metal-organic compounds

cis-Tetracarbonyl[(4-fluorophenyl)-diphenylphosphine-P](piperidine-N)-molybdenum(0)

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The title molecule, $[Mo\{P(C_6H_5)_2(C_6H_4F)\}(HNC_5H_{10})(CO)_4]$ or $[Mo(C_{18}H_{14}FP)(C_5H_{11}N)(CO)_4]$, has irregular octahedral geometry about the Mo atom. The molecules form a complicated hydrogen-bonded network comprising C—H···O, C—H···F and C—H···π hydrogen bonds and π–π interactions. The C—H···π and π–π interactions form chains containing C—H···π/π–π dimers linked via C—H···π interactions and the chains are linked into a three-dimensional network via C—H···O and C—H···F hydrogen bonds.

Comment

The molybdenum(0) complex cis-$[Mo(CO)_4(HNC_5H_{10})_2]$ is a convenient precursor for a range of cis-$[Mo(CO)_4L_2]$ (L = phosphine, phosphite, etc) complexes. Structural studies on a wide range of such complexes have been reported. However, to date, the structures of only three other intermediate piperidine–phosphine complexes, namely cis-$[Mo(CO)_4(HN-C_5H_{10})(PR_3)]$, where R is Me$_2$Ph, MePh$_2$ and Ph$_3$, have been reported (Cotton et al., 1982a). A diffraction study of cis-tetracarbonyl[(4-fluorophenyl)diphenylphosphine-P](piper-N)molybdenum(0), (I) (Fig. 1), reveals a structure similar to that of $[Mo(CO)_4(HNC_5H_{10})(PPhMe_2)]$ [(II); Cotton et al., 1982b], but with a significantly smaller P—Mo—N angle [86.28 (7)° for (I) versus 90.77 (7)° for (II); see Table 1]. The piperidine ligand of (I) exhibits the expected chair conformation, and the distances and angles of this ligand are similar to those found for (II).

The geometry about the P atom is distorted tetrahedral and similar to the analogous complex cis-$[Mo(CO)_4\{P(C_6H_4-F-4)_3\}_2]$ [(III); Alyea et al., 1994]. The molecules of (I) are involved in a number of C—H···O intermolcular interactions from both the piperidine and phenyl groups, forming a three-dimensional network (see Table 2). The ability of C—H to act as a hydrogen-bond donor to oxygen was established by Taylor & Kennard (1982). They showed that C—H···O interactions (i) are essentially electrostatic in nature, (ii) show C···O distances ranging from 3 to 4 Å and (iii) are likely to be

linear. The phosphine ligands are involved in C—H···π and π–π interactions with contacts from the ring centres to H atoms of 3.5 and 3.1 Å, respectively. These C—H···π and π–π interactions combine to form chains along the c axis and these

(I)
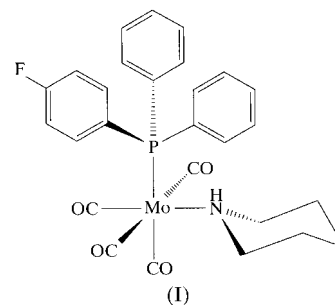
chains can be thought of as containing C—H···π/π–π dimers linked via C—H···π interactions. These C—H···π/π–π interactions between the phenyl rings of phenylphosphines are well known and have been extensively investigated by Dance and co-workers (Dance & Scudder, 1995, 1996a,b; Lewis & Dance, 2000). The steric demands of the Mo coordination sphere promote formation of an unusual intramolecular N—H···π hydrogen bond between one of the phenyl rings and the N atom of the piperidine moiety. The fluoro substitutent of the 4-fluorophenyl ring is disordered over two rings, with a 58.8 (7)% occupancy for the major position, which is involved in an intermolecular C—H···F interaction with the piperidine moiety (Table 2). A comparison of the Mo—P bond lengths for (I), (II) (Cotton et al., 1982b) and the related complex (III) (Alyea et al., 1994), which contains 4-fluorophenyl groups, shows that the Mo—P bond in (I) is shorter than in (II); the values are 2.5670 (10) and 2.576 (2) Å, respectively, and are consistent with the Mo—P bond length of 2.5644 (4) Å in (III). Evidently, while the presence of an F atom in the para position of the phenyl ring has no effect upon the P—C
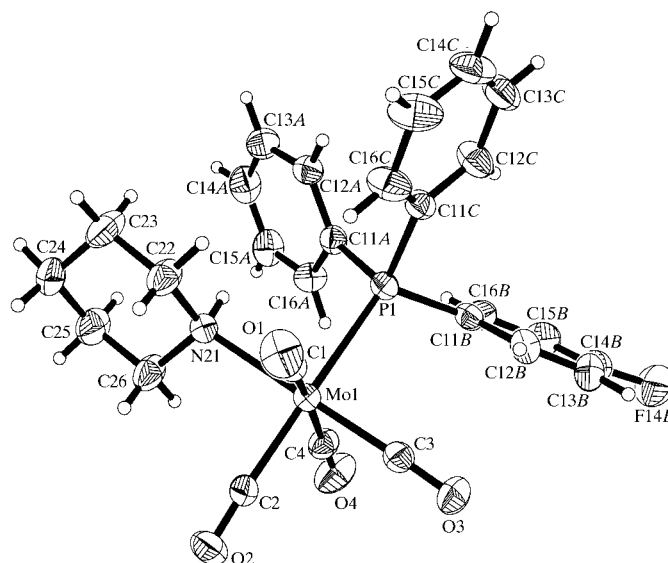

Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids. The minor disorder component is not shown for clarity.

distances and P—C—P angles, it does reduce the Mo—P distance significantly; this is consistent with the steric argument put forward by Alyea *et al.* (1994).

