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***trans*-Bis(dinitrogen)-bis-[1,2-bis(diphenylphosphino)ethane]molybdenum(0)**

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Abstract. Mo(N₂)₂[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]₂, triclinic, $P\bar{1}$, $a = 10.662$ (3), $b = 12.654$ (3), $c = 10.527$ (3) Å, $\alpha = 92.48$ (1), $\beta = 118.89$ (2), $\gamma = 71.20$ (1)°, $D_m = 1.31$ g cm⁻³ (by flotation), $D_x = 1.35$ g cm⁻³, $Z = 1$. The final $R = 0.047$. The molybdenum atom, octahedrally coordinated to four phosphorus atoms and two dinitrogens, occupies the centre of symmetry. Mo–N, N–N and two Mo–P bond lengths are 2.014 (5), 1.118 (8), 2.445 (1) and 2.462 (1) Å, respectively. The Mo–N–N bond angle is 176.6 (5)°.

Introduction. Since the discovery of the first dinitrogen complex of a transition metal (Allen & Senoff, 1965), many such complexes have been prepared and their properties extensively studied in relation to both chemical and biological interest. Among them, the title complex (Hidai, Tominari, Uchida & Misono, 1969; Hidai, Tominari & Uchida, 1972) is receiving special

attention because of the key role of molybdenum in biological nitrogen fixation. This paper gives the refined structure of the title complex initially reported by Uchida, Uchida, Hidai & Kodama (1971).

An orange prismatic crystal of dimensions 0.4 × 0.3 × 0.6 mm, crystallized from toluene/n-hexane solution, was sealed in a Pyrex capillary in an atmosphere of nitrogen and was mounted along [101] on a Rigaku automated diffractometer (LiF-monochromatized Mo K α , $\lambda = 0.7107$ Å; 2θ - ω scan, up to $2\theta = 55^\circ$). Lorentz and polarization corrections were applied, but no absorption correction was made ($\mu = 4.56$ cm⁻¹). Of 5464 reflexions, 3253 ($F_o > 3\sigma F$) were regarded as 'observed' and were used in the analysis.

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations to $R = 0.069$ with anisotropic temperature parameters for the non-hydrogen atoms. At this stage, the

