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trans-Tetracarbonylbis(tricyclohexylphosphine)molybdenum(0), *trans*-$[\mathrm{Mo(CO)_4(PCy_3)_2}]$

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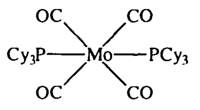
Abstract

The title compound, $[\mathrm{Mo(CO)_4\{P(C_6H_{11})_3\}_2}]$, has crystallographic inversion symmetry and principal dimensions Mo—P 2.5436 (9), Mo—C 2.020 (4) and 2.028 (3) Å. The mean cone angle for the cyclohexylphosphine ligand is 155°, compared with 146° for the *cis* isomer.

Comment

The title compound, (1), was synthesized as part of our studies of $[\mathrm{Mo(CO)}_{(6-n)}(\mathrm{P}Y_3)_n]$ (n = 1–3, Y = alkyl, aryl, OR, SR, NR_2, halide) complexes by ^{95}Mo NMR spectroscopy (Alyea & Song, 1995; Song, 1994). The effect of changes in the P substituent (Y) and the degree of carbonyl substitution have previously been deduced by the X-ray analyses of *cis*-$[\mathrm{Mo(CO)_4\{P(C_6H_4F}\text{-}p)_3\}_2]$ (Alyea, Ferguson, Gallagher & Song, 1994), *cis*-$[\mathrm{Mo(CO)_4\{P(OPh)_3\}_2}]$ (Alyea, Ferguson & Zwikker, 1994), *fac*-$[\mathrm{Mo(CO)_3\{P(OPh)_3\}_3}]$ (Alyea, Ferguson & Song, 1995) and *trans*-$[\mathrm{Mo(CO)_4\{P(O^tBu)_3\}_2}]$ (Alyea, Ferguson & Song, 1996). A search of the October 1995 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed relatively few X-ray data on *trans*-$\mathrm{Mo(CO)_4P_2}$ fragments. Examples of such mononuclear *trans* systems having phosphine ligands are *trans*-$[\mathrm{Mo(CO)_4(PPh_2F)\{PPh_2(NH_2)\}}]$ (Bradley, Wong, Gabe & Lee, 1986), *trans*-$[\mathrm{Mo(CO)_4\{PPh_2(NHMe)\}_2}]$ (Gray & Zhang, 1993), *trans*-$[\mathrm{Mo(CO)_4\{Ph_2P\text{-}CH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_4\text{-}CH_2\text{-}PPh_2\}}]$ (Gray & Duffey, 1994). Relevant dinuclear *trans* systems with bridging bidentate phosphine ligands are *trans*-$[\mathrm{Mo(CO)_4\{Ph_2P(CH_2)}_n\mathrm{PPh_2\}_2Mo(CO)_4}]$ (n = 5: Ueng & Hwang, 1994; n = 6: Ueng & Hwang, 1991). Although the structure of *cis*-$[\mathrm{Mo(CO)_4(PCy_3)_2}]$, (2), was reported recently (Watson, Woodward, Conole, Kessler & Sykara, 1994), there has been no report on the structure of the corresponding *trans* isomer, for which synthetic and spectroscopic data are known (Alyea & Somogyvari, 1988). In order to compare the effect of changing from *cis* to *trans* geometry, we now report structural details of *trans*-$[\mathrm{Mo(CO)_4(PCy_3)_2}]$, (1).



(1)

A view of (1) together with atomic numbering scheme is shown in Fig 1; one of the cyclohexyl rings (C31–C36) is disordered over two orientations (see *Experimental*). The molecule has a crystallographic inversion centre at the Mo atom which has slightly distorted octahedral geometry.

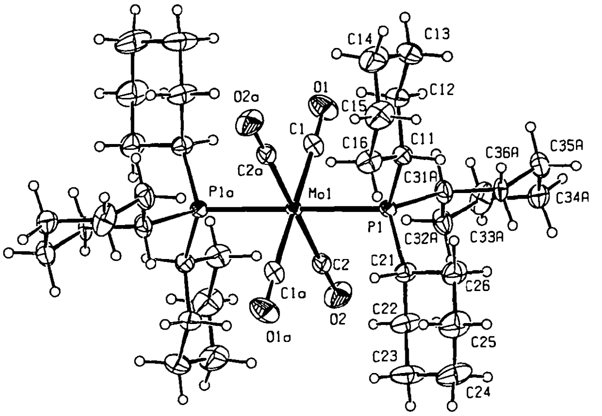


Fig. 1. A view of (1) with our numbering scheme; only one of the two orientations of the disordered cyclohexane ring (C31*A*—C36*A*/C31*B*—C36*B*) is shown. Displacement ellipsoids are drawn at the 30% probability level. Atoms P1a, C1a, C2a, O1a and O2a are at equivalent positions $-x$, $-y$, $-z$.

