

R. Gregory Peters,^a
Jason D. Palcic^a and
Russell G. Baughman^{b*}^aDepartment of Chemistry, University of
Memphis, TN 38152, USA, and ^bDivision of
Science, Truman State University, Kirksville,
MO 63501, USACorrespondence e-mail:
baughman@truman.edu

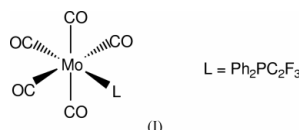
Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
Disorder in main residue
R factor = 0.034
wR factor = 0.077
Data-to-parameter ratio = 11.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Pentacarbonyl[diphenyl(perfluorovinyl)-
phosphine]molybdenum(0)

In the title compound, $[\text{Mo}\{(\text{C}_2\text{F}_3)\text{PPh}_2\}(\text{CO})_5]$, the Mo atom occupies the center of a slightly distorted octahedral environment, bound to five carbonyl groups and one phosphine ligand, so that the local symmetry of the $\text{Mo}(\text{CO})_4\text{P}$ portion of the molecule is approximately C_{4v} . The P atom sits in a distorted-tetrahedral environment; the C–P–Mo angles are much larger than the C–P–C angles. The C_2F_3 group is rotationally disordered by $\sim 180^\circ$.

Comment

Our group has focused on the synthesis and characterization of transition metal complexes ligated with P atoms bearing fluorinated substituents. We have recently described the structure of another group VI (chromium) tetracarbonyl complex bearing two phosphine ligands, both with pentafluoroethyl substituents (Peters *et al.*, 2002). Phosphorus ligands with one fluorinated substituent exhibit electronic properties that approximate those of phosphites. The structure determination of the title compound, (I), was undertaken to establish the connectivity of the ligand to the metal and to compare the structure with other known $\text{Mo}(\text{CO})_5(\text{L})$ complexes.



The metal–phosphorus distance [2.518 (9) Å] in the title compound is only slightly longer than the Mo–P bond distance [2.506 (1) Å] in $(\text{CO})_5\text{MoP}(\text{CH}_2\text{CH}_2\text{CN})_3$ (Cotton *et al.*, 1981), where the $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ ligand is viewed as moderately electron-withdrawing. The Mo–P bond distance in (I) is also significantly shorter than the Mo–P bond length [2.560 (1) Å] in the PPh_3 analog (Cotton *et al.*, 1981). These structural data, coupled with the $\nu(\text{CO})$ IR stretching data (Banger *et al.*, 1999), support the conclusion that $\text{Ph}_2\text{P}(\text{C}_2\text{F}_3)$ is a good π -acceptor ligand, with electronic characteristics that approximate those of phosphites and tris-(2-cyanoethyl)-phosphine.

The average Mo–C_{eq} distance [2.050 (8) Å] in the title compound essentially equals the average distances in the PPh_3 [2.046 (4) Å] and the $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ [2.044 (5) Å] derivatives. Although the Mo–C5 (*i.e.*, axial) distance [1.996 (4) Å] in the title compound essentially equals that in the PPh_3 [1.995 (3) Å] derivative, these distances are $\sim 3\sigma$ shorter than the 2.008 (4) Å reported for the $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ derivative. The slightly elongated Mo–C_{ax} bonds for the $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$

Received 11 November 2003
Accepted 17 November 2003
Online 29 November 2003

derivative compared with those for the title and PPh_3 compounds is likely a direct result of reduced electron density at the metal center, limiting π -backbonding into the empty π^* orbitals on CO; however, the difference is of marginal significance.

The metal sits at the center of a slightly distorted octahedral environment. The P1-Mo1-C5 axis is nearly perpendicular (Table 1) to the planar arrangement of the equatorial $\text{Mo}(\text{CO})_4$ unit, which has an r.m.s. deviation of 0.028 Å. The P1-Mo1-C5 angle is significantly ($>4\sigma$) closer to being linear than either of the two *trans* $\text{C}_{\text{eq}}-\text{Mo1}-\text{C}_{\text{eq}}$ angles (*cf.* Table 1). The geometry of the coordinated P atom is that of a compressed tetrahedron, with average Mo-P-R -group bond angles of 116.1° and average R1-P-R2 bond angles of 102.1° .

In the early stages of refinement, the presence of elongated displacement ellipsoids in the C_2F_3 group strongly suggested disorder. As the group appeared to be rotationally disordered about the P1-C18 bond by nearly 180° , refinement of the separate orientations was performed. The distances and angles of the two disordered components were initially fixed based on the Au analog (Banger *et al.*, 1999). In the final stages of refinement, the atomic positions and displacement parameters were allowed to refine independently. Component 'A', shown in Fig. 1 in bold bond lines, is the predominant species [53 (3)%]; 'B' is shown in dashed lines. Final positions indicate that 'A' and 'B' are rotated $\sim 180^\circ$ about the P1-C18 bond; the Mo1-P1-C18-F1A torsion angle is $175.2 (7)^\circ$, while the Mo1-P1-C18-F1B torsion angle is $-9.1 (8)^\circ$. The least-squares plane containing the P atom and the rotationally disordered atoms in the C_2F_3 group [*i.e.*, $\text{P1/C18/C19A/F1A/F2A/F3A/C19B/F1B/F2B/F3B}$] has an r.m.s. deviation of