Table 1(a). The positional ($\times 10^4$) and thermal parameters ($\times 10^5$) with their standard deviationsThe anisotropic temperature factor is of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0 (0)	0 (0)	0 (0)	588 (9)	378 (4)	748 (7)	-282 (8)	671 (11)	-34 (8)
P(1)	-1903 (1)	1516 (1)	319 (1)	753 (16)	408 (9)	868 (15)	-353 (19)	955 (25)	-157 (17)
P(2)	-1133 (1)	-1102 (1)	735 (1)	789 (17)	408 (10)	941 (16)	-379 (19)	970 (26)	-52 (18)
N(1)	1394 (5)	-58 (4)	2164 (5)	757 (57)	555 (35)	937 (54)	-181 (68)	780 (88)	-4 (65)
N(2)	2106 (6)	-79 (5)	3373 (6)	1352 (81)	973 (53)	1180 (37)	-554 (103)	873 (120)	-84 (93)
C(1)	-2124 (6)	917 (4)	1750 (5)	879 (68)	544 (64)	860 (61)	-326 (80)	1027 (103)	-152 (73)
C(2)	-2463 (6)	-166 (4)	1337 (6)	1028 (76)	461 (40)	1128 (70)	-294 (83)	1292 (117)	21 (78)
C(11)	-1651 (5)	2827 (4)	1082 (5)	811 (67)	459 (38)	876 (60)	-402 (77)	941 (100)	-136 (70)
C(12)	-2826 (6)	3722 (5)	1041 (7)	1081 (81)	428 (41)	1407 (81)	-384 (87)	1054 (128)	-304 (86)
C(13)	-2576 (8)	4663 (5)	1695 (7)	1536 (100)	405 (44)	1610 (95)	-151 (98)	1338 (157)	-282 (96)
C(14)	-1106 (7)	4714 (5)	2387 (7)	1468 (95)	445 (44)	1419 (85)	-455 (98)	1255 (144)	-302 (92)
C(15)	78 (7)	3830 (5)	2447 (6)	1345 (91)	682 (50)	1223 (78)	-977 (106)	1256 (136)	-247 (94)
C(16)	-186 (6)	2885 (5)	1789 (6)	1125 (82)	625 (46)	1254 (77)	-721 (96)	1386 (129)	-324 (90)
C(21)	-3876 (5)	2028 (4)	-1228 (5)	721 (63)	339 (35)	1040 (64)	-318 (70)	928 (101)	-144 (69)
C(22)	-5150 (6)	2115 (4)	-1104 (6)	893 (70)	389 (38)	1105 (68)	-240 (77)	1028 (111)	-11 (75)
C(23)	-6602 (6)	2445 (5)	-2337 (6)	831 (72)	527 (43)	1364 (79)	-321 (85)	1070 (120)	-165 (88)
C(24)	-6800 (7)	2723 (6)	-3677 (7)	914 (78)	836 (54)	1192 (79)	-224 (100)	867 (124)	-138 (99)
C(25)	-5563 (7)	2682 (7)	-3805 (6)	1150 (91)	1289 (73)	879 (74)	-275 (126)	836 (129)	64 (112)
C(26)	-4098 (6)	2338 (5)	-2593 (6)	1039 (80)	734 (50)	1108 (74)	-368 (97)	1158 (123)	33 (91)
C(31)	195 (6)	-2215 (4)	2334 (5)	860 (69)	521 (40)	990 (65)	-587 (81)	1078 (107)	5 (75)
C(32)	363 (7)	-2088 (5)	3694 (6)	1314 (90)	564 (46)	1122 (74)	-590 (99)	884 (129)	-271 (88)
C(33)	1402 (8)	-2936 (6)	4878 (7)	1578 (104)	874 (60)	1048 (78)	-822 (125)	559 (139)	-46 (103)
C(34)	2277 (8)	-3927 (5)	4691 (7)	1418 (98)	696 (54)	1255 (84)	-692 (113)	504 (142)	296 (100)
C(35)	2151 (8)	-4064 (5)	3337 (8)	1390 (96)	585 (49)	1670 (98)	-394 (106)	1494 (158)	242 (103)
C(36)	1107 (7)	-3212 (7)	2137 (7)	1246 (88)	598 (46)	1388 (84)	-394 (98)	1628 (141)	-8 (93)
C(41)	-2457 (6)	-1776 (4)	-588 (5)	976 (72)	522 (41)	956 (63)	-688 (84)	1163 (108)	-324 (76)
C(42)	-2329 (7)	-2903 (5)	-389 (7)	1532 (97)	655 (49)	1470 (86)	-1083 (109)	2067 (153)	-743 (100)
C(43)	-3432 (9)	-3315 (6)	-1446 (8)	2135 (132)	1036 (68)	2012 (116)	-2181 (159)	2898 (213)	-1670 (146)
C(44)	-4618 (8)	-2617 (7)	-2680 (8)	1614 (117)	1579 (93)	1857 (115)	-2384 (178)	2000 (193)	-1858 (170)
C(45)	-4764 (8)	-1512 (8)	-2903 (7)	1053 (91)	1690 (92)	1231 (87)	-1258 (147)	1221 (142)	-785 (140)
C(46)	-3683 (7)	-1082 (6)	-1861 (7)	988 (81)	900 (57)	1204 (78)	-776 (106)	1038 (125)	-257 (101)

