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Tetracarbonyl[difluoromethylenebis(diisopropoxyphosphine-*P*)]molybdenum(0)

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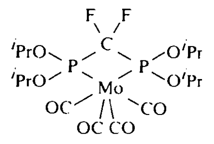
Abstract

The title compound, $[\{(^i\mathrm{PrO})_2\mathrm{PCF_2P}(\mathrm{O}^i\mathrm{Pr})_2\}\mathrm{Mo(CO)_4}]$ or $[\mathrm{Mo}(\mathrm{C_{13}H_{28}F_2O_4P_2})(\mathrm{CO})_4]$, crystallizes without imposed symmetry. The four-membered ring is folded by 21.2 (1)° about the P···P axis. The Mo—P bonds are short [2.4351 (7) and 2.4445 (8) Å] and the P—C bonds long [1.889 (2) and 1.892 (3) Å] compared with systems lacking electronegative substituents.

Comment

We are interested in the structures of diphosphines containing the P—CF$_2$—P moiety, and of their metal complexes (Fild *et al.*, 1994; Jones, 1996; Jones & Bembenek, 1996; Jones & Thöne, 1997). The structure of the CH$_2$ analogue of the title compound, (I), is known (Fild *et al.*, 1980).



(I)

The title compound crystallizes with no imposed symmetry (Fig. 1); it is not isostructural with the CH$_2$ analogue (Fild *et al.*, 1980), which crystallizes in the orthorhombic space group *Pccn*, also without imposed symmetry. The structure of the free ligand is not available for comparison.

The four-membered Mo–P–C–P ring is folded by 21.2 (1)° about the P···P axis; the ring in the CH$_2$ analogue is flatter, with a fold angle of 15.8°. The presence of a small ring is necessarily associated with large deviations from ideal bond angles. The P1—Mo—P2 'bite' angle is only 69.64 (2)°, with the corresponding P1···P2 distance being 2.7863 (9) Å; other angles at Mo are affected in turn, *e.g.* C11—Mo—P2 162.14 (7)°.

In the title compound, the Mo—P bond lengths [2.4351 (7) and 2.4445 (8) Å] are significantly shortened with respect to the CH$_2$ analogue [2.463 (2) and 2.473 (2) Å]; we and others have already noted that phosphines bearing electronegative substituents tend to form short metal–phosphorus bonds (Heuer *et al.*, 1989, and references therein). A shortening of the Mo—C bond *trans* to phosphorus is observed [2.012 (2) and 2.014 (2) Å, relative to the *cis*-Mo—C values of 2.035 (2) and 2.043 (2) Å]; in the CH$_2$ analogue, the differences were less clear-cut because of higher s.u.'s (Fild *et al.*, 1980).

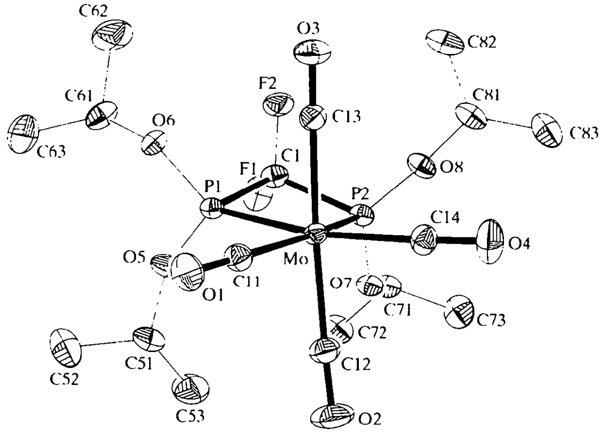


Fig. 1. The molecular structure of the title compound in the crystal. Ellipsoids represent 30% probability levels and H atoms have been omitted for clarity.

The P—C bonds are long [1.889 (2) and 1.892 (3) Å, *cf.* 1.823 (6) and 1.843 (6) Å in the CH$_2$ analogue]; we have previously observed that P—C bonds involving halogenated carbon are systematically lengthened with respect to non-halogenated systems (Jones & Bembenek, 1996, and references therein).

Experimental

The title compound was obtained from [(norbornadiene)Mo(CO)$_4$] and the disphosphine in toluene (Reichert, 1985), and recrystallized by slow cooling of a saturated solution in petroleum ether (313–333 K boiling fraction).

Crystal data

$[\mathrm{Mo}(\mathrm{C_{13}H_{28}F_2O_4P_2})(\mathrm{CO})_4]$
$M_r = 556.27$
Monoclinic
$P2_1/c$
$a = 9.887$ (2) Å
$b = 12.666$ (3) Å
$c = 20.345$ (4) Å
$\beta = 102.78$ (2)°
$V = 2484.7$ (9) Å^3
$Z = 4$
$D_x = 1.487$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0$–11.5°
$\mu = 0.708$ mm^{-1}
$T = 178$ (2) K
Irregular tablet
0.60 × 0.55 × 0.35 mm
Colourless

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Data collection

Nicolet $R3$ diffractometer
ω scans
Absorption correction:
  ψ scans (*XEMP*; Siemens 1994*a*)
  $T_{min} = 0.732$, $T_{max} = 0.817$
11 818 measured reflections
5729 independent reflections
4696 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.56°$
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -26 \rightarrow 25$
3 standard reflections every 147 reflections intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 1.029$
5729 reflections
280 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.0618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0052 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mo—C11	2.012 (2)	Mo—P1	2.4351 (7)
Mo—C14	2.014 (2)	Mo—P2	2.4445 (8)
Mo—C13	2.035 (2)	P1—C1	1.889 (2)
Mo—C12	2.043 (2)	P2—C1	1.892 (3)
P1—Mo—P2	69.64 (2)	F1—C1—F2	105.89 (18)
C1—P1—Mo	95.75 (8)	P1—C1—P2	94.93 (10)
C1—P2—Mo	95.37 (7)		

Methyl H atoms were included using rigid groups (starting positions were taken from difference syntheses and then allowed to rotate but not tip). Methine H atoms were treated using a riding model starting from calculated positions.

Data collection: *P*3 *Software* (Nicolet, 1987). Cell refinement: *P*3 *Software*. Data reduction: *XDISK* in *P*3 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

The title compound was synthesized and entrusted to me by Dr J. Martens and Professor M. Fild, to whom I am grateful. I thank the Fonds der Chemischen Industrie for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1251). Services for accessing these data are described at the back of the journal.

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