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trans-Bis(dinitrogen)tetrakis(methyldiphenylphosphine)molybdenum(0) Benzene Solvate, $[Mo(N_2)_2\{P(CH_3)(C_6H_5)_2\}_4].1{\cdot}5(C_6H_6)$

By Robert H. Morris, Joel M. Ressner and Jeffery F. Sawyer

Department of Chemistry and the Scarborough Campus, University of Toronto, 80 *St George Street, Toronto, Ontario, Canada M5S 1A*1

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Abstract. $M_r = 1069{\cdot}9$, triclinic, $P\bar{1}$, $a = 11{\cdot}776\ (2)$, $b = 14{\cdot}353\ (2)$, $c = 17{\cdot}425\ (2)$ Å, $\alpha = 76{\cdot}51\ (1)$, $\beta = 71{\cdot}45\ (1)$, $\gamma = 82{\cdot}52\ (1)°$, $U = 2710$ Å^3, $Z = 2$, $D_x = 1{\cdot}31$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}0$ cm^{-1}, $F(000) = 1114$, $T = 295$ K, $R = 0{\cdot}052$ for 5693 observed $[I > 3\sigma(I)]$ reflections. The molybdenum atom is approximately octahedrally coordinated by four phosphorus atoms $[\langle Mo{-}P\rangle = 2{\cdot}496\ (2)$ Å] and two nitrogen atoms [Mo—N = 1·989 (5), 2·000 (5) Å]. The N—N bond lengths are 1·133 (7) and 1·154 (7) Å. Bulky ligands pack around the metal with four pairs of adjacent phenyl rings on different P atoms nearly parallel thus resulting in an approximate D_{2d} symmetry for the complex.

Introduction. The title complex undergoes a variety of unusual substitution reactions where the phosphine ligands are replaced by P-, N-, or S-donor ligands while the labile dinitrogen ligands are retained (Morris & Ressner, 1983; Morris, Ressner, Sawyer & Shiralian, 1984, and references therein). The lability of the bulky phosphine ligands can be attributed to a weakening of the molybdenum–phosphorus bonds by inter-ligand steric interactions. This structure determination supports this conclusion.

Experimental. Preparation of the complex $Mo(N_2)_2(PMePh_2)_4$ as reported (George & Noble, 1979; Lazarowych, Morris & Ressner, 1985). Crystals obtained by slow evaporation of a benzene solution in a nitrogen-filled glovebox. Dark red block-shaped crystal, overall dimensions 0·19 × 0·21 × 0·24 mm, sealed in Lindemann capillary. Precession photographs gave preliminary cell and space-group information. Further work on Enraf–Nonius CAD-4 diffractometer, graphite monochromatized Mo $K\bar{\alpha}$ radiation. Accurate unit-cell dimensions by least-squares fit of diffracting positions of 25 reflections ($8{\cdot}7 < \theta < 15{\cdot}4°$). Data collected using ω–2θ scans, ω scan ranges $(0{\cdot}70 + 0{\cdot}35\tan\theta)°$. Scan rates conditional on information collected in prescans selected to give $I/\sigma(I)$ of 25 within max. scan time of 80 s. Gradual decrease in intensities of 3 standard reflections monitored every 12 000 s of exposure time corrected for after data reduction [max. rescale factor (on F) 1·23]. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect peak. 8792 reflections in quadrants $(h, \pm k, \pm l)$ with $2\theta \leq 50°$ measured. Correction for Lorentz, polarization and crystal decay. 644 zero $F_{\rm obs}$ excluded, 447 symmetry-equivalent data averaged ($R_{\rm merge} = 0{\cdot}02$) to give 7515 reflections. Structure solved using Patterson, least-squares and Fourier methods. Least-squares refinement of occupancy factors for solvent molecules indicated 1·5 molecules of benzene in asymmetric unit. All hydrogen atoms in $Mo(N_2)_2(PMePh_2)_4$ molecule located in difference Fourier map but, owing to program limitations, only methyl hydrogen atoms refined. Blocked least-squares refinement minimizing $\sum w||F_o| - |F_c||^2$, with all non-hydrogen atoms except those in solvent with anisotropic thermal parameters, converged (max. $\Delta/\sigma = 0{\cdot}07$) to $R = 0{\cdot}052$ ($wR = 0{\cdot}054$) for 5693 observed data with $I > 3\sigma(I)$. $w = [\sigma^2(F) + 0{\cdot}0006F^2]^{-1}$. Most significant features in final difference Fourier map attributable to phenyl hydrogen atoms ($\leq 0{\cdot}57$ e Å^{-3}). Programs: Enraf–Nonius (1979) *SDP* and *SHELX* (Sheldrick, 1976) on PDP 11/23 and SEL75 computers. Atomic scattering factors from *SHELX*. The final atomic positional and thermal parameters are included in Table 1, selected bond

