

The atoms N(1), N(2) and C(1)–C(10), defining the bipyridine ligand, are planar within  $\pm 0.08$  Å, and the Rh atom lies 0.2 Å from the mean plane. The other bipyridine ligand, defined by the N(3), N(4) and C(11)–C(20) atoms, is planar within  $\pm 0.02$  Å, the Rh atom being 0.2 Å from this plane. The mean planes make a dihedral angle of 79.0 (1)°.

Both the bipyridine-ligand rigidity and the Rh—N equilibrium distance result in the angles Rh—N(1)—C(5), Rh—N(2)—C(6), Rh—N(3)—C(15) and Rh—N(4)—C(16) being smaller than Rh—N(1)—C(1), Rh—N(2)—C(10), Rh—N(3)—C(11) and Rh—N(4)—C(20), as well as in the N—Rh—N angles differing from the theoretical value of 90°.

For the bipyridine ligands, the C—C bond distances range from 1.352 (11) to 1.494 (9) Å, averaging 1.389 (9) Å. The N—C bond distances range from 1.330 (8) to 1.361 (8) Å, averaging 1.347 (8) Å.

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## Structures of [1,3-Bis(diphenylphosphino)propane]tetracarbonylmolybdenum(0) (1) and [1,4-Bis(diphenylphosphino)butane]tetracarbonylmolybdenum(0) (2)

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**Abstract.** (1) C<sub>31</sub>H<sub>26</sub>MoO<sub>4</sub>P<sub>2</sub>, [Mo{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>3</sub>-H<sub>6</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}(CO)<sub>4</sub>], *M<sub>r</sub>* = 620.4, orthorhombic, *Pnma*, *a* = 16.854 (4), *b* = 21.970 (4), *c* = 7.723 (2) Å, *V* = 2860 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.47 (3), *D<sub>x</sub>* = 1.48 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.7093 Å, μ = 0.59 mm<sup>-1</sup>, *F*(000) = 1264, *T* = 298 K, final *R* = 0.033 for 1871 observed reflections. (2) C<sub>32</sub>H<sub>28</sub>MoO<sub>4</sub>P<sub>2</sub>, [Mo{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>4</sub>H<sub>8</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}(CO)<sub>4</sub>], *M<sub>r</sub>* = 634.3, monoclinic, *P2<sub>1</sub>/n*, *a* =

12.072 (2), *b* = 15.379 (5), *c* = 16.607 (5) Å, β = 104.65 (2)°, *V* = 2983 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.36 (3), *D<sub>x</sub>* = 1.35 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.7093 Å, μ = 0.57 mm<sup>-1</sup>, *F*(000) = 1296, *T* = 298 K, final *R* = 0.032 for 3888 observed reflections. The molecular structures of both compounds are similar, but the numbers of the ring members are six in (1) and seven in (2). In the order of compound (1), (2), the following changes occur: P—Mo—P = 89.74 (4), 91.65 (4)°; *cis* C—Mo—C = 88.7 (2), 86.1 (2)°; *trans* C—Mo—C = 174.8 (3), 176.8 (2)°. The increase in

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P—Mo—P and the decrease in *cis* C—Mo—C angle are attributed to the ring effect. The variety of the *trans* C—Mo—C angle is probably due to the rotational orientations of the phenyl groups of the bidentate ligands.

**Introduction.** Crystal structures of [bis(diphenylphosphino)methane]tetracarbonylmolybdenum(0) (Cheung, Lai & Mok, 1971), [1,2-bis(diphenylphosphino)ethane]tetracarbonylmolybdenum(0) (Bernal, Reiser, Dobson & Dobson, 1986), *cis*-bis[1,3-bis(diphenylphosphino)propane]tetracarbonylmolybdenum(0) (Chow, Wang, Sheu & Peng, 1986) have been published. In order to understand the ring effect on the structure of bidentate phosphine derivatives of molybdenum(0) carbonyl, the structure determination of the title compounds was undertaken.

