Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Re(1)—P(1)	2·474 (5)	C(1)—O(1)	1·208 (28)
—O(8)	2·173 (13)	C(2)—O(2)	1·196 (28)
—C(1)	1·889 (21)	C(3)—O(3)	1·211 (30)
—C(2)	1·823 (23)	C(4)—O(4)	1·189 (28)
—C(3)	1·841 (24)	C(5)—O(5)	1·137 (30)
—C(63)	2·179 (11)	C(6)—O(6)	1·155 (29)
		C(7)—O(7)	1·183 (32)
Re(2)—P(2)	2·437 (5)	C(8)—O(8)	1·293 (25)
—C(4)	1·899 (23)	C(8)—C(62)	1·451 (24)
—C(5)	1·988 (24)		
—C(6)	1·918 (31)	O(8)—Re(1)—C(63)	74·9 (4)
—C(7)	1·917 (25)	Re(1)—O(8)—C(8)	121·2 (12)
—C(8)	2·116 (22)	O(8)—C(8)—C(62)	110·9 (16)
		C(8)—C(62)—C(63)	121·6 (13)
P(1)—C(16)	1·828 (14)	C(62)—C(63)—Re(1)	111·0 (8)
—C(26)	1·826 (13)		
—C(36)	1·812 (12)	C(8)—Re(2)—P(2)	79·7 (6)
		Re(2)—P(2)—C(61)	101·6 (4)
P(2)—C(46)	1·803 (13)	P(2)—C(61)—C(62)	117·0 (9)
—C(56)	1·819 (14)	C(61)—C(62)—C(8)	118·3 (13)
—C(61)	1·817 (12)	C(62)—C(8)—Re(2)	123·2 (13)

and the analogous Re—O—C—C—C ring in $[C_6H_5CO(o\text{-}C_6H_4)Re(CO)_3\{P(C_6H_5)_3\}]$ [C—Re—O 74·4 (4), Re—O—C 117·7 (9), O—C—C 119·1 (12), C—C—C 115·7 (10), C—C—Re 112·6 (7)°] (Preut & Haupt, 1980) are different. These variations of the internal bond angles at the non-metal ring atoms are connected with the change in substituent attached to the benzoylic C(8) atom, from $Re(CO)_4$ to a phenyl group. The Re(1) ring, like the corresponding ring of the above-mentioned metalation product of benzophenone, is planar. This ring property and the comparable bond lengths $\{[Re(C_{13}H_9O)(C_{18}H_{15}P)(CO)_3]$: Re—O 2·174 (9), Re—C 2·199 (10), C—O 1·240 (17) and C—C 1·427 (17) Å$\}$ seem to be compatible with delocalized π electrons in such heterocyclic rings, as was suggested for an analogous Mn ring in $[CH_3CO(o\text{-}C_6H_4)Mn(CO)_4]$ (Knobler, Crawford & Kaesz 1975).

The Re(1) ring of the title compound is one part of an extended planar tricyclic ring system that includes the bridging benzoyl ligand and the Re(1) and Re(2) atoms. This indicates that the Re(2) ring also has π-electron delocalization. The structural parameters of the Re(2) ring support this proposal. For example the Re(2)—P(2) bond shows a significant shortening compared with the Re(1)—P(1) bond. This may be ascribed to a stronger σ, π bond between the Re(2)—P(2) ring atoms.

The coordination around both Re atoms is distorted octahedral. Each of the three CO ligands at the Re(1) atom is *trans* to a different atom. Two of the four carbonyl ligands at the Re(2) atom are arranged *trans* to the ring atoms and the remaining two in apical positions. The two rhenium atoms are bridged by the quadridentate ligand, which is bidentate to each Re atom.

Intramolecular distances do not indicate interactions exceeding van der Waals forces.

