

METAL-ORGANIC COMPOUNDS

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[Bis(3-aminopropyl)phenylphosphine-*N,P*]-tetracarbonylmolybdenum(0)

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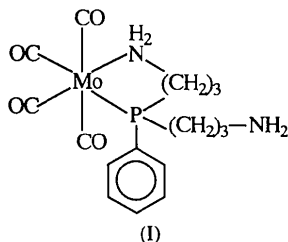
Abstract

The Mo atom in the title complex, $[\text{Mo}(\text{C}_{12}\text{H}_{21}\text{N}_2\text{P})(\text{CO})_4]$, has distorted octahedral coordination geometry with a bidentate chelating bap [bap = bis(3-aminopropyl)phenylphosphine] ligand. The Mo—P and Mo—N distances are 2.4979 (12) and 2.326 (4) Å, respectively. The Mo—C(CO) distances vary according to the nature of the *trans* ligand, with the Mo—CO distance *trans* to N [1.933 (5) Å] being significantly shorter than that *trans* to P [1.983 (5) Å], or when the CO ligands are mutually *trans* [2.029 (5) and 2.015 (5) Å].

Comment

Synthesis of the hybrid NPN donor ligand bap has been reported in high yield from the photochemically induced free-radical reaction between PhPH₂ and two equivalents of allylamine (Uriarte, Mazanec, Tau & Meek, 1980). The reaction of bap with *cis*-[Mo(CO)₄(pip)₂] was reported to give the tricarbonyl product *fac*-[Mo(CO)₃(bap)] in which the bap ligand was suggested to be tridentate (Beckett, Cassidy & Duffin, 1991). An X-ray structure determination of this product was undertaken in order to determine the correct stoichiometry and exact mode of bonding.

The present study identifies the product (I) as a tetracarbonyl rather than a tricarbonyl species, with the bap



ligand being bidentate through P and one N donor atom. The structure of a single molecule is shown in Fig. 1. The Mo⁰ centre has slightly distorted octahedral coordination geometry, with the P and N donor atoms of the bap ligand mutually *cis*. The angles at Mo involving the *cis* ligands vary from 85.53 (13) to 92.6 (2)° and those involving the *trans* ligands from 176.4 (2) to 179.1 (2)°. The Mo—P and Mo—N distances are 2.4979 (12) and 2.326 (4) Å, respectively. The four Mo—C(CO) distances show considerable variation, with that *trans* to N [1.933 (5) Å] being significantly shorter than that *trans* to P [1.983 (5) Å], or when the CO ligands are mutually *trans* [2.029 (5) and 2.015 (5) Å]. The four C—O bond lengths [1.140 (5)–1.163 (5) Å] are equal within experimental error, and the Mo—C—O moieties are almost linear with angles at the C atom varying from 174.3 (4) to 179.0 (5)°. The angles at C7 and C8 in the two —CH₂CH₂CH₂N— moieties are basically the same [115.2 (3) and 115.7 (3)°, respectively] but those at C5 and C6 [114.1 (3) and 115.1 (4)°, respectively] are *ca* 4° larger than those at C9 and C10 [111.7 (5) and 110.1 (7)°, respectively], which probably reflect some strain in the chelating moiety. It is also observed that one of the tetrahedral angles at P [Mo—P—C11 118.5 (1)°] is considerably larger than the others [102.7 (2)–112.8 (2)°], which may result from steric interactions involving the phenyl group. Other bond lengths and angles are as expected.