**Experimental.** (1) Crystal 0.20 × 0.20 × 0.20 mm, CAD-4 diffractometer,  $\theta/2\theta$  scan, unit cell: 24 reflections,  $2\theta$  range 15.90 to 22.48°,  $D_m$  by flotation ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{Cl}$ ),  $2\theta_{\text{max}} = 49.8^\circ$ , ranges of *hkl*: 0 to 20, 0 to 26, 0 to 9, respectively. Three standard reflections monitored every 2 h: variation on  $I < 3\%$ , 2574 unique reflections,  $R_{\text{int}} = 0.020$ , 1871 observed with  $I \geq 2.0\sigma(I)$ , quantity minimized  $w(KF_o - F_c)^2$ ,  $R(F) = 0.033$ ,  $wR = 0.028$ ,  $S = 1.92$ , weighting scheme from counting statistics. Structure solved by heavy-atom method, H atoms of phenyl groups calculated after isotropic refinement, the others found in difference Fourier map,  $(\Delta/\sigma)_{\text{max}} = 0.102$ , Peaks in final  $\Delta F$  map 0.630 to  $-0.350 \text{ e } \text{\AA}^{-3}$ , secondary-extinction coefficient 0.76 (4) (length in  $\mu\text{m}$ ). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computing programs: *NRCC SDP VAX* package (Gabe & Lee, 1981). *ORTEP* from Enraf-Nonius (1979) *Structure Determination Package*. (2) Crystal 0.20 × 0.25 × 0.20 mm, CAD-4 diffractometer, unit cell: 24 reflections,  $2\theta$  range 18.58 to 29.06°,  $D_m$  by flotation ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{Cl}$ ),  $2\theta_{\text{max}} = 49.8^\circ$ , ranges of *hkl*: -14 to 13, 0 to 18, 0 to 19, respectively. Three standard reflections monitored every 2 h: variation on  $I < 3\%$ , 5237 unique reflections,  $R_{\text{int}} = 0.010$ , 3888 observed with  $I \geq 2.0\sigma(I)$ ,  $R(F) = 0.032$ ,  $wR = 0.031$ ,  $S = 2.23$ , weighting scheme from counting statistics. Structure solved by heavy-atom method. H atoms of phenyl groups calculated after isotropic refinement, the others found in difference Fourier map,  $(\Delta/\sigma)_{\text{max}} = 0.066$ . Peaks in final  $\Delta F$  map 0.290 to  $-0.630 \text{ e } \text{\AA}^{-3}$ , secondary-extinction coefficient 2.26 (4) (length in  $\mu\text{m}$ ). Other details as for (1).

