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Acta Cryst. (1997). **C53**, 1251–1254

[Mo(C₂₅H₂₂P₂)(C₃₄H₃₃P₃)(CO)]

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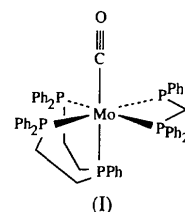
Abstract

The crystal structure of [bis(2-diphenylphosphino-ethyl)phenylphosphine-*P,P',P''*][bis(diphenylphosphino)methane-*P,P'*] carbonylmolybdenum(0), [Mo(dpepp)(dppm)(CO)] [where dppm = Ph₂PCH₂PPh₂ and dpepp = Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂], is reported. In the distorted octahedral complex, the tridentate ligand adopts a facial arrangement with the monodentate ligand *trans* to the central P atom. All Mo—P distances are statistically dissimilar.

Comment

Dinitrogen complexes of molybdenum and tungsten containing organophosphine ligands have played a key role in model studies of biological nitrogen fixation (George, 1983; Henderson, Leigh & Pickett, 1983; Hidai & Mizobe, 1995). We synthesized a series of mono(dinitrogen) complexes of molybdenum containing a tridentate phosphine and either two monodentate

phosphines or one bidentate phosphine (George & Tisdale, 1988). These complexes afforded ammonia upon treatment with acid demonstrating that it was not necessary to have two dinitrogen ligands per metal center in order to produce ammonia. There is some ambiguity about the structure of these complexes because of the various isomers that can be formed. For example, the tridentate ligand can be *fac* (facial) or *mer* (meridional). Previous structural assignments are based upon ³¹P NMR spectroscopy. The crystal structure of [MoBr(dpepp)(dmpm)], (II) (dmpm = Me₂PCH₂PMe₂) (George, Ma, Shailh, Tisdale & Zubietta, 1990), was determined but since the complex is paramagnetic no relationship between the ³¹P NMR spectrum and X-ray structure could be established.



The molecular structure of the title compound, (I), is shown with the atom-numbering scheme in Fig. 1. The structure is well resolved and shows several disordered atomic positions, bridging atoms C5 and P4, and the phenyl group bonded to the axial P atom (C91–C96). For clarity, lower occupancy sites are omitted in Fig. 1. The complex displays a distorted octahedral coordination environment about Mo with four P atoms

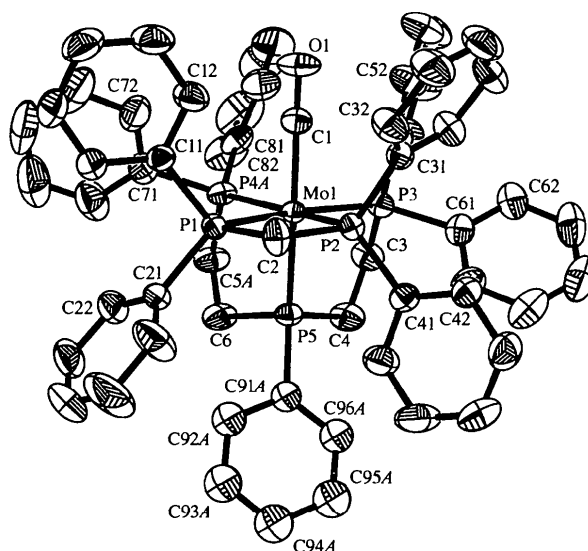


Fig. 1. Structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity and only high-occupancy sites are shown. All ring C atoms are numbered sequentially as shown explicitly in C91A–C96A.

loosely defining an equatorial plane about molybdenum, while the central P atom of dpepp and the C atom of the CO ligand occupy axial positions. Most angles differ from 90 or 180° about molybdenum (Table 2); Mo—C1—O1 is 178.1(3)°.

