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cis-Tetracarbonylbis(tricyclohexylphosphine)molybdenum(0) and pentacarbonyl(tricyclohexylphosphine)molybdenum(0)

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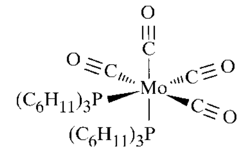
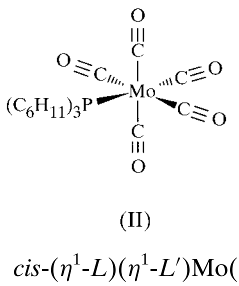
In the present redetermination of the complex *cis*-tetracarbonylbis(tricyclohexylphosphine)molybdenum(0), (I), $[Mo(C_{18}H_{33}P)_2(CO)_4]$ or *cis*-$\{\eta^1$-$[P(C_6H_{11})_3]_2\}Mo(CO)_4$, the Mo atom has a distorted octahedral geometry with a large P—Mo—P angle of 104.8 (1)°. A strong *trans* influence on the carbonyls in (I) is seen in a shortening of the Mo—C and a lengthening of the C—O distances opposite the phosphines compared with those that are *cis*. This influence is greatly diminished in the complex pentacarbonyl(tricyclohexylphosphine)molybdenum(0), (II), $[Mo(C_{18}H_{33}P)(CO)_5]$ or $\{\eta^1$-$[P(C_6H_{11})_3]\}Mo(CO)_5$, the core of which has a slightly distorted C_{4v} geometry.

Comment

Tricyclohexylphoshine dissociates from *cis*-$\{\eta^1$-$[P(cy)_3]_2\}$tetracarbonylmolybdenum(0) (cy is cyclohexyl) to produce a mixture of $\{\eta^2$-$[P(cy)_3]_2\}$tetracarbonylmolybdenum(0) and $[\eta^1$-$P(cy)_3]$pentacarbonylmolybdenum(0) (Cortes-Figueroa *et al.*, 1997). Ligand dissociation from *cis*-$(\eta^1$-$L)(\eta^1$-$L')Mo(CO)_4$ produces $(\eta^2$-$L')Mo(CO)_4$, for $L = P(cy)_3$, triphenylphosphine or piperidine and $L' = P(cy)_3$ or triphenylphosphine, where L and L' have cone angles greater than 45° (Tolman, 1977). The lability of the Mo—$P(cy)_3$ bond in such complexes may arise, in part, from the ligand cone angle of 170° and may account for the difficulty in preparation of the analogous complex *cis*-$\{[\eta^1$-$P(cy)_3]_2\}W(CO)_4$ by Boyles *et al.* (1985). Rates of ligand dissociation reactions from *cis*-$(\eta^1$-$L)(\eta^1$-$L')Mo(CO)_4$ also point to the type of metal ion and the size of the ligand as important kinetic controlling factors (Laboy *et al.*, 1995; Cortes-Figueroa *et al.*, 1997). As part of a systematic study testing the relationships between structure and reactivity in these complexes, the synthesis and structures of the title compounds, *cis*-tetracarbonylbis(tricyclohexylphosphine)molybdenum(0), (I), and pentacarbonyl(tricyclohexylphosphine)molybdenum(0), (II), are reported. The structure of (I) is a redetermination of that reported by Watson *et al.* (1994), which was based on a very limited data set.



(I)



(II)

The structures of (I) and (II) are shown in Figs. 1 and 2, respectively. In (I), the Mo atom has a considerably distorted octahedral coordination geometry, as indicated by the P1—Mo—P2 bond angle of 104.8 (1)° (ideal value 90°) and the molecular distortion from C_{2v} symmetry. This is accompanied by a contraction of the opposite C2—Mo—C3 angle to 84.2 (2)°, and of the adjacent P1—Mo—C3 and P2—Mo—C2 angles to 86.5 (2) and 84.8 (2)°, respectively. The sterically crowded environment at the Mo atom is further indicated by the distortions of the equatorial *trans* bond angles for P1—Mo—C2 [169.9 (2)°], P2—Mo—C3 [167.6 (2)°] and C4—Mo—C1 [171.8 (3)°] from the 180° ideal. The Mo—C_{ax} bond lengths, averaging 2.040 (8) Å, are *trans* to each other and are significantly (about 10 s.u.'s) longer than the Mo—C_{eq} distances, which average 1.924 (8) Å and are both *trans* to P. Both Mo—P bond distances are similar and average 2.655 (2) Å, which is significantly longer than the average Mo—P distance in phosphine–pentacarbonyl–molybdenum complexes such as (II) [2.594 (1) Å], $[\eta^1$-$PPh_3]Mo(CO)_5$