**Discussion.** Atomic positional parameters and equivalent isotropic temperature factors are listed in

Table 1. *Atomic positional and isotropic thermal parameters of (1) and (2)*

$$B_{\text{iso}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{iso}}$ ( $\text{\AA}^2$ )
(1)				
Mo	0.31988 (3)	$\frac{1}{2}$	0.24258 (7)	2.47 (2)
P	0.41248 (6)	0.83149 (5)	0.3580 (1)	2.5 (0)
C1	0.2464 (4)	$\frac{1}{2}$	0.4516 (9)	3.8 (3)
C2	0.3839 (4)	$\frac{1}{2}$	0.0211 (9)	4.0 (3)
C3	0.2525 (3)	0.6874 (2)	0.1352 (6)	3.7 (2)
C4	0.4864 (2)	0.8085 (2)	0.5193 (5)	2.8 (2)
C5	0.5319 (3)	$\frac{1}{2}$	0.4823 (8)	3.0 (3)
C11A	0.3695 (2)	0.8973 (2)	0.4702 (5)	2.9 (2)
C12A	0.3122 (3)	0.8868 (2)	0.5955 (6)	4.3 (2)
C13A	0.2800 (3)	0.9343 (2)	0.6890 (6)	5.1 (3)
C14A	0.3036 (3)	0.9932 (2)	0.6560 (7)	5.1 (3)
C15A	0.3604 (3)	1.0039 (2)	0.5358 (6)	5.1 (3)
C16A	0.3935 (3)	0.9563 (2)	0.4440 (6)	3.9 (2)
C11B	0.4703 (2)	0.8676 (2)	0.1849 (5)	2.7 (2)
C12B	0.5522 (3)	0.8656 (2)	0.1812 (6)	4.1 (2)
C13B	0.5933 (3)	0.8911 (2)	0.0443 (7)	5.3 (3)
C14B	0.5537 (3)	0.9193 (2)	-0.0860 (7)	5.0 (3)
C15B	0.4731 (3)	0.9222 (2)	-0.0836 (6)	4.4 (2)
C16B	0.4313 (3)	0.8959 (2)	0.5002 (6)	3.6 (2)
O1	0.2001 (3)	$\frac{1}{2}$	0.5606 (7)	6.7 (3)
O2	0.4145 (4)	$\frac{1}{2}$	-0.1087 (7)	8.7 (4)
O3	0.2132 (2)	0.6518 (1)	0.0649 (5)	6.1 (2)
(2)				
Mo	0.42304 (3)	0.73204 (2)	0.12568 (2)	2.55 (2)
P1	0.56209 (9)	0.72690 (7)	0.03294 (6)	2.66 (5)
P2	0.2788 (1)	0.81592 (7)	0.01784 (6)	2.75 (5)
C1	0.5075 (4)	0.8409 (3)	0.1719 (2)	3.7 (2)
C2	0.3347 (4)	0.6206 (3)	0.0849 (3)	3.5 (2)
C3	0.5297 (4)	0.6610 (3)	0.2101 (3)	3.4 (2)
C4	0.3278 (4)	0.7387 (3)	0.2068 (2)	3.8 (2)
C5	0.6102 (4)	0.8331 (2)	0.0016 (2)	3.1 (2)
C6	0.5339 (4)	0.8796 (2)	-0.0718 (2)	3.2 (2)
C7	0.4173 (4)	0.9111 (2)	-0.0628 (3)	3.5 (2)
C8	0.3217 (3)	0.8426 (2)	-0.0773 (2)	2.9 (2)
O1	0.5584 (3)	0.9015 (2)	0.1994 (2)	6.1 (2)
O2	0.2834 (3)	0.5583 (2)	0.0670 (2)	5.8 (2)
O3	0.5889 (3)	0.6199 (2)	0.2615 (2)	5.0 (2)
O4	0.2745 (3)	0.7388 (2)	0.2546 (2)	6.2 (2)
C11A	0.5370 (4)	0.6665 (2)	-0.0652 (2)	2.8 (2)
C12A	0.4377 (4)	0.6198 (3)	-0.0946 (3)	3.8 (2)
C13A	0.4175 (4)	0.5763 (3)	-0.1704 (3)	4.8 (3)
C14A	0.4975 (5)	0.5796 (3)	-0.2162 (3)	4.9 (3)
C15A	0.5954 (4)	0.6251 (3)	-0.1875 (3)	4.4 (3)
C16A	0.6165 (4)	0.6691 (3)	-0.1126 (3)	3.7 (2)
C11B	0.6987 (3)	0.6814 (2)	0.0937 (2)	2.8 (2)
C12B	0.7700 (4)	0.7306 (3)	0.1555 (2)	3.7 (2)
C13B	0.8677 (4)	0.6948 (3)	0.2062 (3)	4.5 (3)
C14B	0.8938 (4)	0.6096 (3)	0.1958 (3)	4.8 (3)
C15B	0.8248 (4)	0.5604 (3)	0.1352 (3)	4.8 (3)
C16B	0.7265 (4)	0.5963 (3)	0.0840 (3)	3.7 (2)
C21A	0.2266 (4)	0.9216 (2)	0.0458 (3)	3.2 (2)
C22A	0.2488 (4)	0.9474 (3)	0.1283 (3)	4.3 (2)
C23A	0.2071 (5)	1.0265 (3)	0.1484 (3)	5.3 (3)
C24A	0.1453 (4)	1.0795 (3)	0.0865 (4)	5.1 (3)
C25A	0.1242 (4)	1.0545 (3)	0.0055 (3)	4.8 (3)
C26A	0.1631 (4)	0.9761 (3)	-0.0158 (3)	4.1 (2)
C21B	0.1451 (3)	0.7557 (2)	-0.0175 (2)	2.8 (2)
C22B	0.0728 (4)	0.7502 (3)	0.0346 (3)	4.0 (2)
C23B	-0.0232 (4)	0.6985 (3)	0.0149 (3)	4.8 (3)
C24B	-0.0495 (4)	0.6515 (3)	-0.0580 (3)	4.6 (2)
C25B	0.0206 (4)	0.6566 (3)	-0.1104 (3)	4.3 (2)
C26B	0.1171 (4)	0.7092 (3)	-0.0911 (2)	3.6 (2)

Table 1.\* The selected bond lengths and angles are shown in Table 2.