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lengths and angles in Table 2.* Fig. 1 shows the molecule.

Discussion. The crystal structure contains isolated $Mo(N_2)_2(PMePh_2)_4$ molecules and benzene solvent. The coordination geometry about the molybdenum is distorted octahedral with one pair of *trans* phosphorus atoms above [+0·223 (1) Å] and the other pair below [−0·225 (1) Å] the mean plane described by the molydenum and the four phosphorus atoms.

The four equivalent Mo—P distances are significantly longer than the majority of the Mo—P distances in related compounds: *trans*-$Mo(N_2)_2(dppe)_2$, dppe = 1,2-bis(diphenylphosphino)ethane [2·445 (1), 2·462 (1) Å; Uchida, Uchida, Hidai & Kodama (1975)]; *cis*-$Mo(N_2)_2(PMe_3)_4$ [2·441 (3)–2·459 (3) Å; Carmona, Marin, Poveda, Atwood & Rogers (1983)]; $Mo(N_2)(CO)(dppe)_2$ and $Mo(CO)(dppe)_2$ [2·435 (4)–2·468 (2) Å; Sato, Tatsumi, Kodama, Hidai, Uchida & Uchida (1978)]; $Mo(N_2)(PMe_3)_5$ [2·460 (5) Å equatorial and 2·483 (7) Å *trans* to N_2; Carmona, Marin, Poveda, Rogers & Atwood (1982)]; *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ [2·443 (9), 2·457 (9) and 2·500 (8) Å; Morris *et al.* (1984)]. Recent studies of a series of tetracarbonyl-*cis*-phosphine-molybdenum complexes $Mo(CO)_4(PRR^{I}R^{II})(PR^{III}R^{IV}R^{V})$ have shown that the Mo—P distances (which, being *trans* to CO, are longer than those in the present compounds) do correlate with increasing cone angle of the phosphine while the PMoP angle correlates with cone angle only for symmetrical phosphines with three identical *R* groups (Cotton, Darensbourg, Klein & Kolthammer, 1982*a*,*b*,*c*). Since the cone angle for the ligand $PMePh_2$ (136°; Tolman, 1977) is larger than that for PMe_3 (118°) or 0·5 dppe (125°), the lengthening of the Mo—P bonds in the title compound is principally steric in origin.

By contrast, the Mo—N distances in $Mo(N_2)_2(PMePh_2)_4$ are significantly shorter than the Mo—N bond lengths in $Mo(N_2)_2(dppe)_2$ [2·014 (5) Å] and $Mo(N_2)(CO)(dppe)_2$ [2·068 (12) Å *trans* to CO], but are comparable with the Mo—N distances in *cis*-$Mo(N_2)_2(PMe_3)_4$ [1·97 (1) and 1·97 (1) Å], $Mo(N_2)(PMe_3)_5$ [2·02 (3) Å] and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ [1·98 (2) and 2·00 (3) Å]. Consistent with the shorter Mo—N bond, the N—N distances in $Mo(N_2)_2(PMePh_2)_4$ are greater than analogous distances in $Mo(N_2)_2(dppe)_2$ [1·118 (8) Å] and $Mo(N_2)(CO)(dppe)_2$ [1·087 (18) Å] and equal to or greater than those in $Mo(N_2)(PMe_3)_5$ [1·12 (3) Å], $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2SMe)$ [1·04 (3), 1·10 (3) Å] and probably *cis*-$Mo(N_2)_2(PMe_3)_4$ [1·14 (1), 1·15 (1) Å]. The elongation of the N—N distance over that in free N_2 (1·098 Å) is explained by back-donation of electrons from Mo into antibonding $1\pi_g^*$ orbitals of dinitrogen. The Mo—N—N angles are both 178·8 (4)°.