positions of hydrogen atoms were calculated assuming a C-H bond distance of 1.08 Å, since a difference synthesis revealed none of the hydrogen positions. The final R was 0.047 including hydrogen atoms with a constant isotropic temperature parameter. The quantity minimized was $w(|F_o| - k|F_c|)^2$ and the weighting scheme was $w = 1.0$ for $F_o < 80$, and $w = (80/|F_o|)^2$ for $F_o \geq 80$, where the scale of F_o is about five times absolute scale. In the final cycle, the average parameter shifts were less than the corresponding standard deviations. The atomic scattering factors and anomalous dispersion factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic parameters, with their estimated standard deviations, are given in Table 1. Tables 2 and 3 give the bond distances and angles respectively. Fig. 1 shows the numbering of the atoms.*

Table 1(b). The atomic parameters of the hydrogen atoms ($\times 10^3$)

Isotropic thermal parameter $B = 4.5 \text{ \AA}^2$.			
	x/a	y/b	z/c
H(1a)	-302 (8)	144 (6)	179 (7)
H(1b)	-112 (9)	76 (7)	278 (8)
H(2a)	-236 (8)	-56 (6)	221 (7)
H(2b)	-352 (8)	1 (6)	47 (8)
H(12)	-393 (8)	372 (6)	49 (8)
H(13)	-342 (9)	530 (7)	173 (9)
H(14)	-93 (8)	541 (6)	287 (7)
H(15)	123 (10)	382 (7)	299 (9)
H(16)	69 (7)	223 (6)	180 (7)
H(22)	-500 (8)	191 (6)	-4 (8)
H(23)	-752 (8)	248 (6)	-224 (7)
H(24)	-792 (9)	295 (7)	-459 (8)
H(25)	-573 (9)	287 (6)	-481 (8)
H(26)	-317 (9)	229 (7)	-269 (9)
H(32)	-21 (8)	-140 (6)	385 (8)
H(33)	156 (9)	-283 (7)	588 (8)
H(34)	299 (10)	-452 (8)	554 (9)
H(35)	280 (9)	-479 (6)	313 (8)
H(36)	105 (7)	-330 (5)	111 (7)
H(42)	-143 (8)	-346 (6)	54 (7)
H(43)	-327 (9)	-414 (7)	-127 (9)
H(44)	-538 (9)	-293 (7)	-343 (8)
H(45)	-568 (9)	-95 (7)	-382 (9)
H(46)	-375 (9)	-26 (7)	-202 (8)

Discussion. The complex is centrosymmetric and the molybdenum atom at the centre of symmetry is coordinated to four phosphorus and two nitrogen atoms in a typical d_6 configuration. The central molybdenum and the four phosphorus atoms lie on the same plane, and two dinitrogens are *trans* to each other (Fig. 2). The observed distances of two Mo-P and Mo-N are 2.445, 2.462 and 2.014 Å, respectively, which are all normal values (Pauling, 1960). The N-N distance of 1.118 Å is a little longer than that in the free nitrogen molecule

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30810 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. The bond distances (Å)

Mo—P(1)	2.445 (1)	Mo—P(2)	2.462 (1)
Mo—N(1)	2.014 (5)	N(1)—N(2)	1.118 (8)
P(1)—C(1)	1.857 (6)	P(2)—C(2)	1.877 (7)
P(1)—C(11)	1.851 (6)	P(2)—C(31)	1.850 (6)
P(1)—C(21)	1.840 (6)	P(2)—C(41)	1.849 (6)
C(1)—C(2)	1.518 (9)		
C(11)—C(12)	1.372 (9)	C(31)—C(32)	1.361 (9)
C(12)—C(13)	1.382 (11)	C(32)—C(33)	1.392 (11)
C(13)—C(14)	1.393 (11)	C(33)—C(34)	1.370 (12)
C(14)—C(15)	1.364 (11)	C(34)—C(35)	1.372 (11)
C(15)—C(16)	1.393 (10)	C(35)—C(36)	1.405 (11)
C(16)—C(11)	1.392 (9)	C(36)—C(31)	1.398 (9)
C(21)—C(22)	1.393 (8)	C(41)—C(42)	1.400 (10)
C(22)—C(23)	1.391 (9)	C(42)—C(43)	1.397 (12)
C(23)—C(24)	1.364 (10)	C(43)—C(44)	1.363 (13)
C(24)—C(25)	1.371 (11)	C(44)—C(45)	1.372 (13)
C(25)—C(26)	1.391 (11)	C(45)—C(46)	1.397 (12)
C(26)—C(21)	1.388 (9)	C(46)—C(41)	1.392 (9)
Mo...N(2)	3.131 (7)	P(1)...P(2)	3.135 (2)
P(1)...P(2)	3.776 (2)		