The dpepp ligand adopts a facial configuration with P—Mo—P angles close to 80° and similar to those found in *fac*-[Mo(CO)₃(dpepp)], (III) (Favas, Kepert, Skelton & White, 1980). Qualitatively, (I) is isostructural with (II), which is a molybdenum(I) complex. All Mo—P distances are statistically different in (I), with Mo—P_{3,4} being shorter than Mo—P_{1,2}. The longest Mo—P distance, 2.5100(15) Å, is associated with the P atom *trans* to CO. This distance is in the order of 0.1 Å longer than the corresponding Mo—P distance in (II) where the P atom is *trans* to a Br atom. One consequence of the large difference in Mo—P(central) distance is the angle subtended at molybdenum by the two end P atoms of dpepp; 93.01(7) for (I) and 105.0(1)° for (II). In (III), each P atom is *trans* to a CO ligand, with the Mo—P(terminal) distances being longer [2.504(3) and 2.542(3) Å] than the Mo—P(central) distance [2.479(2) Å] (Favas, Kepert, Skelton & White, 1980).

Several bond lengths not listed here but available in the supplementary material require mentioning. The distances from the low-occupancy P-atom site (P4B) to the nearest phenyl groups are chemically nonsensical; P4B—C71 is 1.58(3) Å, whereas P4B—C81 is 2.18(2) Å. It is likely that second positions for these phenyl groups exist but are not visible due to low occupancy (and probably libration) and the quality of our crystals. P5—C91A is the longest of the remaining P—Ph bonds [1.875(3) Å]. This is expected based on previous structural reports. However, P5—C91B is significantly shorter [1.849(5) Å]. The P—Ph bonds (excluding those to C91B) are normally distributed with an

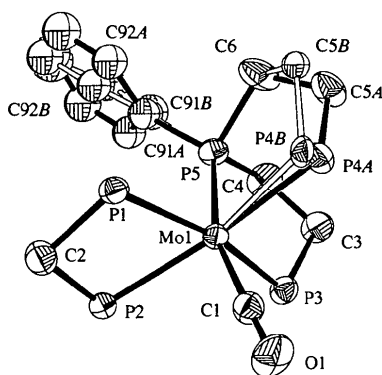


Fig. 2. Structure of the core of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. In addition, all phenyl rings except the disordered phenyl group have been omitted. Bonds to low-occupancy sites are shown as hollow lines.

average value of 1.850(14) Å and range from 1.831(4) (P4A—C81) to 1.875(3) Å (P5—C91A).

Phenyl C—C bond lengths divide into two distinct groups. The disordered phenyl group is restrained as a planar rigid group, with C—C distances of 1.39 Å and a standard deviation of 0.005 Å. The average C—C bond length in the ordered phenyl groups is 1.379(14) Å. They range from 1.340(8) (C23—C24) to 1.408(9) Å (C73—C74).

Examination of the packing of this molecule in the crystal reveals no close contacts, which is consistent with disorder at the mentioned positions. It is interesting to note that all observed disordered positions are in the dpepp ligand. We cannot rule out minor compositional disorder but expect that the presence of other isomers would also cause disorder of the P atoms, all of which are well localized.

Experimental

Complex (I) [$\nu(\text{CO}) = 1782 \text{ cm}^{-1}$] is best prepared by irradiating (366 nm) a sample of [Mo(N₂)(dpepp)(dppm)] (George & Tisdale, 1988) in CO-saturated tetrahydrofuran in a quartz vessel cooled to 195 K under 1 atm of CO (1 atm = 101 325 Pa). The reaction can be effectively monitored by IR spectroscopy. Red–orange crystals were obtained by reducing the volume and adding methanol at room temperature. Crystals were collected under dinitrogen. The crystals studied in this paper had been stored for seven years in the dark in a sealed tube under dry pentane without any visible change or any change in the IR spectrum.

