Preparation and *X*-Ray Crystal Structure of $[(OC)_3Mo\{P_2[MeNC(O)NMe]_2\}_3Mo(CO)_3]$ †

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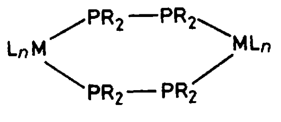
Two new complexes $[(OC)_3Mo(\mu\text{-}L)_3Mo(CO)_3]$ (1) and $[Mo(CO)_3L_3]$ (2) have been isolated from the reaction of $[Mo(CO)_3(C_7H_8)]$ (C_7H_8 = cycloheptatriene) with the diphosphine ligand $P_2[MeNC(O)NMe]_2$ (L). Crystals of (1) are tetragonal with *a* = *b* = 2 271.9(2), *c* = 3 212.1(4) pm, *Z* = 16, and space group *I*4₁/*acd*. The structure has been refined to *R* = 0.038 for 2 309 unique observed diffractomer data. The molecule possesses approximate 32 (D_3) symmetry, with a crystallographic two-fold axis perpendicular to the Mo · · · Mo vector. Mean Mo–P and P–P bond lengths are 246.2(2) and 221.7(2) pm.

The preparation of polynuclear transition-metal carbonyl complexes containing diphosphine ligands which bridge or cap the metal atoms is of interest because such ligands may confer stability on the cluster unit and prevent it breaking up into monomeric units. The presence of more than one metal atom improves the catalytic potential in reactions in which multicentre interaction is important.[1] Elegant syntheses of homobinuclear six-membered rings of type (A) with diphosphine ligands were reported by Vahrenkamp and coworkers.[2-4]



(A)

In this paper we report the preparation of mono- and binuclear molybdenum tricarbonyl complexes with three diphosphine ligands.

Experimental

The diphosphine ligand $P_2[MeNC(O)NMe]_2$ (L)[5] and $[Mo(CO)_3(C_7H_8)]$[6] (C_7H_8 = cycloheptatriene) were prepared according to previously reported procedures. All manipulations were carried out under dry oxygen-free nitrogen. Solvents were dried, deoxygenated, and distilled before use according to standard literature methods.

Table 1. Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo	8 416(1)	2 500(1)	458(1)
P(1)	7 481(1)	3 007(1)	607(1)
P(2)	6 648(1)	2 863(1)	262(1)
N(1)	7 141(2)	2 830(2)	1 064(1)
C(1)	7 422(3)	2 940(3)	1 472(2)
C(2)	6 595(2)	2 565(3)	1 067(2)
O(2)	6 359(2)	2 386(2)	1 378(1)
N(3)	6 355(2)	2 483(2)	670(1)
C(3)	5 793(3)	2 178(4)	652(2)
N(4)	7 406(2)	3 751(2)	564(1)
C(4)	7 867(4)	4 169(3)	686(3)
C(5)	6 853(3)	3 991(3)	480(2)
O(5)	6 752(2)	4 507(2)	512(1)
N(6)	6 448(2)	3 577(2)	345(1)
C(6)	5 848(3)	3 796(3)	254(2)
P(1′)	7 845(1)	1 630(1)	244(1)
N(1′)	8 220(2)	1 089(2)	−13(1)
C(1′)	8 712(3)	774(3)	183(2)
C(2′)	8 082(3)	949(2)	−420(2)
O(2′)	8 360(2)	605(2)	−628(2)
N(3′)	7 393(2)	1 266(2)	582(1)
C(3′)	7 539(4)	1 159(4)	1 019(2)
C(11)	8 914(2)	3 192(3)	645(2)
O(11)	9 202(2)	3 547(2)	776(1)
C(12)	9 194(2)	2 095(3)	363(2)
O(12)	9 653(2)	1 903(2)	328(1)
C(13)	8 507(2)	2 217(2)	1 047(2)
O(13)	8 602(2)	2 053(2)	1 374(1)

