Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (*XSCANS*; Siemens, 1994)
$T_{min} = 0.691$, $T_{max} = 0.892$
10659 measured reflections
9197 independent reflections
4804 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.51°$
$h = -1 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = -23 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.121$
$S = 0.810$
9197 reflections
577 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 1.03$ e Å^{-3} (0.93 Å from Mo2)
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mo1—C19	2.017 (5)	P2—C33	1.825 (5)
Mo1—C20	2.024 (5)	P2—C27	1.838 (5)
Mo1—P1	2.4900 (12)	P2—C21	1.844 (5)
Mo2—C40	2.017 (5)	Cl1—C4	1.743 (5)
Mo2—C39	2.029 (6)	Cl2—C10	1.732 (5)
Mo2—P2	2.4760 (12)	Cl3—C16	1.746 (5)
P1—C13	1.836 (4)	Cl4—C24	1.739 (6)
P1—C7	1.838 (5)	Cl5—C30	1.750 (5)
P1—C1	1.843 (5)	Cl6—C36	1.733 (5)
C19—Mo1—C20	90.6 (2)	C7—P1—Mo1	111.85 (15)
C19—Mo1—P1	89.45 (14)	C1—P1—Mo1	116.71 (15)
C20—Mo1—P1	87.15 (13)	C33—P2—C27	103.9 (2)
C40—Mo2—C39	89.8 (2)	C33—P2—C21	103.0 (2)
C40—Mo2—P2	88.86 (13)	C27—P2—C21	97.8 (2)
C39—Mo2—P2	87.00 (14)	C33—P2—Mo2	110.96 (14)
C13—P1—C7	102.3 (2)	C27—P2—Mo2	118.6 (2)
C13—P1—C1	100.5 (2)	C21—P2—Mo2	120.3 (2)
C7—P1—C1	103.8 (2)	O3—C39—Mo2	177.5 (5)
C13—P1—Mo1	119.5 (2)	O4—C40—Mo2	179.4 (5)

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All the H atoms were located from difference Fourier maps and refined isotropically. Computer program *PARST* (Nardelli, 1983) was used for geometrical calculations.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1322). Services for accessing these data are described at the back of the journal.

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Tetracarbonyl[2-(diphenylphosphino)aniline-*N*,*P*]molybdenum(0)

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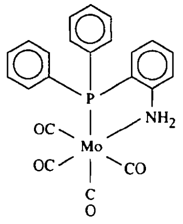
Abstract

In the title complex, $[Mo(CO)_4(C_{18}H_{16}NP)]$, coordination about the central metal is distorted octahedral. The five-membered $MoNC_2P$ chelate ring has an 'envelope' conformation with the Mo atom deviating from the plane defined by the four non-metal atoms.

Comment

The title compound, (I), $[Mo(CO)_4\{(C_6H_5)_2PC_6H_4\text{-}NH_2\}]$, was prepared as part of a series of our continuing studies on transition metal derivatives containing NH, OH and SH functional PR_3 ligands (Dahlenburg, Herbst & Kühnlein, 1997; Dahlenburg & Kühnlein, 1997; Dahlenburg & Herbst, 1997; Dahlenburg, Herbst & Liehr, 1997). This crystal structure was determined in order to make comparisons with related tetracarbonylmolybdenum complexes bearing bidentate ligands with NH_2 and $P(C_6H_5)_2$ donor groups.



(I)

