro-1,2-benzenediolato)oxotechnetate(V),  $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Tc}(\text{C}_6\text{H}_3\text{NO}_4)_2(\text{O})]$ ,  $M_r = 663.57$ , orthorhombic,  $P2_12_12$ ,  $a = 14.457(4)$ ,  $b = 21.380(6)$ ,  $c = 10.209(3)$  Å,  $V = 3155(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.39(1)$ ,  $D_x = 1.392$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.49$  mm<sup>-1</sup>,  $F(000) = 1384$ ,  $T = 295$  K and  $R = 0.065$  for 2658 observed reflections. The geometry around the Tc atom is square pyramidal with a short Tc—O(oxo) bond [ $1.634(4)$  Å] in the apical position. The Tc—O bonds with the diolato ligands are longer with distances of  $1.952(4)$  to  $1.979(5)$  Å. The Tc atom lies  $0.6947(5)$  Å out of the plane of the four diolato O atoms. The nitro groups are in the same planes as the catecholato ligands. The nitro group of one ligand is disordered.

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**Introduction.** The chemistry of Tc has recently become very important especially in relation to the use of the isotope <sup>99m</sup>Tc in nuclear medicine as an organ-imaging agent. The element has been combined with different types of ligands to produce very specific radiopharmaceuticals for imaging the bones, the heart, the brain, the kidneys, the liver and other organs, and also tumor tissue (Clarke & Podbielski, 1987; Nicolini, Bandoli & Mazzi, 1990).

Several of the <sup>99m</sup>Tc radiopharmaceuticals contain purely O donor ligands [see Davison, DePamphilis, Jones, Franklin & Lock (1987) and references therein] but few have been characterized. Recently, oxotechnetium(V) complexes of ethyleneglycol and catechol were reported and the crystal structure of the catechol compound was determined (Davison *et*

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