Table 1. *Final atomic positional* (×10⁴, ×10⁵ *for* Mo) *and thermal parameters* (Å² ×10³) *with e.s.d.'s in parentheses*

	x	y	z	U or U_{eq}†
Mo(1)	26088 (4)	26164 (3)	24248 (3)	23·6 (3)
N(11)	3936 (4)	3516 (3)	1950 (3)	31 (3)
N(12)	4702 (5)	4013 (4)	1678 (4)	52 (4)
N(21)	1272 (4)	1737 (3)	2900 (3)	33 (3)
N(22)	482 (5)	1241 (4)	3179 (3)	49 (4)
P(1)	1795 (1)	3586 (1)	1304 (1)	27·9 (8)
C(1)	1939 (7)	4877 (4)	1148 (4)	38 (4)
C(111)	2531 (5)	3485 (4)	211 (3)	31 (3)
C(112)	1950 (6)	3128 (4)	−240 (4)	47 (4)
C(113)	2556 (7)	3081 (5)	−1073 (4)	52 (5)
C(114)	3681 (7)	3408 (5)	−1443 (4)	56 (5)
C(115)	4261 (6)	3770 (4)	−999 (4)	48 (4)
C(116)	3682 (6)	3800 (4)	−168 (4)	42 (4)
C(121)	216 (5)	3538 (4)	1350 (3)	30 (3)
C(122)	−474 (5)	4360 (4)	1126 (4)	41 (4)
C(123)	−1677 (6)	4259 (5)	1159 (4)	50 (5)
C(124)	−2146 (6)	3374 (5)	1394 (4)	49 (5)
C(125)	−1444 (6)	2554 (5)	1604 (4)	49 (5)
C(126)	−267 (6)	2628 (4)	1605 (4)	42 (4)
P(2)	1329 (1)	3609 (1)	3416 (1)	29·6 (8)
C(2)	643 (7)	2900 (5)	4452 (4)	38 (4)
C(211)	1937 (5)	4589 (4)	3656 (3)	34 (3)
C(212)	1709 (6)	4713 (4)	4466 (4)	44 (4)
C(213)	2180 (6)	5478 (5)	4617 (4)	52 (5)
C(214)	2874 (6)	6122 (4)	3964 (4)	49 (4)
C(215)	3082 (6)	6011 (4)	3160 (4)	49 (4)
C(216)	2638 (5)	5231 (4)	3008 (4)	41 (4)
C(221)	−103 (5)	4209 (4)	3259 (3)	35 (3)
C(222)	−317 (6)	5200 (4)	3113 (4)	45 (4)
C(223)	−1456 (7)	5591 (5)	3020 (4)	56 (5)
C(224)	−2327 (7)	4995 (6)	3081 (4)	59 (5)
C(225)	−2094 (6)	3995 (5)	3225 (4)	52 (5)
C(226)	−975 (5)	3615 (4)	3313 (4)	38 (4)
P(3)	3582 (1)	1417 (1)	1542 (1)	28·9 (8)
C(3)	2531 (6)	972 (4)	1145 (4)	39 (4)
C(311)	4862 (5)	1708 (4)	608 (3)	33 (3)
C(312)	4983 (6)	1412 (4)	−128 (4)	44 (4)
C(313)	5989 (7)	1640 (5)	−815 (4)	55 (5)
C(314)	6878 (7)	2166 (5)	−770 (4)	56 (5)
C(315)	6771 (6)	2462 (5)	−47 (4)	56 (5)
C(316)	5746 (6)	2230 (4)	645 (4)	43 (4)
C(321)	4125 (6)	220 (4)	2020 (4)	36 (4)
C(322)	5323 (6)	−131 (4)	1773 (4)	48 (5)
C(323)	5659 (7)	−1060 (5)	2180 (5)	58 (5)
C(324)	4792 (8)	−1602 (5)	2788 (5)	60 (6)
C(325)	3563 (7)	−1266 (4)	3037 (4)	53 (5)
C(326)	3267 (6)	−335 (4)	2643 (4)	42 (4)
P(4)	3714 (1)	1841 (1)	3437 (1)	28·4 (8)
C(4)	5322 (6)	1629 (5)	2956 (4)	39 (4)
C(411)	3302 (5)	675 (4)	4130 (3)	32 (3)
C(412)	4163 (6)	−44 (4)	4321 (4)	44 (4)
C(413)	3794 (7)	−911 (5)	4871 (4)	53 (5)
C(414)	2584 (7)	−1050 (5)	5223 (4)	58 (5)
C(415)	1719 (7)	−353 (5)	5040 (4)	56 (5)
C(416)	2078 (6)	508 (4)	4482 (4)	42 (4)
C(421)	3852 (5)	2504 (4)	4198 (4)	34 (4)
C(422)	4517 (6)	3343 (4)	3883 (4)	45 (4)
C(423)	4678 (7)	3838 (5)	4444 (5)	59 (5)
C(424)	4175 (7)	3519 (6)	5296 (5)	59 (5)
C(425)	3522 (6)	2724 (5)	5593 (4)	55 (5)
C(426)	3350 (6)	2205 (5)	5053 (4)	43 (4)
C(11)	−1306 (16)	−1619 (12)	2489 (9)	155 (5)
C(12)	−193 (24)	−1967 (16)	2348 (14)	241 (9)
C(13)	304 (26)	−1952 (22)	2926 (20)	321 (14)
C(14)	−148 (19)	−1193 (17)	3315 (13)	221 (8)
C(15)	−685 (25)	−546 (19)	2747 (16)	271 (11)
C(16)	−1642 (30)	−801 (27)	2724 (20)	358 (17)
C(21)	−51 (29)	731 (16)	251 (15)	241 (9)
C(22)	932 (28)	571 (23)	−281 (17)	272 (11)
C(23)	1053 (22)	−290 (21)	−225 (13)	236 (9)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j U_{ij}$.