\* Lists of structure factors, anisotropic thermal parameters, packing diagrams, full bond lengths and angles, dihedral angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53437 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°) of some bidentate phosphine derivatives of molybdenum carbonyl

Compound*	Mo—P (Å)		P—Mo—P (°)	<i>cis</i> C—Mo—C (°)		<i>trans</i> C—Mo—C (°)	
	(1)	(2)		(1)	(2)	(1)	(2)
(1)	2.538 (1)	1.968 (5)	89.74 (4)	88.7 (2)	174.8 (3)		
	2.538 (1)	1.968 (5)					
(2)	2.550 (1)	1.976 (4)	91.65 (4)	86.1 (2)	176.8 (2)		
	2.515 (1)	1.983 (4)					
		2.009 (4)					
		2.041 (4)					
		2.023 (7)					
(3)	2.535 (3)	1.94 (1)	67.3 (1)	94.0 (4)	167.9 (5)		
	2.501 (2)	1.92 (1)					
		2.02 (2)					
		2.07 (1)					
(4)	2.500 (2)	1.999 (8)	80.2 (1)	90.4 (3)	176.6 (3)		
	2.495 (2)	1.974 (8)					
		2.030 (9)					
		2.053 (9)					
		2.025 (4)					
(5)	2.468 (2)	1.913 (8)	85.55 (8)	81.3 (3)			
	2.476 (2)	1.938 (9)					
	2.564 (2)						
	2.582 (2)						

\* Compound (3) = [bis(diphenylphosphino)methane]tetracarbonylmolybdenum(0) (Cheung, Lai & Mok, 1971); compound (4) = [1,2-bis(diphenylphosphino)ethane]tetracarbonylmolybdenum(0) (Bernal, Reisner, Dobson & Dobson, 1986); compound (5) = bis[1,3-bis(diphenylphosphino)propane]dicarbonylmolybdenum(0) (Chow, Wang, Sheu & Peng, 1986).

The coordination geometries of both compounds, in Figs. 1 and 2, are the same, but not the numbering of the ring members, since each Mo atom is bonded to four carbonyl groups and a bidentate ligand having two P atoms as donors.

The coordination around the metal is a distorted octahedron for both compounds, the equatorial plane being formed by two CO groups and two P atoms. The deviations of the Mo atom from this plane are 0.087 (1) and 0.009 (2) Å for (1) and (2), respectively. Distortion is due to the formation of the chelate ring and also to the differences between the Mo—P and Mo—CO bond lengths.

There are four CO groups in both compounds. The mutually *cis* CO groups (*trans* to the bidentate phosphine ligand) have average Mo—C distances of 1.968 (5) and 1.979 (4) Å while the mutually *trans* CO ligands exhibit average bonding distances of 2.029 (7) and 2.025 (4) Å for (1) and (2) respectively. The two mutually *trans* CO groups have longer Mo—C distances than those of the other two carbonyls. This feature is expected on the basis of the directional nature of  $\pi$  bonding in substituted octahedral metal carbonyls, since phosphorus is known to be a poorer  $\pi$  acceptor than CO (Cotton & Kraihanzel, 1962; Cotton, Darensbourg, Klein & Kolthammer, 1982).

The bond angles of P—Mo—P are 89.74 (4) and 91.65 (4)° and of *cis* C—Mo—C are 88.7 (2) and 86.1 (2)° for (1) and (2) respectively. The increase in P—Mo—P and the decrease in the *cis* C—Mo—C angle for (2) are attributed to the ring effect: the seven-membered ring is more bulky than the

six membered one. It is obvious from Table 2 that the angle of P—Mo—P increases from the four-membered ring in (3) to the seven-membered ring in (2) for the four bidentate phosphine derivatives of molybdenum tetracarbonyl as the size of the ring increases [67.3 (1), 80.2 (1), 89.74 (4) and 91.65 (4)° for (3), (4), (1) and (2), respectively]. In contrast, the angle of *cis* C—Mo—C decreases for the same order [94.0 (4), 90.4 (3), 88.7 (2) and 86.1 (2)° respectively]. The average bond length of *cis* Mo—C of (5) is smaller than that of (1) [1.926 (9) vs 1.968 (5) Å]. This may be due to the smaller number of strong  $\pi$ -withdrawing carbonyl groups in (5). The smaller angles of P—Mo—P [85.55 (8), 86.76 (8) vs 89.74 (4)°], and hence *cis* C—Mo—C [81.3 (3) vs 88.7 (2)°] for (5), compared with (1) are attributed to the more bulky substituent for (5) [two bidentate phosphine ligands in (5) vs only one in (1)].

