



**HAL**  
open science

# Tricarbonyl( $\eta^5$ -cyclopentadienyl)(trimethylphosphine-P)molybdenum(II) Tetrafluoroborate

James C Fettinger, Heinz-Bernhard Kraatz, Rinaldo Poli

► **To cite this version:**

James C Fettinger, Heinz-Bernhard Kraatz, Rinaldo Poli. Tricarbonyl( $\eta^5$ -cyclopentadienyl)(trimethylphosphine-P)molybdenum(II) Tetrafluoroborate. Acta Crystallographica Section C: Crystal Structure Communications [1968-2013], 1998, 54, pp.181-183. 10.1107/S0108270197012651. hal-03368458

**HAL Id: hal-03368458**

**<https://hal.science/hal-03368458>**

Submitted on 7 Oct 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Tricarbonyl( $\eta^5$ -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*

*(Received 24 April 1997; accepted 26 September 1997)*

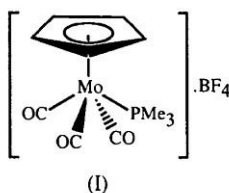
## Abstract

The title compound,  $[\text{Mo}(\text{C}_5\text{H}_5)(\text{C}_3\text{H}_9\text{P})(\text{CO})_3]\text{BF}_4$ , forms by a ligand-redistribution reaction from  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PMe}_3)\text{FBF}_3]$ , which is produced at low temperature by protonation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{-}$

(PMe<sub>3</sub>)H] with HBF<sub>4</sub>. The cation has a typical four-legged piano-stool geometry, with Mo—P 2.496 (2) and Mo—C<sub>nt</sub> 2.00 (2) Å, where C<sub>nt</sub> is the centre of gravity of the cyclopentadienyl ring.

### Comment

The title compound, (I), crystallizes in the orthorhombic space group *Pca*2<sub>1</sub> 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<sub>4</sub> compounds (Kubáček *et al.*, 1982), *i.e.* a four-legged piano stool. This structural type is highly documented for neutral half-sandwich derivatives of Mo<sup>II</sup> (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)<sub>4</sub>]<sup>+</sup> compound with other neutral ligands.

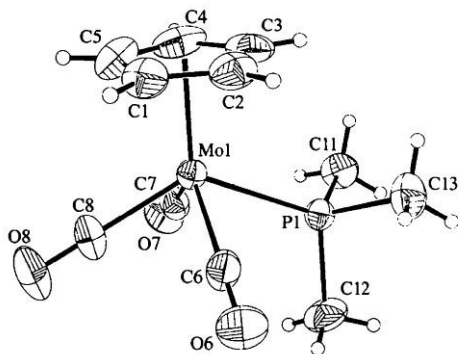


Fig. 1. The molecular configuration and labelling scheme for the cation in (I). Ellipsoids are drawn at the 30% probability level.

A previously reported example of this type is [CpMo(CO)(CN<sup>t</sup>Bu)<sub>3</sub>]<sup>+</sup> (Lawless *et al.*, 1986). When the [CpMo(CO)<sub>3</sub>(PMe<sub>3</sub>)]<sup>+</sup> cation is viewed along the Mo—C<sub>nt</sub> axis (C<sub>nt</sub> 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<sub>Cp</sub>—C<sub>nt</sub>—Mo—L (L = CO or PMe<sub>3</sub>) dihedral angles are all non-zero; C3—C<sub>nt</sub>—Mo1—P1 8.1 (8) and C<sub>nt</sub>—Mo1—P1—C12 170.6 (5)°. These values clearly indicate the acentric-

ity of the structure and its subsequent lack of a mirror plane. The Mo—C<sub>nt</sub> 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<sub>3</sub>)<sub>3</sub>]<sup>+</sup>; 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<sub>3</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)] [2.473 (3) Å; Churchill & Fennessey, 1968], *trans*-[CpMoI(CO)<sub>2</sub>(PPh<sub>3</sub>)] [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)<sub>3</sub>(P<sup>t</sup>Bu<sub>3</sub>)] [2.50 (1) Å; Fenn & Cross, 1971], *cis*-[CpMoBr(CO)<sub>2</sub>(PPh<sub>3</sub>)] [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<sub>3</sub>. The C<sub>nt</sub>—Mo—L (L = CO and PMe<sub>3</sub>) 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)<sub>2</sub>(PMe<sub>3</sub>)] with HBF<sub>4</sub>, which was carried out in an attempt to isolate a classical dihydride or a dihydrogen complex of formula [CpMoH<sub>2</sub>(CO)<sub>2</sub>(PMe<sub>3</sub>)]<sup>+</sup> or a complex with the weakly coordinating BF<sub>4</sub><sup>-</sup> counterion, [CpMo(FBF<sub>3</sub>)(CO)<sub>2</sub>(PMe<sub>3</sub>)], as described earlier (Quadrelli *et al.*, 1996). Evidence for the formation of [CpMo(FBF<sub>3</sub>)(CO)<sub>2</sub>(PMe<sub>3</sub>)] 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<sub>5</sub>H<sub>5</sub>)(C<sub>3</sub>H<sub>9</sub>P)(CO)<sub>3</sub>]-  
BF<sub>4</sub>  
M<sub>r</sub> = 407.94  
Orthorhombic  
*Pca*2<sub>1</sub>  
a = 14.8333 (8) Å  
b = 7.6010 (9) Å  
c = 14.109 (2) Å  
V = 1590.7 (3) Å<sup>3</sup>  
Z = 4  
D<sub>x</sub> = 1.703 Mg m<sup>-3</sup>  
D<sub>m</sub> not measured