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and bond angles in the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39984 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A striking feature in the title compound is the symmetrical (approximately D_{2d}) way in which the phenyl rings are arranged in four pairs of parallel rings: (11)–(31), (12)–(22), (21)–(42) and (32)–(41), with angles between pairs of planes of 8·4 (5), 8·9 (5), 1·6 (5) and 11·1 (5)°, respectively. The average perpendicular inter-ring separations are 3·1–3·6 Å with individual C···C contacts as short as 3·26 (1) Å [C(326)···C(411)]. These separations are typical for such energetically favourable interactions and similar interactions have been observed in $Mo(CO)_4(PMePh_2)_2$* (Cotton *et al.*, 1982*a*), the $Au(PPh_3)_3^+$ cation (Tolman, 1977), $Pt(PCy_2Ph)_2(CF_3C{\equiv}CCF_3)$ (Cy = cyclohexyl) (Farrar & Payne, 1981) and other complexes (Al-Karaghouli, Day & Wood, 1978; Ball & Payne, 1976). This efficient packing arrangement of the bulky ligands may explain the deviations of the P positions from octahedral geometry. The ±0·224 (1) Å distortion of the P atoms from the MoP_4 plane results in PMoN angles of 84–96° {*cf.* also the structure of $[Ir(PMePh_2)_4]BF_4.C_6H_{12}$ (Clark, Skelton & Waters, 1975)}. The P atoms deviate from the planes of the attached phenyl rings by 0·016 (2)–0·066 (1) Å.