The Mo—P bond distance in (1) [2.5436 (9) Å] is much shorter than the average Mo—P bond distance in *cis*-$[\mathrm{Mo(CO)_4(PCy_3)_2}]$, (2) [2.654 (4) Å], and longer than in any of the related *trans*-$[\mathrm{Mo(CO)_4(P}Y_3)_2]$ compounds cited above, *e.g.* *trans*-$[\mathrm{Mo(CO)_4\{P(O^tBu)_3\}_2}]$, (3) [2.4699 (7) Å], *trans*-$[\mathrm{Mo(CO)_4(PPh_2F)\{PPh_2(NH_2)\}}]$, (4) [2.414 (1), 2.471 (1) Å], *trans*-$[\mathrm{Mo(CO)_4\{PPh_2(NHMe)\}_2}]$, (5) [2.4585 (7) Å], *trans*-$[\mathrm{Mo(CO)_4\{Ph_2P(CH_2)_5PPh_2\}_2Mo(CO)_4}]$, (6) [2.478 (2) and 2.488 (2) Å], *trans*-$[\mathrm{Mo(CO)_4\{Ph_2P(CH_2)_6PPh_2\}_2Mo(CO)_4}]$, (7) [2.468 (2) and 2.470 (2) Å], and *trans*-$[\mathrm{Mo(CO)_4(Ph_2P\text{-}CH_2\text{-}(CH_2\text{-}O\text{-}CH_2)_4\text{-}CH_2\text{-}PPh_2)}]$, (8) [2.472 (1) and 2.484 (1) Å]. The elongated Mo—P bond distance in (1) can be attributed to the steric hindrance caused by the bulkier cyclohexyl group of the $\mathrm{PCy_3}$ ligand.

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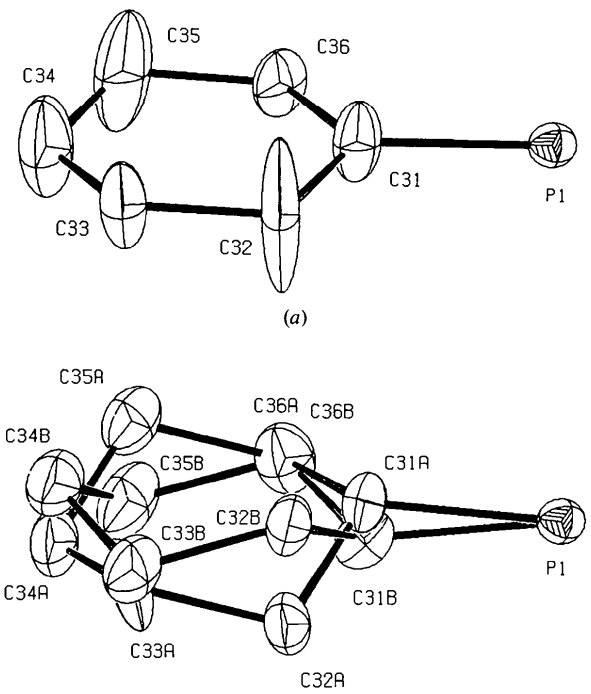
The P—Mo—P angles in (1), (3) and (5) are required to be exactly 180° by crystallographic symmetry constraints, as compared with 173.1 (1) in (4), 177.38 (8) in (6), 173.26 (7) in (7) and 175.69 (4)° in (8), where the molecules lie in general positions in their unit cells. The slight non-linearity of the Mo—C—O angles in (1) [176.9 (3), 177.7 (3)°] presumably accommodates the bulk of the $\mathrm{PCy_3}$ ligands; similar small deviations were also found in (3) (Alyea, Ferguson & Song, 1996). The other angles around the Mo atom show small deviations from the values for idealized octahedral geometry [C1—Mo—C2 92.17 (13)°, P1—Mo—C2 87.07 (9)°]. Distortion of the tetrahedral geometry at the P atom is shown by the disparity of the enlarged Mo—P—C and the reduced C—P—C angles (Table 2). In the case of *cis*-$[\mathrm{Mo(CO)_4(PCy_3)_2}]$ the C—P—C angles are in the range 98.8 (7)–107.1 (7)°. In non-coordinated $\mathrm{PCy_3}$ (Davies, Dutremez & Pinkerton, 1991), the C—P—C angles are 103.1 (3), 103.2 (3) and 105.1 (3)°. The other dimensions in (1) are normal and have been deposited as Supplementary Material.