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Structure of Tetracarbonyl(phenanthroline)molybdenum(0), $[Mo(CO)_4(C_{12}H_8N_2)]$, at 185 K

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Abstract. $M_r = 388·2$, monoclinic, $C2/m$, $a = 15·482\,(5)$, $b = 11·980\,(3)$, $c = 8·177\,(3)$ Å, $\beta = 106·58\,(3)°$, $V = 1453·6$ Å^3, $Z = 4$, $D_x = 1·77$ Mg m^{-3}, $\lambda(\text{Mo }K\bar{\alpha}) = 0·71069$ Å, $\mu = 0·869$ mm^{-1}, $F(000) = 768$, $T = 185$ K. $R = 0·0183$ for 923 unique observed reflections. The molecule possesses crystallographically imposed C_s symmetry, with the mirror plane bisecting the N—Mo—N angle. The geometry at Mo is distorted

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octahedral. The *trans*-standing CO groups are less strongly bound to Mo than those *trans* to N and, additionally, the former are bent away from the phenanthroline ligand to afford C—Mo—C 167·55 (13)°.

Introduction. The title compound was first reported by Stiddard (1962). It is an important starting material in the synthesis of numerous phenanthroline molybdenum complexes, most recently in our laboratories asymmetric η-bonded allyl species of the general formula $[MoX(CO)_2(\eta\text{-}1\text{-}RC_3H_4)(C_{12}H_8N_2)]$ where X = halide or pseudohalide and R = Me, Ph, or C(O)OEt.

As a *cis*-disubstituted derivative of $Mo(CO)_6$ it is, furthermore, a representative example of a class of compound whose structures shed important light on competitive metal—ligand bonding influences. Thus we have performed an accurate, low-temperature diffraction study described herein.

Experimental. Red blocks, 0·04 × 0·02 × 0·02 cm, from solvent diffusion using CH_2Cl_2 and *n*-hexane; preliminary unit cell from oscillation and Weissenberg photography; systematic absence (hkl: $h + k = 2n + 1$) implied space group $C2$, Cm, or $C2/m$, the last proving to be correct by successful refinement; CAD-4 diffractometer, 185 K (ULT-1 apparatus), 25 reflections ($14·0 < \theta < 14·5°$) centred, graphite-monochromated Mo $K\alpha$; for data collection $\theta_{max} = 22°$, ω–2θ scans in 96 steps, ω-scan width 0·8° + 0·35°tanθ, rapid prescan after which reflections with $I \geq 0·5\sigma(I)$ remeasured such that final net intensity had $I > 50\sigma(I)$ subject to a maximum measuring time of 60 s; two quadrants of data ($hk\pm l$ and $-h-k\pm l$) measured over 38 X-ray hours with no detectable decay or movement; derived structure factors merged to give 947 unique data, $R_{int} = 0·0151$; for structure solution and refinement 923 amplitudes with $F \geq 2\sigma(F)$ retained (h −16→16, k 0→12, l 0→8), Patterson synthesis (Mo) and difference-Fourier methods; post-solution empirical absorption correction, full-matrix least-squares refinement (on F), $w = [\sigma^2(F) + 0·0002(F)^2]^{-1}$, anisotropic thermal parameters for non-H atoms, isotropic for H atoms, $R = 0·0183$, $wR = 0·0266$, $S = 1·695$, data: variable ratio 7:1, max. peak and min. trough in final ΔF synthesis 0·133 and −0·196 e Å^{-3} respectively, max. shift/e.s.d. in final cycle 0·007; neutral scattering factors for C,O,N and Mo (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965); computer programs: *SHELX*76 (Sheldrick, 1976), *DIFABS* (Walker & Stuart, 1983), *XANADU* (Roberts & Sheldrick, 1976), *CALC* (Gould & Taylor, 1984), *ORTEP*II (Johnson, 1976), and *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens, Parthasarathi, Bruins Slot & Haltiwanger, 1984).