Mo Kα radiation  
λ = 0.71073 Å  
Cell parameters from 25  
reflections  
θ = 11.9–18.5°  
μ = 0.969 mm<sup>-1</sup>  
T = 293 (2) K  
Block  
0.30 × 0.30 × 0.20 mm  
Red

#### Data collection

Enraf–Nonius CAD-4  
diffractometer

1287 reflections with  
I > 2σ(I)

$\omega/2\theta$  scans  
 Absorption correction:  
 $\psi$  scans (*SHELXTL*;  
 Sheldrick, 1994)  
 $T_{\min} = 0.767$ ,  $T_{\max} = 0.824$   
 3355 measured reflections  
 1903 independent reflections

$R_{\text{int}} = 0.038$   
 $\theta_{\max} = 27.50^\circ$   
 $h = -17 \rightarrow 20$   
 $k = 0 \rightarrow 10$   
 $l = 0 \rightarrow 19$   
 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

Extinction correction:  
*SHELXL93*  
 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 ( $\text{\AA}$ ,  $^\circ$ )

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 *XCAD4* (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<sub>1</sub>b* (non-standard setting of *Pca2<sub>1</sub>*; 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*  $\rightarrow$  *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<sub>1</sub>*. The structure was determined with the successful location of the Mo atom using *SHELXS86* (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  $\text{BF}_4$  molecule. *SHELXL93* (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  $d(\text{C—H}) = 0.930 \text{ \AA}$  and  $U_{\text{H}} = 1.2U_{\text{parent}}$ ; methyl H atoms were initially located by circular difference Fourier about the C atom in question, then optimized for tetrahedral geometry and located with  $d(\text{C—H}) = 0.960 \text{ \AA}$  and  $U_{\text{H}} = 1.5U_{\text{parent}}$ . The disordered  $\text{BF}_4$  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  $|\Delta\rho| = 0.36 \text{ e } \text{\AA}^{-3}$ . 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: *XCAD4* and *NRCVAX*. Molecular graphics: *SHELXTL* (Sheldrick, 1994). Software used to prepare material for publication: *SHELXTL*.

We are grateful to the DOE-OER (grant DEFG-0295ER14550) for support of this work.

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.

### References

- Abugideiri, F., Kelland, M. A., Poli, R. & Rheingold, A. L. (1992). *Organometallics*, **11**, 1303–1311.
- Bush, M. A., Hardy, A. D. U., Manojlovic-Muir, L. & Sim, G. A. (1971). *J. Chem. Soc. A*, pp. 1003–1009.
- Churchill, M. R. & Fennessey, J. P. (1968). *Inorg. Chem.* **7**, 953–959.
- Enraf-Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands.
- Fenn, R. H. & Cross, J. H. (1971). *J. Chem. Soc. A*, pp. 3312–3315.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Harms, K. (1993). *XCAD4. Program for the Lp-Correction of Nonius CAD-4 Diffractometer Data*. University of Marburg, Germany.
- Kubáček, P., Hoffmann, R. & Havlas, Z. (1982). *Organometallics*, **1**, 180–188.
- Lawless, G., McNally, G., Manning, A. R., Cunningham, D. & McArdle, P. (1986). *Polyhedron*, **5**, 1741–1746.
- Poli, R. (1990). *Organometallics*, **9**, 1892–1900.
- Quadrelli, A., Kraatz, H.-B. & Poli, R. (1996). *Inorg. Chem.* **35**, 5154–5162.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sim, G. A., Sime, J. G., Woodhouse, D. I. & Knox, G. R. (1979). *Acta Cryst.* **B35**, 2403–2406.
- Treichel, P. M. & Shubkin, R. L. (1967). *Inorg. Chem.* **6**, 1328–1334.