(1.098 Å; Wilkinson & Houk, 1956). Elongation of the N-N distance is explained by back donation of electrons from the metal non-bonding d orbitals into the anti-bonding $1\pi_g^*$ -orbital of dinitrogen (Chatt & Richards, 1971). The N-N bond elongations are also observed in other dinitrogen complexes (Bottomley & Nyburg, 1968; Davis & Ibers, 1970; Davis, Payne & Ibers, 1969; Ferguson, Lover & Robinson, 1972; Treitel, Flood, Marsh & Gray, 1969). The P-C bond distances, average 1.847 Å, are a little longer than those of the uncomplexed triphenylphosphine molecule (1.828 Å; Daly, 1964).

The bond angle of P(1)-Mo-P(2) is 79.4° ; such a deviation from the octahedral angle is not uncommon in complexes with bidentate ligands (Davis & Ibers, 1970; Hall, Kilbourn & Taylor, 1970; Snyder & Weaver, 1970). The observed angle which the Mo-N bond makes with the plane containing the molybdenum atom and four phosphorus atoms, 84.5° , is significantly smaller than the octahedral value. The Mo-N(1)-N(2)

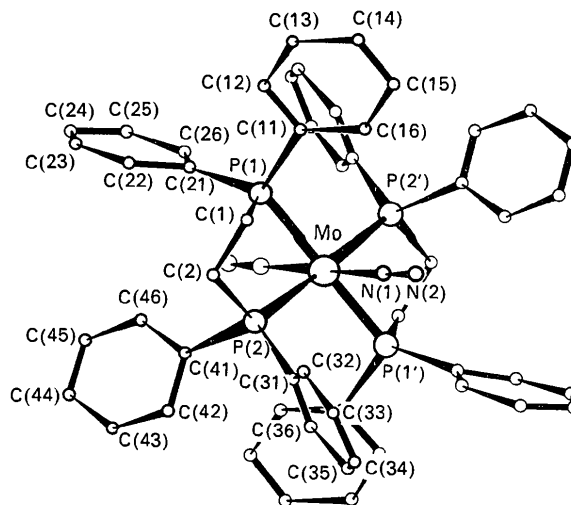


Fig. 1. A drawing of the molecule viewed along the c axis and atomic numbering.

Table 3. *The bond angles*(°)