Reaction of $[Mo(CO)_3(C_7H_8)]$ *with* L.—(*a*) *In a mol ratio of* 2 : 3. A solution of $[Mo(CO)_3(C_7H_8)]$ (1.1 g) in tetrahydrofuran (thf) (20 cm^3) was added slowly to L (1.15 g) dissolved in thf (30 cm^3) and heated to 50 °C for 2 h. The light yellow precipitate which formed was filtered off and washed with thf (10 cm^3). Recrystallization from CH_2Cl_2 yielded 0.5 g (29%) of $[(OC)_3Mo(\mu\text{-}L)_3Mo(CO)_3]$ (1), m.p. 289 °C (Found: C, 27.7; H, 3.3; N, 16.2; P, 17.7. $C_{24}H_{36}Mo_2N_{12}O_{12}P_6$ requires C, 27.15; H, 3.40; N, 15.85; P, 17.50%). The i.r. spectrum of a Nujol mull showed ν(C=O) bands at 1 980, 1 940, and 1 690 cm^{-1}; n.m.r. chemical shifts were τ(CH_3) 3.01 and δ(^{31}P) 69.48 p.p.m. in CH_2Cl_2.

(*b*) *In a mol ratio of* 1 : 3. A solution of $[Mo(CO)_3(C_7H_8)]$ (3.5 g) in toluene (20 cm^3) was added to L (0.9 g) in toluene (20 cm^3) and heated to 70 °C for 3 h. After cooling to 20 °C the precipitated solid was filtered off and recrystallized from CH_2Cl_2–thf to yield 0.6 g (53%) of white $[Mo(CO)_3L_3]$ (2), m.p. 263 °C (Found: C, 28.3; H, 4.05; N, 18.8; P, 20.4. $C_{21}H_{36}MoN_{12}O_9P_6$ requires C, 28.60; H, 3.10; N, 19.05; P, 21.10%). The i.r. spectrum of a Nujol mull showed ν(C=O) bands at 1 965, 1 880, and 1 680 cm^{-1}; n.m.r. chemical shifts were τ(CH_3) 3.03, 3.08; δ(^{31}P) 11.50, 69.48 p.p.m. in CH_2Cl_2.

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† Tris[μ-(2,4,6,8-tetramethyl-2,4,6,8-tetra-aza-1,5-diphosphabicyclo[3.3.0]octane-3,7-dione-*PP*′)]-bis(tricarbonylmolybdenum).

Supplementary data available (No. SUP 23501, 24 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Bond lengths (pm) and angles (°); A denotes atoms generated by the two-fold axis (1.5 − x, y, −z)

Mo–P(1)	246.2(2)	Mo–P(1′)	246.3(2)
Mo–C(11)	202.8(6)	Mo–C(12)	201.6(6)
Mo–C(13)	200.9(5)	Mo–P(2A)	246.1(1)
P(1)–P(2)	221.7(2)	P(1)–N(1)	170.9(4)
P(1)–N(4)	170.6(5)	P(2)–N(3)	170.3(5)
P(2)–N(6)	170.7(5)	N(1)–C(2)	137.8(7)
N(1)–C(1)	147.6(7)	C(2)–N(3)	140.1(7)
C(2)–O(2)	120.4(7)	N(4)–C(4)	146.7(9)
N(3)–C(3)	145.4(9)	C(5)–O(5)	120.0(7)
N(4)–C(5)	139.4(8)	N(6)–C(6)	148.1(8)
C(5)–N(6)	138.5(8)	P(1′)–N(3′)	170.6(5)
P(1′)–N(1′)	170.8(4)	N(1′)–C(1′)	147.1(8)
P(1′)–P(1′A)	221.6(3)	C(2′)–O(2′)	120.7(7)
N(1′)–C(2′)	138.1(7)	N(3′)–C(3′)	146.4(8)
C(2′)–N(3′A)	139.8(7)	C(11)–O(11)	112.1(7)
C(12)–O(12)	113.7(7)	C(13)–O(13)	113.5(6)