Crystal data

[Mo(C₂₅H₂₂P₂)(C₃₄H₃₃P₃)-
(CO)]

$M_r = 1042.83$

Triclinic

$P\bar{1}$

$a = 12.108(2) \text{ \AA}$

$b = 12.155(2) \text{ \AA}$

$c = 18.884(4) \text{ \AA}$

$\alpha = 104.37(3)^\circ$

$\beta = 100.67(3)^\circ$

$\gamma = 100.80(3)^\circ$

$V = 2565.0(9) \text{ \AA}^3$

$Z = 2$

$D_x = 1.350 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 22
reflections

$\theta = 11.5\text{--}12.5^\circ$

$\mu = 0.453 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prismatic

$0.45 \times 0.30 \times 0.15 \text{ mm}$

Scarlet

Data collection

Siemens P4 diffractometer

θ – 2θ scans

Absorption correction:

analytical, face-indexed

$T_{\min} = 0.70$, $T_{\max} = 0.90$

16 658 measured reflections

14 709 independent

reflections

10 695 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 30.0^\circ$

$h = -1 \rightarrow 16$

$k = -16 \rightarrow 16$

$l = -26 \rightarrow 26$

3 standard reflections

every 97 reflections

intensity decay: <3%

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.051$$

$$wR(F^2) = 0.134$$

$$S = 1.02$$

14 704 reflections

607 parameters

H atoms riding

$$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 1.067P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.014$$

$$\Delta\rho_{\max} = 1.101 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.685 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

C91A§	0.6207 (3)	0.2822 (2)	0.1619 (2)	0.043 (4)
C92A§	0.5279 (3)	0.2757 (2)	0.1963 (2)	0.052 (2)
C93A§	0.4713 (5)	0.1679 (4)	0.2007 (4)	0.063 (2)
C94A§	0.5047 (8)	0.0675 (4)	0.1696 (6)	0.068 (5)
C95A§	0.6013 (6)	0.0750 (4)	0.1388 (5)	0.067 (2)
C96A§	0.6567 (6)	0.1825 (4)	0.1330 (4)	0.053 (2)
C91B¶	0.6205 (6)	0.2806 (5)	0.1556 (4)	0.035 (4)
C92B¶	0.5700 (6)	0.2728 (5)	0.2153 (4)	0.047 (2)
C93B¶	0.5167 (8)	0.1645 (6)	0.2208 (4)	0.057 (2)
C94B¶	0.519 (1)	0.0626 (5)	0.1680 (7)	0.089 (7)
C95B¶	0.560 (1)	0.0701 (5)	0.1049 (5)	0.074 (3)
C96B¶	0.6187 (9)	0.1780 (6)	0.1016 (5)	0.062 (3)
C2	0.8470 (3)	0.5570 (3)	0.4144 (2)	0.0407 (7)
C3	0.8329 (3)	0.4959 (3)	0.0627 (2)	0.0449 (8)
C4	0.7470 (3)	0.3917 (3)	0.0698 (2)	0.0504 (9)
C5A†	0.5805 (4)	0.5830 (3)	0.1014 (2)	0.0479 (13)
C5B‡	0.542 (2)	0.589 (2)	0.144 (2)	0.027 (7)
C6	0.5540 (3)	0.4680 (3)	0.1176 (2)	0.0528 (9)
C1	0.9233 (3)	0.7635 (3)	0.3020 (2)	0.0347 (6)
O1	0.9836 (2)	0.8579 (2)	0.3308 (1)	0.0546 (7)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

