Crystal data

$[MnCl_3(C_{12}H_{12}N_2)].C_2H_3N$
$M_r = 386.58$
Monoclinic
$P2_1/n$
$a = 7.4118\ (1)$ Å
$b = 16.7280\ (3)$ Å
$c = 13.5168\ (1)$ Å
$\beta = 90.748\ (1)^\circ$
$V = 1675.73\ (4)$ Å^3
$Z = 4$
$D_x = 1.532$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8132 reflections
$\theta = 2.0$–27.5°
$\mu = 1.261$ mm^{-1}
$T = 173\ (2)$ K
Needle
$0.25 \times 0.19 \times 0.19$ mm
Dark blue

Data collection

Siemens SMART platform diffractometer
ω scans
Absorption correction: empirical from ψ scans (*SHELXTL5*; Sheldrick, 1995)
$T_{min} = 0.703$, $T_{max} = 0.787$
11 406 measured reflections

3840 independent reflections
3476 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$
$\theta_{max} = 27.50^\circ$
$h = -9 \rightarrow 8$
$k = -13 \rightarrow 22$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.081$
$S = 1.07$
3822 reflections
197 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 1.0062P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.01$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXTL5* (Sheldrick, 1995)
Extinction coefficient: 0.0034 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn—N1	2.096 (1)	Mn—Cl2	2.2187 (5)
Mn—N12	2.035 (1)	Mn—Cl3	2.3117 (5)
Mn—Cl1	2.2587 (5)		
N1—Mn—N12	77.95 (6)	N12—Mn—Cl2	168.86 (4)
N1—Mn—Cl1	137.16 (4)	N12—Mn—Cl3	91.65 (4)
N1—Mn—Cl2	92.63 (4)	Cl1—Mn—Cl2	92.65 (2)
N1—Mn—Cl3	110.55 (4)	Cl1—Mn—Cl3	110.85 (2)
N12—Mn—Cl1	90.36 (4)	Cl2—Mn—Cl3	97.28 (2)

A hemisphere of frames, 0.3° in ω, was collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. Intensity decay was <1%. ψ-Scan empirical absorption corrections were applied based on the entire data set. Full data-collection details are in the archived CIF and are also reported elsewhere (Abboud *et al.*, 1997). The H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.96 and 0.93 Å were used for methyl and sp^2 C atoms, respectively. H-atom displacement parameters were set at $1.2U_{eq}$ of the parent C atom or $1.5U_{eq}$ for methyl H atoms.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART* and *SAINT* (Siemens, 1995). Data reduction: *SHELXTL5* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL5*. Program(s) used to refine structure: *SHELXTL5*. Molecular graphics: *SHELXTL5*. Software used to prepare material for publication: *SHELXTL5*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1372). Services for accessing these data are described at the back of the journal.

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Tricarbonyl(η^5-cyclopentadienyl)(trimethylphosphine-*P*)molybdenum(II) Tetrafluoroborate

James C. Fettinger, Heinz-Bernhard Kraatz and Rinaldo Poli

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA. E-mail: jf96@umail.umd.edu

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Abstract

The title compound, $[Mo(C_5H_5)(C_3H_9P)(CO)_3]BF_4$, forms by a ligand-redistribution reaction from $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PMe_3)FBF_3]$, which is produced at low temperature by protonation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2$-

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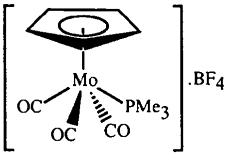
$(PMe_3)H]$ with HBF_4. The cation has a typical four-legged piano-stool geometry, with Mo—P 2.496 (2) and Mo—*Cnt* 2.00 (2) Å, where *Cnt* is the centre of gravity of the cyclopentadienyl ring.

Comment

The title compound, (I), crystallizes in the orthorhombic space group $Pca2_1$ with the tetrafluoroborate anion highly disordered. A model with three orientations was employed, but the disorder and the high thermal motion of the F atoms does not afford significant structural parameters for this unit. The cation is ordered and is shown in Fig. 1. The geometry is typical of $CpML_4$ compounds (Kubácek *et al.*, 1982), *i.e.* a four-legged piano stool. This structural type is highly documented for neutral half-sandwich derivatives of Mo^{II} (Poli, 1990), but to a much lesser extent for cationic derivatives, *i.e.* products of formal substitution of one or more carbonyl ligands from the known (Treichel & Shubkin, 1967) $[CpMo(CO)_4]^+$ compound with other neutral ligands.