P(1)–Mo–P(1′)	88.6(1)	P(1)–Mo–C(11)	93.5(2)
P(1′)–Mo–C(11)	177.4(2)	P(1)–Mo–C(12)	177.4(2)
P(1′)–Mo–C(12)	93.0(2)	C(11)–Mo–C(12)	84.8(2)
P(1)–Mo–C(13)	93.2(2)	P(1′)–Mo–C(13)	93.4(2)
C(11)–Mo–C(13)	84.9(2)	C(12)–Mo–C(13)	84.6(2)
P(1)–Mo–P(2A)	88.6(1)	P(1′)–Mo–P(2A)	88.6(1)
C(11)–Mo–P(2A)	93.0(2)	C(12)–Mo–P(2A)	93.6(2)
C(13)–Mo–P(2A)	177.4(2)	Mo–P(1)–P(2)	124.8(1)
Mo–P(1)–N(1)	116.6(2)	P(2)–P(1)–N(1)	90.5(2)
Mo–P(1)–N(4)	122.3(2)	P(2)–P(1)–N(4)	91.2(2)
N(1)–P(1)–N(4)	104.9(2)	P(1)–P(2)–N(3)	91.4(2)
P(1)–P(2)–N(6)	90.5(2)	N(3)–P(2)–N(6)	105.0(2)
P(1)–P(2)–Mo(A)	124.7(1)	N(3)–P(2)–Mo(A)	122.0(2)
N(6)–P(2)–Mo(A)	116.7(1)	P(1)–N(1)–C(1)	121.8(4)
P(1)–N(1)–C(2)	121.0(3)	C(1)–N(1)–C(2)	117.1(4)
N(1)–C(2)–O(2)	123.7(5)	N(1)–C(2)–N(3)	113.7(4)
O(2)–C(2)–N(3)	122.4(5)	P(2)–N(3)–C(2)	118.7(4)
P(2)–N(3)–C(3)	123.7(4)	C(2)–N(3)–C(3)	116.2(5)
P(1)–N(4)–C(4)	123.2(4)	P(1)–N(4)–C(5)	119.5(4)
C(4)–N(4)–C(5)	116.2(5)	N(4)–C(5)–O(5)	122.5(6)
N(4)–C(5)–N(6)	113.2(5)	O(5)–C(5)–N(6)	124.2(6)
P(2)–N(6)–C(5)	121.1(4)	P(2)–N(6)–C(6)	122.3(4)
C(5)–N(6)–C(6)	116.5(5)	Mo–P(1′)–N(1′)	116.7(2)
Mo–P(1′)–N(3′)	121.9(2)	N(1′)–P(1′)–N(3′)	105.0(2)
Mo–P(1′)–P(1′A)	124.7(1)	N(1′)–P(1′)–P(1′A)	90.6(2)
N(3′)–P(1′)–P(1′A)	91.4(2)	P(1′)–N(1′)–C(1′)	121.5(4)
P(1′)–N(1′)–C(2′)	120.7(4)	C(1′)–N(1′)–C(2′)	117.8(5)
N(1′)–C(2′)–O(2′)	123.6(5)	N(1′)–C(2′)–N(3′A)	114.1(5)
O(2′)–C(2′)–N(3′A)	122.2(5)	P(1′)–N(3′)–C(3′)	123.7(4)
P(1′)–N(3′)–C(2′A)	118.6(4)	Mo–C(11)–O(11)	174.3(5)
Mo–C(12)–O(12)	174.3(5)	Mo–C(13)–O(13)	174.9(5)

Crystal Data.—$C_{24}H_{36}Mo_2N_{12}O_{12}P_6$, M = 1 062.35, Tetragonal, space group $I4_1/acd$, $a = b$ = 2 271.9(2), c = 3 212.1(4) pm, U = 16.580 nm³, Z = 16, D_c = 1.702 mg m⁻³, $F(000)$ = 8 544, μ = 0.885 mm⁻¹ for Mo-K_α radiation, λ = 71.069 pm.