Table 1. *Fractional coordinates of atoms with standard deviations and isotropic thermal parameters*

	x	y	z	U_{eq}*/U_{iso}(Å^2)
Mo(1)	−0·19346 (2)	0·50000	0·36482 (3)	0·0208
N(1)	−0·28860 (13)	0·38782 (17)	0·1776 (3)	0·0223
C(1)	−0·29201 (18)	0·27711 (22)	0·1835 (4)	0·0273
C(2)	−0·35174 (18)	0·21369 (24)	0·0603 (3)	0·0314
C(3)	−0·41022 (18)	0·26521 (22)	−0·0763 (3)	0·0301
C(4)	−0·41013 (15)	0·38208 (21)	−0·0872 (3)	0·0252
C(5)	−0·34782 (15)	0·43993 (21)	0·0438 (3)	0·0233
C(6)	−0·47140 (17)	0·44354 (24)	−0·2211 (3)	0·0318
C(13)	−0·12132 (17)	0·38123 (24)	0·5037 (3)	0·0288
O(13)	−0·08197 (13)	0·30711 (18)	0·57992 (24)	0·0437
C(14)	−0·2645 (3)	0·50000	0·5378 (5)	0·0344
O(14)	−0·29176 (24)	0·50000	0·6535 (4)	0·0652
C(15)	−0·09893 (24)	0·50000	0·2371 (4)	0·0211
O(15)	−0·03898 (18)	0·50000	0·1812 (3)	0·0349
H(1)	−0·2478 (19)	0·2373 (22)	0·290 (3)	0·0350
H(2)	−0·3515 (16)	0·1388 (24)	0·077 (3)	0·0231
H(3)	−0·4504 (15)	0·2243 (21)	−0·162 (3)	0·0145
H(6)	−0·5116 (19)	0·398 (3)	−0·319 (3)	0·0466

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Bond lengths* (Å) *and angles* (°)

Mo(1)—N(1)	2·2434 (21)	C(4)—C(6)	1·431 (4)
Mo(1)—C(13)	1·958 (3)	C(5)—C(5′)	1·439 (3)
Mo(1)—C(14)	2·024 (3)	C(6)—C(6′)	1·353 (4)
Mo(1)—C(15)	2·026 (3)	C(13)—O(13)	1·155 (3)
N(1)—C(1)	1·329 (3)	C(14)—O(14)	1·141 (4)
N(1)—C(5)	1·362 (3)	C(15)—O(15)	1·146 (4)
C(1)—C(2)	1·384 (4)	C(1)—H(1)	1·06 (3)
C(2)—C(3)	1·368 (4)	C(2)—H(2)	0·91 (3)
C(3)—C(4)	1·403 (4)	C(3)—H(3)	0·932 (24)
C(4)—C(5)	1·403 (3)	C(6)—H(6)	1·02 (3)
N(1)—Mo(1)—N(1′)	73·62 (7)	C(5)—C(4)—C(6)	119·42 (22)
N(1)—Mo(1)—C(13)	96·60 (10)	N(1)—C(5)—C(4)	123·04 (22)
N(1)—Mo(1)—C(13′)	170·20 (10)	N(1)—C(5)—C(5′)	117·29 (21)
N(1)—Mo(1)—C(14)	95·47 (11)	C(4)—C(5)—C(5′)	119·61 (21)
N(1)—Mo(1)—C(15)	94·49 (10)	C(4)—C(6)—C(6′)	120·95 (24)
C(13)—Mo(1)—C(13′)	93·18 (11)	Mo(1)—C(13)—O(13)	176·27 (24)
C(13)—Mo(1)—C(14)	85·88 (12)	Mo(1)—C(14)—O(14)	169·4 (3)
C(13)—Mo(1)—C(15)	85·57 (11)	Mo(1)—C(15)—O(15)	172·9 (3)
C(14)—Mo(1)—C(15)	167·55 (13)	H(1)—C(1)—N(1)	117·3 (15)
Mo(1)—N(1)—C(1)	126·76 (18)	H(1)—C(1)—C(2)	119·6 (15)
Mo(1)—N(1)—C(5)	115·72 (16)	H(2)—C(2)—C(1)	117·4 (17)
C(1)—N(1)—C(5)	117·52 (22)	H(2)—C(2)—C(3)	122·9 (17)
N(1)—C(1)—C(2)	123·1 (3)	H(3)—C(3)—C(2)	121·4 (15)
C(1)—C(2)—C(3)	119·7 (3)	H(3)—C(3)—C(4)	119·3 (15)
C(2)—C(3)—C(4)	119·32 (25)	H(6)—C(6)—C(4)	116·6 (17)
C(3)—C(4)—C(5)	117·24 (22)	H(6)—C(6)—C(6′)	122·3 (17)
C(3)—C(4)—C(6)	123·32 (23)		