Mol	x	y	z	U_{eq}
P1	0.73779 (6)	0.61539 (6)	0.36208 (4)	0.02737 (14)
P2	0.93907 (6)	0.53989 (6)	0.34655 (4)	0.02805 (15)
P3	0.93351 (7)	0.57956 (7)	0.15581 (4)	0.0328 (2)
P4A†	0.6920 (2)	0.6952 (2)	0.18062 (15)	0.0324 (4)
P4B‡	0.680 (2)	0.697 (2)	0.201 (1)	0.038 (4)
P5	0.68881 (7)	0.42950 (6)	0.15462 (4)	0.0334 (2)
C11	0.74336 (3)	0.7525 (2)	0.4342 (2)	0.0322 (6)
C12	0.8487 (3)	0.8340 (3)	0.4638 (2)	0.0496 (9)
C13	0.8593 (4)	0.9376 (3)	0.5197 (2)	0.0602 (11)
C14	0.7663 (4)	0.9604 (3)	0.5465 (2)	0.0625 (11)
C15	0.6620 (4)	0.8795 (4)	0.5179 (3)	0.0721 (13)
C16	0.6497 (3)	0.7758 (3)	0.4620 (2)	0.0559 (10)
C21	0.5986 (3)	0.5263 (3)	0.3638 (2)	0.0358 (6)
C22	0.4975 (3)	0.5359 (3)	0.3202 (2)	0.0499 (8)
C23	0.3901 (3)	0.4712 (4)	0.3196 (3)	0.0681 (13)
C24	0.3820 (5)	0.3949 (5)	0.3599 (4)	0.097 (2)
C25	0.4796 (5)	0.3850 (6)	0.4045 (4)	0.110 (2)
C26	0.5869 (4)	0.4509 (4)	0.4072 (3)	0.0736 (14)
C31	1.0850 (3)	0.6288 (3)	0.3997 (2)	0.0322 (6)
C32	1.1186 (3)	0.6725 (3)	0.4774 (2)	0.0468 (8)
C33	1.2313 (4)	0.7366 (4)	0.5134 (2)	0.0619 (11)
C34	1.3097 (3)	0.7584 (4)	0.4729 (3)	0.0621 (11)
C35	1.2791 (3)	0.7158 (4)	0.3962 (2)	0.0578 (10)
C36	1.1663 (3)	0.6520 (3)	0.3592 (2)	0.0447 (8)
C41	0.9594 (3)	0.3916 (3)	0.3427 (2)	0.0335 (6)
C42	1.0633 (3)	0.3674 (3)	0.3711 (2)	0.0389 (7)
C43	1.0702 (4)	0.2531 (3)	0.3665 (2)	0.0533 (9)
C44	0.9735 (4)	0.1621 (3)	0.3331 (3)	0.0626 (11)
C45	0.8701 (4)	0.1843 (3)	0.3035 (3)	0.0666 (12)
C46	0.8626 (3)	0.2981 (3)	0.3087 (2)	0.0497 (8)
C51	1.0184 (3)	0.7032 (3)	0.1338 (2)	0.0408 (7)
C52	1.0990 (3)	0.7904 (3)	0.1925 (2)	0.0509 (9)
C53	1.1668 (4)	0.8850 (4)	0.1789 (3)	0.0676 (12)
C54	1.1563 (5)	0.8925 (5)	0.1071 (3)	0.083 (2)
C55	1.0772 (5)	0.8065 (4)	0.0482 (3)	0.0770 (15)
C56	1.0086 (4)	0.7133 (4)	0.0613 (2)	0.0561 (10)
C61	1.0386 (3)	0.4854 (3)	0.1544 (2)	0.0401 (7)
C62	1.1423 (3)	0.5091 (4)	0.1323 (2)	0.0514 (9)
C63	1.2114 (4)	0.4305 (5)	0.1273 (2)	0.0685 (12)
C64	1.1809 (5)	0.3276 (5)	0.1449 (3)	0.0743 (14)
C65	1.0809 (5)	0.3041 (4)	0.1685 (2)	0.0698 (13)
C66	1.0095 (4)	0.3811 (3)	0.1729 (2)	0.0537 (9)
C71	0.6075 (3)	0.7835 (3)	0.2338 (2)	0.0475 (8)
C72	0.6691 (4)	0.8784 (3)	0.2948 (2)	0.0584 (10)
C73	0.6125 (6)	0.9468 (5)	0.3385 (3)	0.086 (2)
C74	0.4904 (6)	0.9160 (6)	0.3195 (4)	0.092 (2)
C75	0.4302 (5)	0.8220 (6)	0.2608 (4)	0.096 (2)
C76	0.4874 (4)	0.7572 (5)	0.2180 (3)	0.0725 (13)
C81	0.7406 (4)	0.7974 (3)	0.1295 (2)	0.0452 (8)
C82	0.6804 (5)	0.7936 (4)	0.0583 (2)	0.0737 (14)
C83	0.7254 (7)	0.8719 (6)	0.0218 (3)	0.099 (2)
C84	0.8256 (7)	0.9550 (5)	0.0548 (4)	0.099 (2)
C85	0.8837 (5)	0.9617 (4)	0.1246 (3)	0.082 (2)
C86	0.8424 (3)	0.8837 (2)	0.1618 (2)	0.0598 (10)