As indicated in Fig. 1, the overall molecular geometry about the central Mo atom of (I) corresponds to distorted octahedral. The $(C_6H_5)_2PC_6H_4NH_2$ ligand acts as an *N,P*-bidentate ligand, giving rise to a five-membered chelate structure. The chelate ring exhibits a bend along the N···P direction of 25.2 (1)°, *i.e.* it adopts an envelope conformation with the metal atom deviating by 0.81 (1) Å from the plane defined by atoms N, P, C17 and C18. The structure of (I) can be compared to those previously reported for [$Mo(CO)_4\{H_2NCH_2CH_2N(H)CH_2C_6H_5\}$] (II) (Shiu, Wang & Liao, 1991), [$Mo(CO)_4\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}$] (III) (Bernal, Reisner, Dobson & Dobson, 1986), and [$Mo(CO)_4\{(C_6H_5)_2CH{=}CHP(C_6H_5)_2\}$] (IV) (Ueng & Leu, 1991). As a consequence of the distinct *trans* bond-weakening influence of strong σ-donor/π-acceptor ligands, the two mutually *trans* carbonyl ligands of all four complexes show longer Mo—C distances [2.012 (3) and 2.041 (3) Å for (I) *versus* 2.022 (5) and 2.028 (5) Å for (II), 2.030 (9) and 2.053 (9) Å for (III), and 2.022 (5) and 2.038 (5) Å for (IV)] than do the two *trans* to $P(C_6H_5)_2$ [1.986 (2) Å for (I) *versus* 1.974 (8) and 1.999 (8) Å for (III), and 1.976 (5) and 1.993 (5) Å for (IV)] and NH_2 [1.949 (3) Å for (I) *versus* 1.953 (4) Å for (II)]. The significant difference in Mo—CO bond lengths observed for the latter two groups of carbonyl ligands is expected, because an NH_2 group is at the *trans* position for the shorter one and is known to be a weaker *trans*-influencing group than the $P(C_6H_5)_2$ residue which is *trans* to the longer metal-to-carbonyl bonds. The Mo—NH_2 distance in (I), 2.326 (2) Å, is close to that reported for compound (II), 2.342 (3) Å, and also to the lengths of the two Mo—NH_2 bonds in *fac*-[$Mo(CO)_3\{HN(CH_2CH_2NH_2)_2\}$], 2.311 (19) and 2.348 (18) Å (Cotton & Wing, 1965). The Mo—$P(C_6H_5)_2$ bond length measured for the title compound, 2.4994 (8) Å, also compares favorably with those in both (III), 2.495 (2) and 2.500 (2) Å, and (IV), 2.494 (1) and 2.501 (1) Å. The chelate bite angle of (I), 75.70 (5)°, is slightly smaller than the N—Mo—N and P—Mo—P angles of the other three tetracarbonyl derivatives [77.0 (1) for (II), 78.58 (4) for (IV) and and 80.2 (1)° for (III)].

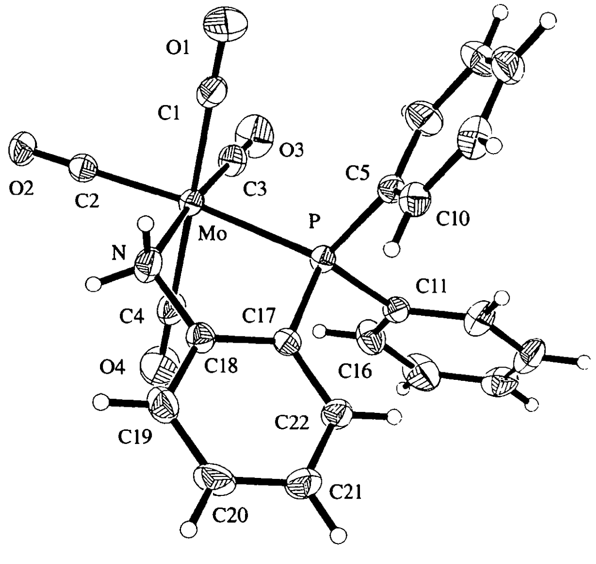


Fig. 1. The structure of the title complex with displacement ellipsoids drawn at the 50% probability level.

Experimental

The synthesis of (I) was carried out by reacting [$Mo(CO)_6$] with *ortho*-$(C_6H_5)_2PC_6H_4NH_2$ in a 1:1 stoichiometry in refluxing toluene for 2 h. IR (KBr): 1843, 1870, 1910, 2020 [all ν(CO)], 3273, 3317 cm^{-1} [both ν(NH)]; ^{1}H NMR (CD_2Cl_2): δ 4.61 (*s*, NH_2); ^{13}C NMR (CD_2Cl_2): δ 208.5 [*d*, *cis*-^2J(P,C) = 8.8 Hz, 2 CO], 217.3 [*d*, *trans*-^2J(P,C) = 32.3 Hz, 1 CO], 220.8 [*d*, *cis*-^2J(P,C) = 7.4 Hz, 1 CO]; ^{31}P NMR (CD_2Cl_2): δ = 43.8 (*s*). Single crystals were obtained from the CD_2Cl_2 solutions used for NMR measurements.