(I)

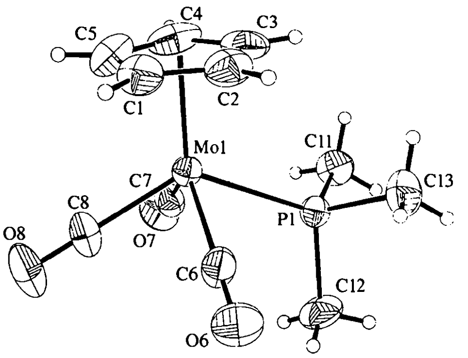


Fig. 1. The molecular configuration and labelling scheme for the cation in (I). Ellipsoids are drawn at the 30% probability level.

A previously reported example of this type is $[CpMo(CO)(CN^tBu)_3]^+$ (Lawless *et al.*, 1986). When the $[CpMo(CO)_3(PMe_3)]^+$ cation is viewed along the Mo—*Cnt* axis (*Cnt* is the center of gravity of atoms C1–C5), the orientation of the cyclopentadienyl ring is such that no C atom exactly overlaps with any basal donor atom. In other words, the C_{Cp}—*Cnt*—Mo—*L* (*L* = CO or PMe_3) dihedral angles are all non-zero; C3—*Cnt*—Mo1—P1 8.1 (8) and *Cnt*—Mo1—P1—C12 170.6 (5)°. These values clearly indicate the acentricity of the structure and its subsequent lack of a mirror plane. The Mo—*Cnt* distance [2.00 (2) Å] is typical of this class of compounds and the ring is symmetrically placed on top of the metal, the difference between the longest and shortest Mo—C bond being only 0.071 (11) Å. For other compounds of this class, such differences may be greater than 0.2 Å (for instance, in $[CpMoCl(PMe_3)_3]^+$; Abugideiri *et al.*, 1992). The Mo—P distance of 2.496 (2) Å is longer than in complexes where the phosphine ligand is *trans* to weak *trans*-labilizing ligands, such as *trans*-$[CpMo(COCH_3)(CO)_2(PPh_3)]$ [2.473 (3) Å; Churchill & Fennessey, 1968], *trans*-$[CpMoI(CO)_2(PPh_3)]$ [2.481 (5) Å; Bush *et al.*, 1971] and [CpMoCl(CO)(dppe)] [*trans* to Cl, 2.439 (5) Å; Bush *et al.*, 1971], but similar to that in compounds where the phosphine ligand is *trans* to a carbonyl ligand, such as *cis*-$[CpMoI(CO)_3(P^nBu_3)]$ [2.50 (1) Å; Fenn & Cross, 1971], *cis*-$[CpMoBr(CO)_2(PPh_3)]$ [2.538 (2) Å; Sim *et al.*, 1979] and [CpMoCl(CO)(dppe)] [2.496 (4) Å; Bush *et al.*, 1971]. The Mo—C values are marginally longer for the two carbonyl ligands *trans* to each other relative to that *trans* to PMe_3. The *Cnt*—Mo—*L* (*L* = CO and PMe_3) angular parameters are larger for the two carbonyl ligands *trans* to each other [122.4 (4) and 123.2 (4)°] than for the other two ligands [115.1 (5) and 115.7 (5)°], in line with the established trend of angular *trans* influence (Poli, 1990).

Experimental

The title compound derives from the protonation reaction of $[CpMoH(CO)_2(PMe_3)]$ with HBF_4, which was carried out in an attempt to isolate a classical dihydride or a dihydrogen complex of formula $[CpMoH_2(CO)_2(PMe_3)]^+$ or a complex with the weakly coordinating BF_4^- counterion, $[CpMo(FBF_3)(CO)_2(PMe_3)]$, as described earlier (Quadrelli *et al.*, 1996). Evidence for the formation of $[CpMo(FBF_3)(CO)_2(PMe_3)]$ is obtained at low temperature, but this rearranges to the title compound by a ligand-redistribution process upon warming to room temperature. The title compound was recrystallized from dichloromethane–heptane.

Crystal data

$[Mo(C_5H_5)(C_3H_9P)(CO)_3]$-$BF_4$
$M_r = 407.94$
Orthorhombic
$Pca2_1$
$a = 14.8333 (8)$ Å
$b = 7.6010 (9)$ Å
$c = 14.109 (2)$ Å
$V = 1590.7 (3)$ Å^3
$Z = 4$
$D_x = 1.703$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.9$–$18.5°$
$\mu = 0.969$ mm^{-1}
$T = 293 (2)$ K
Block
0.30 × 0.30 × 0.20 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer