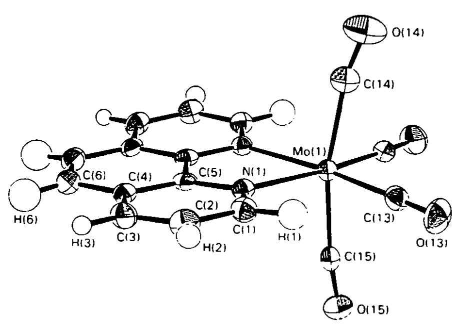

Fig. 1. The molecular structure of (1). Thermal ellipsoids are constructed at the 30% probability level.

Discussion. The final fractional coordinates are listed in Table 1, and Fig. 1 presents a perspective view of the molecule, demonstrating the atomic-numbering scheme adopted. Derived molecular parameters, uncorrected for thermal effects, appear in Table 2, with primed atoms generated by reflection in the crystallographic mirror plane at $y = 0{\cdot}5$. In the crystal (Fig. 2) molecules exist as weakly bound head-to-head dimers *via* quasi-graphitic packing between phenanthroline ligands related through centres of inversion and twofold axes. Closest intermolecular contacts have been deposited in Table 3.*

The $[Mo(CO)_4(phen)]$ molecule (1) (phen = 1,10-phenanthroline) has crystallographically imposed C_s symmetry about the plane bisecting the N—Mo—N′ angle. The phen ligand is not strictly planar (r.m.s.d. 0·050 Å, Table 4 deposited), but rather is of a shallow-boat form, the two peripheral six-membered rings being inclined in the same sense relative to the central one. A similar conformation is seen in molecules of the free ligand that crystallize in the general position (Nishigaki, Yoshioka & Nakatsu, 1978). No dimensions within the chelate differ significantly from corresponding ones in free phenanthroline, and all lie within the appropriate ranges tabulated for a number of phenanthroline metal complexes (Frenz & Ibers, 1972), although the relevance of the latter agreement is somewhat reduced by the relatively high errors in dimensions in many previous determinations. Good correlation also exists between the (relatively long) metal—N bond length and (relatively narrow) N—metal—N′ interbond angle in (1) with those in other complexes previously catalogued.

* Lists of structure factors and anisotropic thermal parameters, and Tables 3 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42273 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

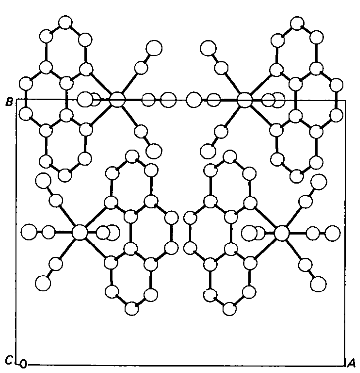

Fig. 2. The crystal structure of (1). H atoms are omitted for the sake of clarity.