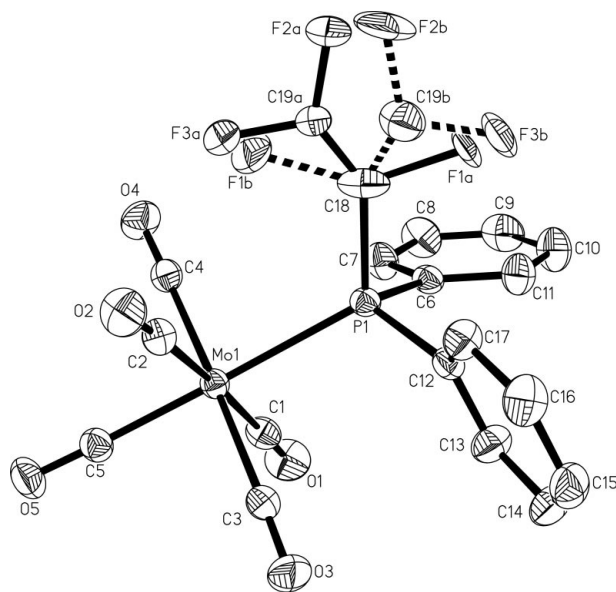


Figure 1
View of the title molecule, showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 20% probability level in order to minimize atom overlap. Component 'A', shown in bold bond lines, is the predominant [53 (3)%] C_2F_3 species; 'B' is shown in dashed lines.

0.066 Å. In addition, this plane is nearly perpendicular to the $\text{Mo}(\text{CO})_{\text{eq}}$ unit, the dihedral angle between them being $87.9 (1)^\circ$.

Experimental

The title complex was prepared by the thermolysis of $\text{Mo}(\text{CO})_6$ with one equivalent of $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_2\text{F}_3)$ in refluxing octane. The alkane solvent was removed under vacuum and the crude complex was isolated from a petroleum ether slurry at 195 K. The crude solid material was dissolved and crystals suitable for X-ray diffraction were prepared by the slow evaporation of an ether/heptane solvent mixture. An alternative method for the preparation of the title complex, as well as other routine characterization data, has been reported by Banger *et al.* (1999).

Crystal data

$[\text{Mo}(\text{C}_{14}\text{H}_{10}\text{F}_3\text{P})(\text{CO})_5]$
 $M_r = 502.18$
 Orthorhombic, *Pbca*
 $a = 10.2463 (4) \text{ \AA}$
 $b = 16.1386 (9) \text{ \AA}$
 $c = 24.5021 (13) \text{ \AA}$
 $V = 4051.7 (3) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.647 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 100 reflections
 $\theta = 7.7\text{--}16.7^\circ$
 $\mu = 0.78 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Parallelepiped, light blue
 $0.58 \times 0.55 \times 0.27 \text{ mm}$

Data collection

Bruker P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: by integration (*XSCALE*; Bruker, 1999)
 $T_{\text{min}} = 0.684$, $T_{\text{max}} = 0.806$
 4476 measured reflections
 3555 independent reflections
 2675 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -12 \rightarrow 1$
 $k = -19 \rightarrow 1$
 $l = -1 \rightarrow 29$
 3 standard reflections every 100 reflections
 intensity decay: 1.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.077$
 $S = 1.09$
 3547 reflections
 299 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.3244P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mo1—P1	2.5168 (9)	P1—C12	1.818 (3)
Mo1—C1	2.042 (4)	P1—C18	1.814 (5)
Mo1—C2	2.057 (4)	O1—C1	1.126 (4)
Mo1—C3	2.055 (4)	O2—C2	1.130 (4)
Mo1—C4	2.044 (4)	O3—C3	1.130 (4)
Mo1—C5	1.996 (4)	O4—C4	1.131 (4)
P1—C6	1.834 (3)	O5—C5	1.150 (4)
P1—Mo1—C1	90.02 (11)	C2—Mo1—C5	88.73 (14)
P1—Mo1—C2	91.43 (10)	C3—Mo1—C4	178.24 (14)
P1—Mo1—C3	90.86 (10)	C3—Mo1—C5	90.41 (15)
P1—Mo1—C4	90.85 (10)	C4—Mo1—C5	87.88 (15)
P1—Mo1—C5	178.72 (11)	Mo1—P1—C6	118.28 (11)
C1—Mo1—C2	176.24 (14)	Mo1—P1—C12	112.66 (10)
C1—Mo1—C3	88.23 (15)	Mo1—P1—C18	117.4 (2)
C1—Mo1—C4	91.34 (14)	C6—P1—C12	105.4 (2)
C1—Mo1—C5	89.9 (2)	C6—P1—C18	98.6 (2)
C2—Mo1—C3	88.27 (15)	C12—P1—C18	102.2 (2)
C2—Mo1—C4	92.11 (14)		

Eight reflections with very negative F^2 or flagged by the user for potential systematic errors were omitted from the refinement. The

C—H bond lengths were constrained at 0.96 Å with a riding model [$U_{\text{iso}}(\text{H}) = 0.080 \text{ \AA}^2$].

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS90* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL/PC* and *SHELXL93*.

This work was supported in part by a grant from the University of Memphis Faculty Research Grant Fund. This support does not necessarily imply endorsement of research conclusions by the university.

References

- Banger, K. K., Banham, R. P., Brisdon, A. K., Cross, W. I., Dament, G., Parsons, S., Pritchard, R. G. & Sousa-Pedrares, A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 427–434.
- Bruker (1996). *XSCANS*. Version 2.2. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *XSHELL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cotton, F. A., Darensbourg, D. J. & Ilsley, W. H. (1981). *Inorg. Chem.* **20**, 578–583.
- Peters, R. G., Golynskiy, M. V. & Baughman, R. G. (2002). *Acta Cryst.* **E58**, m70–m71.
- Sheldrick, G. M. (1990*a*). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1990*b*). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93*. University of Göttingen, Germany.