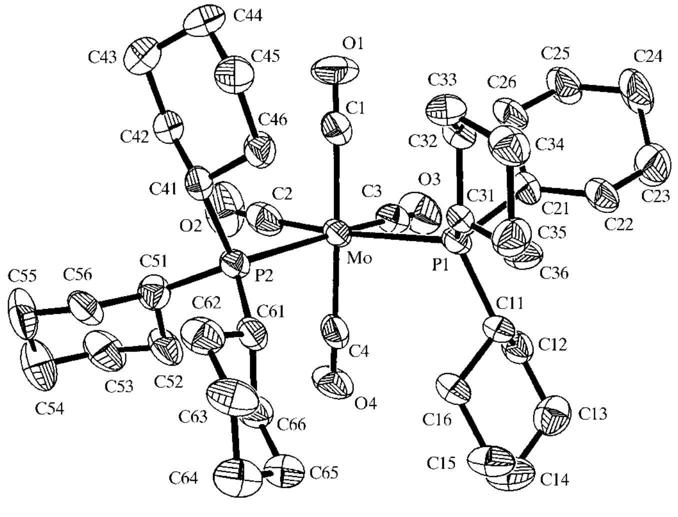


Figure 1
The molecular structure of complex (I) showing the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level and H atoms have been omitted for clarity.

[2.560 (1) Å; Cotton *et al.*, 1981], [η^1-P(CH$_2$CH$_2$CN)$_3$]-Mo(CO)$_5$ [2.506 (1) Å; Cotton *et al.*, 1981], and *trans*-{bis[η^1-P(cy)$_3$]}Mo(CO)$_4$ [2.544 (1) Å; Alyea *et al.*, 1996]. The *trans* influence extends to the carbonyl groups in (I), such that those opposite the shorter Mo—P distances, C2—O2 and C3—O3, average 1.185 (8) Å, while those *cis* to P, C1—O1 and C4—O4, average 1.133 (8) Å. This observation is consistent with the larger π-acceptor ability of carbonyls (Cotton & Wilkinson, 1988; Cortes-Figueroa *et al.*, 1998).

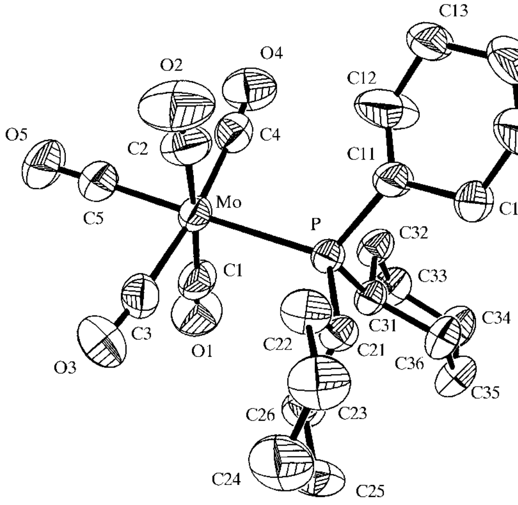


Figure 2
The molecular structure of the major conformer of complex (II) showing the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level and H atoms have been omitted for clarity.

In the pentacarbonyl complex, (II), the Mo geometry is only slightly distorted from the octahedral ideal and is nearly C_{4v}. The *trans* influence is present in (II) but greatly diminished compared with (I). The Mo—C5 distance, *trans* to P and to the shorter Mo—P distance mentioned above, is shorter [1.97 (1) Å] than the average of the remaining Mo—C distances [2.03 (1) Å]. At the carbonyl groups, however, the influence is very weak, with the *trans* C5—O5 distance of 1.154 (6) Å being larger but not statistically distinguishable from the other four [average 1.149 (12) Å]. Disorder in one cyclohexyl ring, between alternate chair conformers, was modelled with the major conformer having an occupancy of 0.64 (1).

Experimental

Complex (I) was prepared from *cis*-[bis(piperidine)]tetracarbonylmolybdenum(0) following the procedure of Darensbourg & Kump (1978); a 2.5 mol excess of tricyclohexylphosphine to the piperidine complex was used, in dichloromethane. Light-yellow crystals of (I) were obtained by recrystallization from dichloromethane–methanol solution. Complex (II) was prepared by refluxing Mo(CO)$_6$ and P(cy)$_3$ in bis(2-methoxyethyl) ether under dinitrogen. Upon cooling to 277 K, colorless crystals of (II) formed in low yield.