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

Mo–N(11)	2·000 (5)	P(2)–C(2)	1·836 (6)
–N(21)	1·989 (5)	–C(211)	1·841 (7)
–P(1)	2·498 (2)	–C(221)	1·862 (6)
–P(2)	2·494 (1)	P(3)–C(3)	1·837 (9)
–P(3)	2·499 (2)	–C(3111)	1·838 (5)
–P(4)	2·492 (2)	–C(321)	1·855 (5)
N(11)–N(12)	1·133 (7)	P(4)–C(4)	1·827 (6)
N(21)–N(22)	1·154 (7)	–C(411)	1·842 (5)
P(1)–C(1)	1·832 (6)	–C(421)	1·859 (7)
–C(111)	1·856 (5)		
–C(121)	1·846 (6)		

N(11)–Mo–N(21)	179·2 (2)	C(1)–P(1)–C(111)	96·5 (3)
–P(1)	84·7 (1)	–C(121)	102·1 (2)
–P(2)	94·7 (1)	C(111)–P(1)–C(121)	99·2 (3)
–P(3)	95·9 (1)	Mo–P(2)–C(2)	113·3 (2)
–P(4)	85·3 (1)	–C(211)	121·5 (2)
N(21)–Mo–P(1)	94·9 (2)	–C(221)	119·3 (2)
–P(2)	84·6 (1)	C(2)–P(2)–C(211)	102·0 (3)
–P(3)	84·8 (1)	–C(221)	95·8 (3)
–P(4)	95·2 (1)	C(211)–P(2)–C(221)	100·6 (3)
P(1)–Mo–P(2)	90·7 (1)	Mo–P(3)–C(3)	112·9 (2)
–P(3)	90·2 (1)	–C(311)	121·6 (2)
–P(4)	170·0 (1)	–C(321)	119·5 (2)
P(2)–Mo–P(3)	169·4 (1)	C(3)–P(3)–C(311)	102·3 (3)
–P(4)	90·3 (1)	–C(321)	96·1 (3)
P(3)–Mo–P(4)	90·6 (1)	C(311)–P(3)–C(321)	100·3 (2)
Mo–N(11)–N(12)	178·8 (4)	Mo–P(4)–C(4)	113·4 (2)
Mo–N(21)–N(22)	178·8 (4)	–C(411)	121·1 (2)
Mo–P(1)–C(1)	113·1 (3)	–C(421)	120·0 (2)
–C(111)	120·5 (2)	C(4)–P(4)–C(411)	102·3 (3)
–C(121)	121·2 (2)	–C(421)	96·6 (3)
		C(411)–P(4)–C(421)	99·4 (3)

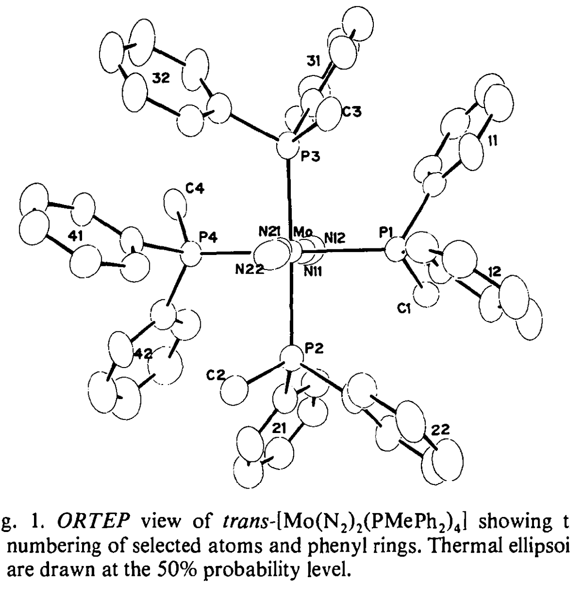

Fig. 1. *ORTEP* view of *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ showing the numbering of selected atoms and phenyl rings. Thermal ellipsoids are drawn at the 50% probability level.

One of the solvent molecules in the lattice sits about the centre of symmetry at the origin while the other is on a general position. Both molecules are only weakly held in the lattice and have large thermal parameters.

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* The attractive Ph···Ph contacts may help explain the discrepancy in the PMoP bond angle in this compound when compared to those in $Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_4(PMe_2Ph)_2$ (Cotton *et al.*, 1982*a*).

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