A better comparison of the steric effect of the change in geometry from the *cis* to the *trans* forms was afforded by calculating the cone angles for each isomer from the available crystallographic data. By calculating semi-cone angles ($\theta/2$) using the 'ligand-profile' concept (Ferguson, Roberts, Alyea & Khan, 1978), with C—H at 1.08 Å, resultant average cone angles (θ) of 146 (*cis*) and 155° (*trans*) were obtained. The latter value is in good agreement with the value (θ = 156°) calculated for the bulky phosphite ligand $\mathrm{P(O^{\mathit{t}}Bu)_3}$ in (3) (Alyea, Ferguson & Song, 1996). These calculated cone angles are significantly smaller than predicted by Tolman (1977) from simple estimates with CPK models [170 for $\mathrm{PCy_3}$, 172° for $\mathrm{P(O^{\mathit{t}}Bu)_3}$]. The flexibility of $\mathrm{PCy_3}$ to adjust to its environment can be attributed to the ability of the cyclohexyl rings to intermesh to relieve steric strain.



(*a*)

(*b*)

Fig. 2. (*a*) A view showing the 'planar' cyclohexyl ring before disorder was allowed for. (*b*) A view showing the two disordered cyclohexyl ring components after refinement. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The title compound was synthesized by the reaction of $\mathrm{Mo(CO)_6}$ with $\mathrm{PCy_3}$ (1:2 ratio) in refluxing *iso*-octane for 24 h. The product was recrystallized from dichloromethane–heptane at 278 K. Relevant spectroscopic data are: ν(CO) = 1870 cm^{-1}, $\delta(^{95}\mathrm{Mo})$ = −1765 p.p.m., *J*(Mo—P) = 134 Hz in $\mathrm{CH_2Cl_2}$ solution (Alyea & Somogyvari, 1988).

Crystal data

$[\mathrm{Mo(CO)_4(C_{18}H_{33}P)_2}]$
M_r = 768.81
Triclinic
$P\overline{1}$
a = 9.9005 (8) Å
b = 10.5082 (12) Å
c = 11.314 (2) Å
α = 62.779 (14)°
β = 72.583 (11)°
γ = 88.966 (8)°
V = 988.9 (2) Å^3
Z = 1
D_x = 1.291 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 11.48–18.08°
μ = 0.450 mm^{-1}
T = 294 (1) K
Plate
0.32 × 0.25 × 0.10 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical by integration from crystal shape
$T_{\min}$ = 0.8899, $T_{\max}$ = 0.9586
4295 measured reflections
4295 independent reflections

2850 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max}$ = 26.86°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -12 \rightarrow 14$
3 standard reflections frequency: 120 min intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0411$
$wR(F^2) = 0.0925$
S = 0.962
4295 reflections
269 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults, C—H 0.97–0.98 Å]