15 684 Profile-fitted[7] intensities from a crystal of size 0.5 × 0.25 × 0.35 mm were recorded in the range $7 < 2\theta < 50°$ on a Stoe-Siemens four-circle diffractometer. After Lorentz polarisation and empirical absorption corrections, equivalents were averaged to give 3 664 unique reflections, 2 309 of which with $F > 3\sigma(F)$ were used for all calculations (performed with the SHELXTL program system written by G.M.S.).

The structure was solved by direct methods and refined to R 0.038, R' 0.043 [weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,88\,F^2$]. Methyl groups were refined as rigid groups with C–H 96 pm, H–C–H 109.5°, and isotropic H [$U(H) = 1.2U_{eq}(C)$]. The remaining atoms were anisotropic. A final difference map showed no peaks higher than 0.35×10^{-6} e pm^{-3}. Final atomic co-ordinates and bond lengths and angles are presented in Tables 1 and 2 respectively.

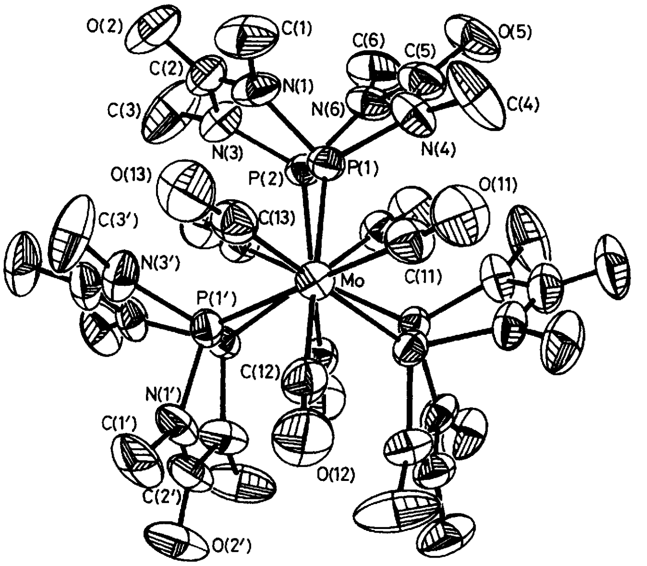

Figure. 50% Probability thermal motion ellipsoids for the molecule of (1), indicating the unique atoms

Discussion

Although lying on a crystallographic two-fold axis and crystallizing in a tetragonal space group, the molecular symmetry approximates closely to 32 (D_3). This can be seen in the Figure, in which the molecule is viewed along the Mo–Mo vector, which coincides with the pseudo-three-fold axis. There is no obvious explanation for the twist away from the idealised $\bar{6}m2$ (D_{3h}) structure. The normal Mo–P and P–P distances [mean values 246.2(2) and 221.7(2) pm respectively] result in a Mo · · · Mo distance of 509.7(1) pm, too long for any bonding interaction.

Complex (2) exhibits two ^{31}P chemical shifts, one of which is very close to the single shift observed in (1). This indicates a structure for (2) in which only one phosphorus atom of each ligand is bonded to an octahedrally co-ordinated Mo.

Acknowledgements

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References

1 E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.
2 L. Staudacker and H. Vahrenkamp, *Chem. Ber.*, 1976, **109**, 218.
3 A. Trenkle and H. Vahrenkamp, *Chem. Ber.*, 1981, **114**, 1366.
4 A. Trenkle and H. Vahrenkamp, *Chem. Ber.*, 1981, **114**, 1343.
5 H. W. Roesky, H. Zamankhan, W. S. Sheldrick, A. H. Cowley, and S. K. Mehrotra, *Inorg. Chem.*, 1981, **20**, 2910.
6 E. W. Abel, J. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 1958, 4559.
7 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

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