Crystal data

[$Mo(CO)_4(C_{18}H_{16}NP)$]
M_r = 485.27
Triclinic
$P\bar{1}$
a = 9.157 (3) Å
b = 10.815 (3) Å
c = 10.855 (4) Å
α = 75.78 (1)°
β = 85.90 (1)°
γ = 84.42 (1)°
V = 1035.9 (6) Å^3
Z = 2
D_x = 1.556 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 26 reflections
θ = 16–21°
μ = 0.738 mm^{-1}
T = 293 (2) K
Block
0.18 × 0.13 × 0.13 mm
Bright yellow

Data collection

Philips PW1100 diffractometer (locally updated; Gomm, 1993)
ω/θ scans
Absorption correction: none
8172 measured reflections
4086 independent reflections
3680 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.078
$\theta_{\rm max}$ = 26.04°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.058$
$S = 1.129$
4079 reflections
262 parameters
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = -0.004$
$\Delta\rho_{\max} = 0.326$ e Å^{-3}
$\Delta\rho_{\min} = -0.776$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Mo—C3	1.949 (3)	Mo—P	2.4994 (8)
Mo—C2	1.986 (2)	O1—C1	1.149 (4)
Mo—C1	2.012 (3)	O2—C2	1.151 (3)
Mo—C4	2.041 (3)	O3—C3	1.160 (4)
Mo—N	2.326 (2)	O4—C4	1.128 (4)
C3—Mo—C2	88.08 (10)	C3—Mo—P	99.42 (7)
C3—Mo—C1	89.89 (12)	C2—Mo—P	172.24 (6)
C2—Mo—C1	91.33 (11)	C1—Mo—P	90.66 (8)
C3—Mo—C4	91.74 (13)	C4—Mo—P	88.72 (8)
C2—Mo—C4	89.08 (11)	N—Mo—P	75.70 (5)
C1—Mo—C4	178.33 (11)	O1—C1—Mo	178.9 (2)
C3—Mo—N	175.00 (7)	O2—C2—Mo	178.3 (3)
C2—Mo—N	96.75 (8)	O3—C3—Mo	179.2 (2)
C1—Mo—N	91.28 (10)	O4—C4—Mo	178.6 (3)
C4—Mo—N	87.07 (11)		

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The final structural model used anisotropic displacement parameters for the non-H atoms. The H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to $1.2U_{eq}$ of their carrier atoms.

Data collection: local diffractometer software (Gomm, 1993). Cell refinement: local diffractometer software. Data reduction: local diffractometer software. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1116). Services for accessing these data are described at the back of the journal.

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(2,2′-Bipyridine)(flavonolato)copper(II) Perchlorate,† [Cu(bpy)(fla)]ClO$_4$

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Abstract

3-Hydroxyflavone coordinates to Cu^{II} together with the auxiliary ligand 2,2′-bipyridine to form a stable cationic flavonolato–copper(II) complex, [Cu(C$_{15}$H$_9$O$_3$)(C$_{10}$H$_8$N$_2$)]ClO$_4$. The complex has distorted square pyramidal geometry. Two O atoms of the flavonol and the N atoms of the chelating bpy ligand are in the basal position, while a perchlorate O atom occupies the apical position.

Comment

Quercetin 2,3-dioxygenase is a Cu^{II}-containing enzyme which catalyses the degradation of quercetin and related compounds into a depside (phenolic carboxylic acid ester) (Westlake, Talbot, Blakely & Simpson, 1959; Takamura & Ito, 1977). Quercetin coordinates to the copper(II) ion and flavonol forms stable Cu^{I} and Cu^{II} compounds (Speier, Fülöp & Párkányi, 1990; Balogh-Hergovich, Speier & Argay, 1991). Simple flavonolato–copper complexes have been used as model compounds and in model reactions (Utaka, Hojo, Fujii & Takeda, 1984; Utaka & Takeda, 1985). Following this, we report here the molecular structure of a cationic mixed-

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† Alternative name: (2,2′-bipyridyl-*N*,*N*′)(4-oxo-2-phenyl-4*H*-chromen-3-olato-*O*^{3},*O*^{4})copper(II) perchlorate.