The conformation of the bidentate phosphine ligands in (1) and (2) is different. Compound (1) has exact mirror molecular symmetry at (x, 0.75, z) through Mo, C(2) and the two *trans* carbonyl groups. But (2) has a pseudo inversion centre at the

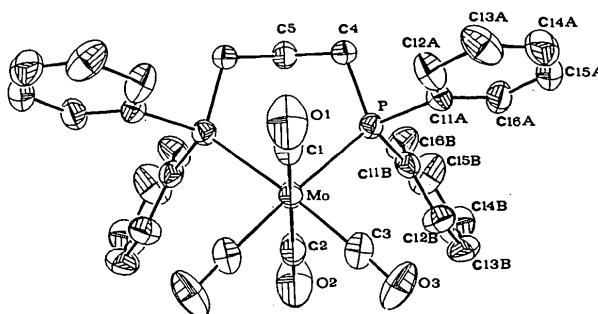


Fig. 1. Molecular structure of (1), [1,3-bis(diphenylphosphino)propane]tetracarbonylmolybdenum(0).

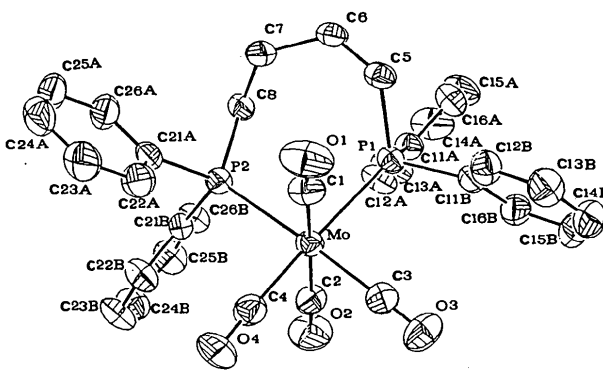


Fig. 2. Molecular structure of (2), [1,4-bis(diphenylphosphino)butane]tetracarbonylmolybdenum(0).

midpoint of the two P atoms for the two PPh<sub>2</sub> units. The smaller bond angles of *trans*-C—Mo—C for (I) [174.8 (3) vs 176.8 (2)<sup>o</sup>] may be due to the rotational orientations of the phenyl groups of the bidentate ligands.

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## Structures of (2-Cyanoethyl)(3-cyanopyridine)bis[dimethylglyoximato(1-)]cobalt(III) Monohydrate (I) and (4-Aminopyridine)(2-cyanoethyl)-bis[dimethylglyoximato(1-)]cobalt(III) (II)

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**Abstract.** (I): [Co(C<sub>3</sub>H<sub>4</sub>N)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>)]·H<sub>2</sub>O, *M<sub>r</sub>* = 465.35, monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 18.425 (4), *b* = 12.073 (3), *c* = 10.038 (2) Å, β = 101.95 (2)<sup>o</sup>, *V* = 2184.1 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.415 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 7.72 cm<sup>-1</sup>, *F*(000) = 968, *R* = 0.061 for 3244 independent reflections. (II): [Co(C<sub>3</sub>H<sub>4</sub>N)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>)], *M<sub>r</sub>* = 437.34, triclinic, *P* $\bar{1}$ , *a* = 15.347 (5), *b* = 15.673 (7), *c* = 8.890 (3) Å, α = 104.46 (3), β = 105.74 (3), γ = 82.38 (5)<sup>o</sup>, *V* = 1988 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.462 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 8.42 cm<sup>-1</sup>, *F*(000) = 912, *R* = 0.080 for 6448 independent reflections. In each crystal, the 2-cyanoethyl group takes a conformation perpendicular to the cobaloxime plane. The size of the cavity for the 2-cyanoethyl group in crystal (II) is significantly greater than that in crystal (I). This explains the greater isomerization rate of (II) compared with (I) on exposure to visible light.

**Introduction.** It has been found that the 2-cyanoethyl group bonded to a Co atom in some cobaloxime complex crystals isomerizes to the 1-cyanoethyl

group on exposure to visible light (Ohgo & Takeuchi, 1985). The isomerization rates are different among the cobaloxime complex crystals. Recently, it has been reported that the complexes with 3-ethylpyridine and 4-ethylpyridine as axial base ligands have the same conformation and that the rate of isomerization is closely related to the size of the cavity for the 2-cyanoethyl group in the two crystals (Sekine, Ohashi, Shimizu & Hori, 1991). Similar relation between the reaction rate and the cavity for the reactive group has been found for the crystalline-state racemization on exposure to X-rays (Ohashi, 1988). In order to examine whether the above relation holds good for the crystals with the other axial base ligands, two complexes with 3-cyanopyridine and 4-aminopyridine as axial ligands were prepared. The analyzed structures revealed that the conformations of the reactive 2-cyanoethyl groups are different from those of the 3-ethylpyridine and 4-ethylpyridine complexes. This paper reports the crystal structures of the two complexes and the relationship between the reaction cavity and the isomerization rate.