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max}$ = 0.441 e Å^{-3}
$\Delta\rho_{\min}$ = −0.545 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Mo1	0	0	0	0.03006 (13)
P1	−0.21010 (8)	−0.17667 (8)	0.20526 (8)	0.0332 (2)
O1	0.2143 (3)	−0.2144 (3)	0.1126 (3)	0.0802 (9)
O2	0.0008 (3)	0.1480 (3)	0.1888 (3)	0.0754 (9)
C1	0.1363 (4)	−0.1357 (4)	0.0748 (3)	0.0459 (8)
C2	0.0036 (4)	0.0957 (3)	0.1195 (3)	0.0441 (8)
C11	−0.2680 (3)	−0.3371 (3)	0.1931 (3)	0.0426 (8)
C12	−0.1493 (4)	−0.4323 (4)	0.1887 (4)	0.0567 (10)
C13	−0.1976 (5)	−0.5638 (4)	0.1800 (5)	0.0819 (14)
C14	−0.2464 (5)	−0.5191 (5)	0.0544 (5)	0.087 (2)
C15	−0.3661 (5)	−0.4296 (5)	0.0597 (5)	0.0803 (14)
C16	−0.3261 (4)	−0.2973 (4)	0.0718 (4)	0.0564 (10)
C21	−0.3794 (3)	−0.0952 (3)	0.2291 (4)	0.0421 (8)
C22	−0.3714 (4)	0.0263 (4)	0.2648 (5)	0.0644 (11)
C23	−0.4991 (4)	0.1096 (5)	0.2524 (6)	0.089 (2)
C24	−0.6390 (4)	0.0126 (5)	0.3396 (6)	0.090 (2)
C25	−0.6466 (4)	−0.1096 (5)	0.3070 (6)	0.0827 (14)
C26	−0.5203 (4)	−0.1942 (4)	0.3239 (4)	0.0640 (11)
C31*A*†	−0.1773 (7)	−0.2757 (6)	0.3775 (4)	0.046 (3)
C32*A*	−0.1071 (7)	−0.1825 (5)	0.4196 (5)	0.057 (2)
C33*A*	−0.0585 (7)	−0.2734 (8)	0.5455 (6)	0.073 (5)
C34*A*	−0.1805 (8)	−0.3840 (7)	0.6694 (4)	0.064 (3)
C35*A*	−0.2483 (7)	−0.4783 (5)	0.6268 (5)	0.062 (2)
C36*A*	−0.2986 (6)	−0.3865 (7)	0.5023 (6)	0.047 (7)
C31*B*	−0.1949 (8)	−0.2485 (10)	0.3849 (3)	0.047 (4)
C32*B*	−0.0439 (7)	−0.2509 (8)	0.3927 (6)	0.050 (3)
C33*B*	−0.0422 (10)	−0.2838 (10)	0.5381 (8)	0.066 (7)
C34*B*	−0.1379 (9)	−0.4248 (9)	0.6515 (6)	0.066 (4)
C35*B*	−0.2900 (8)	−0.4199 (10)	0.6465 (6)	0.075 (4)
C36*B*	−0.2931 (9)	−0.3867 (11)	0.5014 (8)	0.068 (13)

† Disordered cyclohexane ring C31*A*–C36*A*/C31*B*–C36*B* (see below).

Table 2. *Selected geometric parameters (Å, °)*

Mo1—C1	2.020 (4)	P1—C31*A*	1.870
Mo1—C2	2.028 (3)	P1—C31*B*	1.870
Mo1—P1	2.5436 (9)	O1—C1	1.147 (4)
P1—C11	1.866 (3)	O2—C2	1.141 (4)
P1—C21	1.872 (3)		
P1—Mo1—C1	90.10 (9)	C21—P1—C31*B*	100.4 (3)
P1—Mo1—C2	87.07 (9)	Mo1—P1—C11	116.25 (10)
C1—Mo1—C2	92.17 (13)	Mo1—P1—C21	113.45 (11)
C11—P1—C21	101.82 (14)	Mo1—P1—C31*A*	115.7 (2)
C11—P1—C31*A*	97.9 (3)	Mo1—P1—C31*B*	116.8 (3)
C11—P1—C31*B*	106.0 (3)	Mo1—C1—O1	176.9 (3)
C21—P1—C31*A*	109.9 (3)	Mo1—C2—O2	177.7 (3)

Molecule (I) crystallized in the triclinic system; space group $P\bar{1}$ was assumed and confirmed by the analysis. One of the cyclohexane rings is disordered over two orientations; this disorder was allowed for by appropriate constraints (C—C 1.524 Å, P—C 1.870 Å, chair conformation) during the final refinement cycles and led to occupancies of 0.598 (7) and 0.402 (7) for the two conformers. During the initial solution and refinement process, the disordered cyclohexyl ring appeared as a planar ring with abnormal displacement parameters normal to the ring plane (Fig. 2*a*). A view of the two conformers of the disordered ring at the end of the refinement is presented in Fig. 2(*b*). The possibility that the true space group was *P*1 with ordered cyclohexanes as opposed to $P\bar{1}$ with disordered ones was considered and rejected on the following grounds: (*a*) attempted refinement of the structure in the space group *P*1 became quite unstable and (*b*) this situation of 'centrosymmetric or non-centrosymmetric?' has already been the subject of discussion with the conclusion that 'it is better to opt for a centrosymmetric description, even though disorder may result' (Marsh, 1986). Examination of the structures with *PLATON* (Spek, 1994*a*) showed that there were no solvent accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94 (Patterson heavy-atom method). Program(s) used to refine structure: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94; *ORTEP*II (Johnson, 1976) in *PLATON* (Spek, 1994*a*); *PLUTON* (Spek 1994*b*). Software used to prepare material for publication: *NRCVAX*94; *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1347). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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