† Site occupancy = 0.901 (10). ‡ Site occupancy = 0.099 (10). § Site occupancy = 0.542 (9). ¶ Site occupancy = 0.458 (9).

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo1—C1	1.940 (3)	P3—C3	1.861 (3)
Mo1—P4B	2.37 (3)	P4A—C5A	1.863 (4)
Mo1—P3	2.4237 (10)	P4B—C5B	1.87 (4)
Mo1—P4A	2.442 (3)	P5—C6	1.844 (4)
Mo1—P2	2.4788 (10)	P5—C4	1.857 (4)
Mo1—P1	2.4970 (9)	C3—C4	1.531 (5)
Mo1—P5	2.5100 (15)	C5A—C6	1.493 (5)
P1—C2	1.856 (3)	C5B—C6	1.48 (3)
P2—C2	1.847 (3)	C1—O1	1.172 (4)
C1—Mo1—P4B	88.7 (6)	P2—Mo1—P5	107.15 (4)
C1—Mo1—P3	90.99 (10)	P1—Mo1—P5	101.57 (4)
P4B—Mo1—P3	103.3 (6)	C2—P1—Mo1	96.20 (10)
C1—Mo1—P4A	89.15 (11)	C2—P2—Mo1	97.07 (10)
P3—Mo1—P4A	93.01 (7)	C3—P3—Mo1	109.26 (11)
C1—Mo1—P2	86.99 (9)	C5A—P4A—Mo1	112.3 (2)
P4B—Mo1—P2	156.9 (6)	C5B—P4B—Mo1	113.6 (14)
P3—Mo1—P2	99.47 (3)	C6—P5—C4	102.4 (2)
P4A—Mo1—P2	166.99 (6)	C4—P5—Mo1	109.99 (12)
C1—Mo1—P1	90.11 (9)	P2—C2—P1	98.24 (15)
P4B—Mo1—P1	88.8 (6)	C4—C3—P3	110.7 (2)
P3—Mo1—P1	167.82 (3)	C3—C4—P5	112.8 (2)
P4A—Mo1—P1	99.14 (7)	C6—C5A—P4A	111.4 (3)
P2—Mo1—P1	68.47 (3)	C6—C5B—P4B	113.6 (18)
C1—Mo1—P5	164.16 (9)	C5B—C6—P5	120.2 (11)
P4B—Mo1—P5	81.0 (6)	C5A—C6—P5	110.7 (3)
P3—Mo1—P5	79.87 (4)	O1—C1—Mo1	178.1 (3)
P4A—Mo1—P5	78.54 (6)		

The second positions of atoms C5 and P4 were revealed in difference electron-density maps using Biosym's *INSIGHTII* software (Biosym Technologies, 1995). A free variable in *SHELXTL* (Sheldrick, 1994) was used to refine the occupancy of P4B and C5B to the same value [0.099 (10)]. The secondary lower-occupancy site for the C atom was refined with isotropic atomic displacement parameters, whereas anisotropic thermal motion was used to model the low-occupancy P-atom site. At this point, the displacement parameters suggested multiple sites for the axial phenyl group (C91–C96). Assuming equal occupancy of both sites, a second position of this ring was manually fitted to electron density displayed with *INSIGHTII* (Biosym Technologies, 1995). These populations were refined with 0.542 (9)/0.458 (9) occupancy factors with a second free variable. The two positions were refined with isotropic displacement parameters and the ring C atoms were restrained to lie in a flat plane.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve

structure: *XS* (Siemens, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *INSIGHTII*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1241). Services for accessing these data are described at the back of the journal.

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