1287 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans
Absorption correction:
ψ scans (*SHELXTL*; Sheldrick, 1994)
$T_{\min} = 0.767$, $T_{\max} = 0.824$
3355 measured reflections
1903 independent reflections
$R_{\rm int} = 0.038$
$\theta_{\max} = 27.50°$
$h = -17 \rightarrow 20$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.081$
$S = 1.048$
1903 reflections
269 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0088 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.06 (9)

Table 1. *Selected geometric parameters (Å, °)*

Mo1—*Cnt*	2.00 (2)	Mo1—C2	2.331 (9)
Mo1—C6	2.004 (7)	Mo1—C3	2.341 (9)
Mo1—C8	2.005 (9)	Mo1—P1	2.496 (2)
Mo1—C7	2.013 (9)	C6—O6	1.119 (8)
Mo1—C1	2.284 (6)	C7—O7	1.132 (9)
Mo1—C5	2.310 (9)	C8—O8	1.134 (11)
Mo1—C4	2.329 (8)		
Cnt—Mo1—C6	122.4 (4)	C7—Mo1—P1	75.4 (2)
Cnt—Mo1—C8	115.7 (5)	C12—P1—Mo1	113.7 (4)
Cnt—Mo1—C7	123.2 (4)	C13—P1—Mo1	115.3 (3)
C6—Mo1—C7	114.4 (4)	C11—P1—Mo1	115.5 (3)
C8—Mo1—C7	76.7 (3)	O6—C6—Mo1	177.4 (8)
Cnt—Mo1—P1	115.1 (5)	O7—C7—Mo1	176.8 (8)
C6—Mo1—P1	76.4 (3)	O8—C8—Mo1	178.8 (8)
C8—Mo1—P1	129.2 (3)		
C3—*Cnt*—Mo1—P1	8.1 (8)	C8—Mo1—P1—C12	−10.5 (5)
Cnt—Mo1—P1—C12	170.6 (5)		

Normal data-collection procedures were used. Data were corrected for Lorentz and polarization factors, and absorption, and reduced to F_o^2 and $\sigma(F_o^2)$ using *XCAD*4 (Harms, 1993). A parallel reduction was also performed with *NRCVAX* (Gabe *et al.*, 1989), producing reduced observed structure-factor amplitudes. Both outputs were examined closely and systematic absences indicated the centrosymmetric orthorhombic space group *Pcmb* (non-standard setting of *Pbcm*; No. 57) or the non-centrosymmetric orthorhombic space group $Pc2_1b$ (non-standard setting of $Pca2_1$; No. 29) with intensity statistics slightly favouring the non-centrosymmetric case. The molecule was initially believed not to possess a mirror plane and refinement was begun in the non-centrosymmetric space group. Cell constants were rearranged (*abc* → *bca*) and the data were also transformed with the appropriate matrix to allow the structure determination to be performed in the standard setting, *i.e.* $Pca2_1$. The structure was determined with the successful location of the Mo atom using *SHELXS*86 (Sheldrick, 1990). Subsequent difference Fourier maps revealed the location of all remaining non-H atoms within the main molecule and also the atoms comprising the disordered BF_4 molecule. *SHELXL*93 (Sheldrick, 1993) was used to refine the structure using F_o^2 and $\sigma(F_o^2)$. The structure converged well and H atoms were placed in calculated positions; these being dependent on both the type of bonding at the C atom and the temperature (293 K in this case). H atoms were placed on the external bisector of the Cp ring with d(C—H) = 0.930 Å and $U_{\rm H} = 1.2U_{\rm parent}$; methyl H atoms were initially located by circular difference Fourier about the C atom in question, then optimized for tetrahedral geometry and located with d(C—H) = 0.960 Å and $U_{\rm H} = 1.5U_{\rm parent}$. The disordered BF_4 molecule required many cycles of refinement to determine whether further splitting of the molecule's F atoms was fruitful or not. In the end, three orientations were adopted and the structure was now refined to convergence ($\Delta/\sigma < 0.001$) with $R(F) = 8.05$, $wR(F^2) = 8.13\%$ and $S = 1.048$ for all 1903 unique reflections [$R(F) = 3.33$ and $wR(F^2) = 6.45\%$ for those 1287 data with $F_o > 4\sigma(F_o)$]. A final difference Fourier map proved featureless with $|\Delta\rho| = 0.36$ e Å^{-3}. The function minimized during the full-matrix least-squares refinement was $w(F_o^2 - F_c^2)$ where in the non-centrosymmetric structure $w = 1/[\sigma^2(F_o^2) + (0.0271P)^2]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$. An empirical correction for extinction was attempted but found to be negative and not applied.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 and *NRCVAX*. Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1063). Services for accessing these data are described at the back of the journal.

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