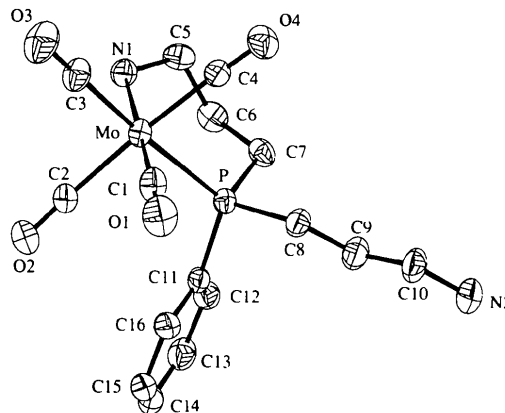


Fig. 1. Structure of $[\text{Mo}(\text{CO})_4(\text{bap})]$ showing 40% probability ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

Group 6 metal complexes of the related NNN or PPP donor ligands $(\text{NH}_2\text{CH}_2\text{CH}_2)\text{NH}$ or $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPH}$ have been reported (Abel, Bennett & Wilkinson, 1959; King, Kapour & Kapour, 1971; King & Cloyd, 1975) and depending upon the reaction conditions either the tricarbonyl or tetracarbonyl complexes are obtained.

Experimental

Single crystals of the title compound were grown from a chloroform solution of the complex layered with hexane and left undisturbed overnight at room temperature.

Crystal data

[Mo(C ₁₂ H ₂₁ N ₂ P)(CO) ₄]	Mo K α radiation
$M_r = 432.26$	$\lambda = 0.71069 \text{ \AA}$
Orthorhombic	Cell parameters from 250 reflections
<i>Pbca</i>	$\theta = 2.83\text{--}29.75^\circ$
$a = 18.479 (4) \text{ \AA}$	$\mu = 0.783 \text{ mm}^{-1}$
$b = 14.511 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 14.389 (4) \text{ \AA}$	Prism
$V = 3858.4 (19) \text{ \AA}^3$	$0.25 \times 0.16 \times 0.10 \text{ mm}$
$Z = 8$	Light yellow
$D_x = 1.488 \text{ Mg m}^{-3}$	

Data collection

FAST area-detector diffractometer	4987 independent reflections
Collection method: see Darr, Drake, Hursthouse & Malik (1993)	2588 observed reflections
Absorption correction: none	$[I > 2\sigma(I)]$
23240 measured reflections	$R_{\text{int}} = 0.0489$
	$\theta_{\text{max}} = 29.75^\circ$
	$h = -19 \rightarrow 25$
	$k = -18 \rightarrow 19$
	$l = -19 \rightarrow 15$

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.650 \text{ e \AA}^{-3}$
$R(F) = 0.0362$	$\Delta\rho_{\text{min}} = -0.448 \text{ e \AA}^{-3}$
$wR(F^2) = 0.1275$	Extinction correction: none
$S = 0.653$	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
4987 reflections	
250 parameters	
H atoms refined isotropically	
$w = 1/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{\text{max}} = -0.405$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Mo	0.10378 (2)	0.12054 (2)	0.15777 (2)	0.05891 (13)
P	0.19620 (6)	0.02902 (7)	0.07099 (7)	0.0590 (3)
C1	0.1183 (3)	0.0504 (4)	0.2705 (3)	0.0846 (13)
O1	0.1264 (3)	0.0071 (3)	0.3378 (3)	0.127 (2)
C2	0.0239 (3)	0.0299 (3)	0.1258 (3)	0.0723 (11)
O2	-0.0191 (2)	-0.0252 (2)	0.1140 (3)	0.1052 (12)
C3	0.0349 (3)	0.1992 (3)	0.2275 (4)	0.0903 (15)
O3	-0.0033 (3)	0.2441 (3)	0.2716 (3)	0.140 (2)
C4	0.1868 (3)	0.2038 (3)	0.1924 (3)	0.0708 (11)
O4	0.2357 (2)	0.2483 (2)	0.2124 (3)	0.1027 (12)
C5	0.1452 (3)	0.2263 (3)	-0.0435 (3)	0.0791 (14)
C6	0.1822 (3)	0.1438 (3)	-0.0860 (3)	0.0792 (13)
C7	0.2358 (3)	0.0959 (3)	-0.0240 (3)	0.0730 (12)
N1	0.0858 (2)	0.2028 (3)	0.0209 (3)	0.0720 (9)
C8	0.2761 (3)	-0.0001 (3)	0.1429 (3)	0.0760 (12)
C9	0.3389 (3)	-0.0415 (4)	0.0917 (4)	0.096 (2)
C10	0.4033 (3)	-0.0571 (6)	0.1554 (6)	0.119 (2)
N2	0.4641 (4)	-0.0986 (5)	0.1024 (9)	0.153 (3)
C11	0.1688 (2)	-0.0809 (2)	0.0194 (3)	0.0621 (10)