P(1)—Mo—P(2)	79.40 (15)	P(1')—Mo—N(1)	94.48 (15)
P(1)—Mo—N(1)	85.57 (15)	P(2')—Mo—N(1)	93.94 (15)
P(2)—Mo—N(1)	86.03 (15)		
Mo—N(1)—N(2)	176.58 (53)		
Mo—P(1)—C(1)	106.39 (20)	Mo—P(2)—C(2)	110.52 (21)
Mo—P(1)—C(11)	125.60 (19)	Mo—P(2)—C(31)	116.91 (20)
Mo—P(1)—C(21)	117.85 (19)	Mo—P(2)—C(41)	122.30 (20)
P(1)—C(1)—C(2)	109.6 (4)	P(2)—C(2)—C(1)	111.1 (4)
C(1)—P(1)—C(11)	98.1 (3)	C(2)—P(2)—C(31)	102.6 (3)
C(1)—P(1)—C(21)	102.3 (3)	C(2)—P(2)—C(41)	97.7 (3)
C(11)—P(1)—C(21)	102.6 (3)	C(31)—P(2)—C(41)	103.7 (3)
P(1)—C(11)—C(12)	123.1 (5)	P(2)—C(31)—C(32)	123.0 (5)
P(1)—C(11)—C(16)	118.2 (5)	P(2)—C(31)—C(36)	117.9 (5)
C(11)—C(12)—C(13)	121.4 (7)	C(31)—C(32)—C(33)	121.3 (7)
C(12)—C(13)—C(14)	119.4 (7)	C(32)—C(33)—C(34)	120.3 (8)
C(13)—C(14)—C(15)	120.0 (7)	C(33)—C(34)—C(35)	119.4 (8)
C(14)—C(15)—C(16)	120.1 (7)	C(34)—C(35)—C(36)	120.7 (7)
C(15)—C(16)—C(11)	120.4 (6)	C(35)—C(36)—C(31)	119.3 (7)
C(16)—C(11)—C(12)	118.6 (6)	C(36)—C(31)—C(32)	119.0 (6)
P(1)—C(21)—C(22)	123.6 (4)	P(2)—C(41)—C(42)	125.2 (5)
P(1)—C(21)—C(26)	117.8 (5)	P(2)—C(41)—C(46)	116.0 (5)
C(21)—C(22)—C(23)	120.6 (6)	C(41)—C(42)—C(43)	120.3 (7)
C(22)—C(23)—C(24)	120.2 (6)	C(42)—C(43)—C(44)	119.8 (9)
C(23)—C(24)—C(25)	119.8 (7)	C(43)—C(44)—C(45)	120.9 (9)
C(24)—C(25)—C(26)	121.0 (7)	C(44)—C(45)—C(46)	120.3 (9)
C(25)—C(26)—C(21)	119.8 (7)	C(45)—C(46)—C(41)	119.9 (7)
C(26)—C(21)—C(22)	118.5 (6)	C(46)—C(41)—C(42)	118.8 (6)

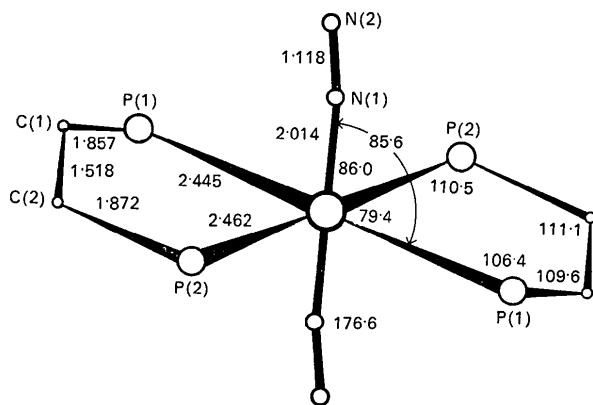


Fig. 2. A perspective drawing of the inner coordination around the molybdenum atom with the bond distances (Å) and bond angles (°).

bond angle, 176.6°, is deviated a little from linearity. Since the Mo—N bond is rather weak and bis(diphenylphosphino)ethane is a fairly bulky ligand, the distortion of the dinitrogen is probably caused by the closed packing effect. The bond-angle enlargements from the tetrahedral value, which are observed about the phosphorus atoms, are due to perturbation of the Mo—P bond. Such enlargements of C—P—C angles are ordinarily found in complexes possessing a phosphorus atom directly coordinated to metal (Debaerdemaeker, Kutoglu, Schmid & Weber, 1973).

The atoms of each phenyl ring are coplanar within 0.01 Å, and the angles between the P—C(phenyl) bonds and the phenyl ring are 1–3°.

All the computations were carried out at the Computer Centre of the University of Tokyo, with the UNICS (1967) program system.

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