Experimental

The title complex was obtained in small yield as a by-product of the reaction between *cis*-[Mo(CO)$_4$(HNC$_5$H$_{10}$)$_2$] and two equivalents of PPh$_2$(C$_6$H$_4$F-4) in dichloromethane. Crystals were obtained by cooling the reaction mixture to 273 K and were separated manually from those of *cis*-[Mo(CO)$_4${PPh$_2$(C$_6$H$_4$F-4)}$_2$].

Crystal data

[Mo(C$_{18}$H$_{14}$FP)(C$_5$H$_{11}$N)(CO)$_4$]	$D_x = 1.454$ Mg m^{-3}
$M_r = 573.39$	Mo $K\alpha$ radiation
Monoclinic, $C2$	Cell parameters from 6006
$a = 13.601$ (3) Å	reflections
$b = 10.981$ (3) Å	$\theta = 2$–24°
$c = 17.973$ (4) Å	$\mu = 0.60$ mm^{-1}
$\beta = 102.598$ (6)°	$T = 301$ (2) K
$V = 2619.9$ (11) Å^3	Block, pale yellow
$Z = 4$	$0.32 \times 0.19 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	4121 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.048$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$\theta_{max} = 25.0°$
	$h = -16 \rightarrow 16$
$T_{min} = 0.831$, $T_{max} = 0.899$	$k = -12 \rightarrow 13$
12 823 measured reflections	$l = -21 \rightarrow 21$
1975 independent reflections (plus 2622 Friedel-related reflections)	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0352P)^2]$
$R(F) = 0.033$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} = 0.004$
$S = 1.00$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
4597 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
327 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.27 (3)

Analysis of the difference map and the displacement parameters of the (4-fluorophenyl)diphenylphosphine ligand revealed that the benzene ring with the *para*-fluoro substituent has two different orientations relative to the piperidine ligand. This has been modelled as a disorder of the F atom over the two rings, with an occupancy factor of 58.8 (7)% for the major component. Refinement of the Flack (1983) parameter showed the crystal to be racemically twinned, with 27 (3)% occupying the minor configuration within the crystal. H atoms were added at idealized positions 0.93 Å from phenyl C atoms, 0.97 Å from methylene C atoms and 0.91 Å from N21; they were then refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

Mo1—C1	2.053 (5)	P1—C11B	1.840 (4)
Mo1—C2	1.971 (4)	P1—C11C	1.829 (4)
Mo1—C3	1.956 (4)	C14A—F14A	1.339 (8)
Mo1—C4	2.024 (4)	C1—O1	1.134 (5)
Mo1—N21	2.339 (3)	C2—O2	1.150 (4)
Mo1—P1	2.5670 (10)	C3—O3	1.164 (4)
P1—C11A	1.827 (4)	C4—O4	1.140 (5)
C1—Mo1—C2	86.87 (15)	C2—Mo1—P1	173.15 (12)
C1—Mo1—C3	88.88 (17)	C3—Mo1—C4	84.32 (16)
C1—Mo1—C4	169.94 (17)	C3—Mo1—N21	178.36 (15)
C1—Mo1—N21	92.50 (13)	C3—Mo1—P1	92.29 (12)
C1—Mo1—P1	99.85 (10)	C4—Mo1—N21	94.42 (13)
C2—Mo1—C3	89.15 (16)	C4—Mo1—P1	87.85 (12)
C2—Mo1—C4	85.63 (16)	N21—Mo1—P1	86.60 (8)
C2—Mo1—N21	91.80 (13)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N21—H21$\cdots$C11A	0.91	2.46	3.231 (4)	142
N21—H21$\cdots$C16A	0.91	2.59	3.398 (5)	148
C14C—H14$C\cdots$O1^{i}	0.93	2.68	3.352 (6)	130
C13C—H13$C\cdots$O3^{i}	0.93	2.93	3.535 (6)	124
C23—H23$A\cdots$O2^{ii}	0.97	2.70	3.467 (6)	137
C24—H24$B\cdots$O4^{iii}	0.97	2.80	3.468 (6)	127
C24—H24$A\cdots$F14A^{iv}	0.97	2.77	3.618 (9)	146

Symmetry codes: (i) $1-x, y, 1-z$; (ii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z$.

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1444). Services for accessing these data are described at the back of the journal.

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