Compound (I)

Crystal data

[Mo(C$_{18}$H$_{33}$P)$_2$(CO)$_4$]
M_r = 768.81
Monoclinic, $P2_1/n$
a = 10.856 (3) Å
b = 25.323 (8) Å
c = 14.795 (7) Å
β = 94.68 (3)°
V = 4054 (3) Å^3
Z = 4
D_x = 1.260 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
θ = 7.5–18.0°
μ = 0.439 mm^{-1}
T = 293 (2) K
Prism, light yellow
0.40 × 0.20 × 0.05 mm

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: semi-zempirical *via* ψ scans (*XEMP*; Siemens, 1989)
$T_{\min}$ = 0.844, $T_{\max}$ = 0.978
12 628 measured reflections
9302 independent reflections
3635 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.092
$\theta_{\max}$ = 27.51°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 32$
$l = -19 \rightarrow 19$
3 standard reflections
every 197 reflections
frequency: 150 min
intensity decay: 3.0 (3)%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.080
S = 0.931
9302 reflections
424 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.59 e Å^{-3}
$\Delta\rho_{\min}$ = −0.70 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Mo—C2	1.921 (6)	Mo—P1	2.6569 (17)
Mo—C3	1.927 (6)	O1—C1	1.123 (6)
Mo—C1	2.039 (5)	O2—C2	1.211 (6)
Mo—C4	2.042 (6)	O3—C3	1.159 (6)
Mo—P2	2.6529 (16)	O4—C4	1.143 (6)
C2—Mo—C3	84.2 (2)	C1—Mo—P2	97.26 (16)
C2—Mo—C1	85.8 (2)	C4—Mo—P2	87.27 (16)
C3—Mo—C1	87.7 (2)	C2—Mo—P1	169.87 (16)
C2—Mo—C4	87.8 (2)	C3—Mo—P1	86.47 (17)
C3—Mo—C4	86.6 (2)	C1—Mo—P1	89.77 (16)
C1—Mo—C4	171.8 (3)	C4—Mo—P1	95.73 (16)
C2—Mo—P2	84.81 (17)	P2—Mo—P1	104.81 (5)
C3—Mo—P2	167.64 (16)		

Compound (II)

Crystal data

[Mo(C$_{18}$H$_{33}$P)(CO)$_5$]
M_r = 516.40
Monoclinic, $P2_1/n$
a = 11.785 (3) Å
b = 16.760 (7) Å
c = 12.779 (4) Å
β = 92.15 (2)°
V = 2522.3 (14) Å^3
Z = 4
D_x = 1.360 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 42 reflections
θ = 12–16°
μ = 0.612 mm^{-1}
T = 293 (2) K
Rod, colorless
0.40 × 0.20 × 0.18 mm

Data collection

Siemens *P*3 diffractometer
ω scans
4655 measured reflections
4435 independent reflections
2498 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.089
$\theta_{\max}$ = 25.01°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = -15 \rightarrow 15$
3 standard reflections
every 197 reflections
frequency: 180 min
intensity increase: 3.2 (4)%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.091$
$S = 0.901$
4435 reflections
308 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Mo—C5	1.972 (6)	Mo—P	2.5938 (14)
Mo—C3	2.009 (7)	O1—C1	1.136 (6)
Mo—C4	2.020 (6)	O2—C2	1.140 (6)
Mo—C2	2.038 (7)	O3—C3	1.163 (6)
Mo—C1	2.046 (7)	O4—C4	1.151 (6)
C5—Mo—C3	86.5 (2)	C4—Mo—C1	91.1 (2)
C5—Mo—C4	86.1 (2)	C2—Mo—C1	176.2 (2)
C3—Mo—C4	172.6 (2)	C5—Mo—P	177.94 (18)
C5—Mo—C2	89.5 (2)	C3—Mo—P	95.38 (16)
C3—Mo—C2	87.9 (2)	C4—Mo—P	92.04 (15)
C4—Mo—C2	92.1 (2)	C2—Mo—P	91.50 (18)
C5—Mo—C1	88.6 (2)	C1—Mo—P	90.52 (15)
C3—Mo—C1	88.6 (2)		

The H atoms of (I) and (II) were treated as riding, with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$ and C—H distances in the range 0.97–0.98 Å.

For both compounds, data collection: *P*3/*PC Diffractometer Program* (Siemens, 1989); cell refinement: *P*3/*PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS*93 (Sheldrick, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1291). Services for accessing these data are described at the back of the journal.

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