C12	0.1775 (3)	-0.1016 (3)	-0.0729 (3)	0.0779 (13)
C13	0.1513 (3)	-0.1830 (4)	-0.1095 (4)	0.094 (2)
C14	0.1178 (3)	-0.2456 (4)	-0.0531 (5)	0.099 (2)
C15	0.1100 (3)	-0.2282 (3)	0.0379 (5)	0.095 (2)
C16	0.1349 (3)	-0.1448 (3)	0.0749 (4)	0.0777 (12)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo—C1	1.933 (5)	C4—O4	1.148 (5)
Mo—C3	1.983 (5)	C5—N1	1.476 (6)
Mo—C4	2.015 (5)	C5—C6	1.508 (6)
Mo—C2	2.029 (5)	C6—C7	1.504 (6)
Mo—N1	2.326 (4)	C8—C9	1.499 (6)
Mo—P	2.4979 (12)	C10—N2	1.484 (10)
P—C7	1.829 (4)	C11—C12	1.372 (6)
P—C11	1.831 (4)	C11—C16	1.375 (6)
P—C8	1.852 (5)	C12—C13	1.381 (6)
C1—O1	1.163 (5)	C13—C14	1.366 (8)
C2—O2	1.140 (5)	C14—C15	1.341 (8)
C3—O3	1.150 (5)	C15—C16	1.401 (6)
C1—Mo—C3	88.1 (2)	C8—P—Mo	112.79 (15)
C1—Mo—C4	90.2 (2)	O1—C1—Mo	179.0 (5)
C3—Mo—C4	91.0 (2)	O2—C2—Mo	174.3 (4)
C1—Mo—C2	87.1 (2)	O3—C3—Mo	176.9 (5)
C3—Mo—C2	91.2 (2)	O4—C4—Mo	177.3 (4)
C4—Mo—C2	176.4 (2)	N1—C5—C6	114.1 (3)
C1—Mo—N1	179.1 (2)	C7—C6—C5	115.1 (4)
C3—Mo—N1	92.4 (2)	C6—C7—P	115.2 (3)
C4—Mo—N1	90.6 (2)	C5—N1—Mo	123.0 (3)
C2—Mo—N1	92.1 (2)	C9—C8—P	115.7 (4)
C1—Mo—P	92.6 (2)	C8—C9—C10	111.7 (5)
C3—Mo—P	176.5 (2)	N2—C10—C9	110.1 (7)
C4—Mo—P	85.53 (13)	C12—C11—C16	118.0 (4)
C2—Mo—P	92.23 (13)	C12—C11—P	123.4 (3)
N1—Mo—P	86.96 (11)	C16—C11—P	118.5 (3)
C7—P—C11	105.7 (2)	C11—C12—C13	121.0 (5)
C7—P—C8	102.7 (2)	C14—C13—C12	120.1 (6)
C11—P—C8	104.4 (2)	C15—C14—C13	120.3 (5)
C7—P—Mo	111.40 (15)	C14—C15—C16	119.9 (5)
C11—P—Mo	118.48 (14)	C11—C16—C15	120.8 (5)

The unit-cell and intensity data were recorded at 293 K on a FAST area-detector diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The amino H atoms were located experimentally and refined isotropically with the N—H distance constrained at 0.95 \AA ; other H atoms were included in idealized positions (C—H = 0.93 \AA) with U_{iso} freely refined.

Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pentacarbonyl(difluoromethyl isocyanide)-chromium at 128 K

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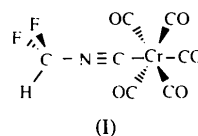
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Abstract

The monomeric molecule of the title compound, [Cr(C₂HF₂N)(CO)₅], is best described as an octahedral complex of chromium(0). The Cr—C bond distance to the difluoromethyl isocyanide ligand [1.956 (2) Å] is longer than the distances to the carbonyl ligands [Cr—CO_{cis} 1.909 (2)–1.915 (2), Cr—CO_{trans} 1.900 (2) Å], indicating a smaller π-acceptor/σ-donor ratio of the isocyanide ligand in comparison with the carbonyl ligands.

Comment

The structural data of complexes of the type (CO)₅CrL can provide important information on the properties of the ligand L, both from the Cr—L distance and from the Cr—C distance to the *trans* carbonyl ligand, which is very sensitive to the σ-donor/π-acceptor ratio of the ligand L. In order to obtain more detailed information on the fluorine-substitution effect in methyl isocyanides, the structure of pentacarbonyl(difluoromethyl isocyanide)-chromium, (I) (m.p. 300 K), was determined at 128 K.



A view of the title molecule and the atom-numbering scheme are given in Fig. 1. The Cr atom is almost octahedrally coordinated by five carbonyl ligands and the difluoromethyl isocyanide ligand. The Cr—C distances to the *cis* carbonyl ligands are similar within 2σ and close to that found for hexacarbonylchromium (Jost, Rees & Yelon, 1975; Whitaker & Jeffery, 1967), whereas this bond distance is slightly shorter for the *trans* carbonyl ligand. The Cr—C distances for related (CO)₅Cr(CNR) complexes are summarized in Table 3 and show that a short Cr—C bond to the isocyanide ligand results in a long Cr—C bond to the *trans* carbonyl ligand and *vice versa*. Short metal–carbon bonds are observed for the strong π-acceptor isocyanide ligand. Although a direct comparison with the trifluoromethyl isocyanide ligand is not possible since the electron-diffraction data for [(CO)₅Cr(CNCF₃)] (Oberhammer & Lentz, 1985) have not allowed determination of individual Cr—C bond lengths, a Cr—C bond of 1.956 (2) Å suggests that, in agreement with the spectroscopic data of Lentz & Preugschat (1992a), the difluoromethyl isocyanide moiety is the weaker π-acceptor ligand. A very short Cr—C bond of 1.814 (6) Å to the strong π-acceptor

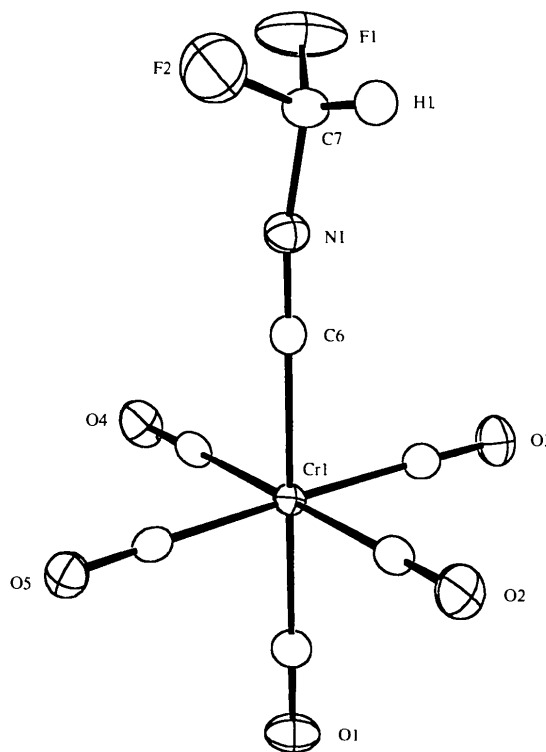


Fig. 1. Molecular structure of the title compound with the crystallographic numbering scheme (ORTEP; Johnson, 1971).