Analysis of distances involving axial [C(14)O(14), C(15)O(15)] and equatorial [C(13)O(13)] carbonyl groups in (1) clearly suggests a greater individual degree of π-back bonding, Mo(d)→CO(π^*), to the latter, readily understood since the axial CO ligands compete with each other whilst the equatorial CO's compete with the less strongly π-acidic phenanthroline ligand. Thus Mo(1)—C is *ca* 0·065 Å shorter, and C—O *ca* 0·010 Å longer, in the equatorial plane. However, Mo(d)→phen(π^*) bonding is clearly evident in (1) since the Mo—N distances in this Mo^0 species are *ca* 0·06 Å shorter than those in the Mo^{VI} complex $[MoCl_2(O)_2(phen)]$ (2) (Viossat & Rodier, 1979).

Apart from the N—Mo—N′ angle, the octahedral metal geometry in (1) is substantially deformed by virtue of the fact that the axial carbonyl groups bend away from the phenanthroline ligand to subtend a C(14)—Mo(1)—C(15) angle of 167·55 (13)°. It is of considerable interest to note that in (2) the *trans*-standing Cl ligands bend *towards* the phen ligand, Cl—Mo—Cl 157·71 (25)°. A similar distortion to that in (2) has also been observed by Fenn (1969) in the closely related complex $[MoBr_2(O)_2(bpy)]$ (3) (bpy = 2,2′-bipyridyl). We interpret these different angular deformations as being a consequence of the greater occupation of the phenanthroline π^* orbitals in (1) (a d^6 complex) *versus* (2) and (3) (d^0 complexes). Thus in (1) we suggest a repulsive interaction between occupied phen(π^*) and axial carbonyl orbitals, whilst in (2) and (3) the halide ligands act as π-donors to the empty phen(π^*) system. Future studies will therefore be directed towards the synthesis and structural study of intermediate Mo^{II} and Mo^{IV} phenanthroline complexes, and to a theoretical analysis of the bonding in this class of complex.

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Structure of *cis-cis*-(*tert*-Butyl isocyanide)dicarbonyl(1,10-phenanthroline)(phenyl isocyanide)manganese(I) Perchlorate, $[Mn(CO)_2(C_5H_9N)(C_7H_5N)(C_{12}H_8N_2)]ClO_4$

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Abstract. $M_r = 576{\cdot}9$, monoclinic, $P2_1/n$, $a = 15{\cdot}343\ (3)$, $b = 12{\cdot}910\ (3)$, $c = 14{\cdot}511\ (3)$ Å, $\beta = 105{\cdot}51\ (2)°$, $V = 2770\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}383$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 644$ m^{-1}, $F(000) = 1184$, room temperature, $R = 0{\cdot}054$ for 2698 observed reflections. The Mn ion displays distorted octahedral coordination with the *tert*-butyl isocyanide, the phenanthroline and a carbonyl ligand in the equatorial plane. The Mn—N and Mn—C bond distances alter according to the electronegative or π-acceptor character of the *trans* ligand. The Mn—C (*tert*-butyl isocyanide) bond length is the shortest observed in the literature for similar ligands.

Introduction. Crystal structure determination of the title compound has been undertaken in order to elucidate the ligand arrangement and the distortion of the coordination polyhedron.

The results obtained show that the reaction of *fac*-$\{Mn(CO)_3(CNR)(NN)\}.ClO_4$ and CNR' in the presence of $ONMe_3$, in chloroform at room temperature, moves the *cis*-CNR ligand to the *trans* position, and does not give the expected *cis-trans* configuration predicted by Howell & Burkinshaw (1983). This result will be related to the formation of *mer*-$\{Mn(CO)_3(CNR)(NN)\}.ClO_4$ and *cis-cis*-$\{Mn(CO)_2(CNR)_2(NN)\}.ClO_4$ from *fac*-$\{Mn(CO)_3(CNR)(NN)\}.ClO_4$ (Garcia-Alonso, Riera, Villafañe & Vivanco, 1985).

Experimental. Red prisms (0·2 × 0·2 × 0·1 mm), Philips PW 1100, Mo $K\alpha$, graphite monochromator, cell parameters from 25 reflections ($4 \leq \theta \leq 8°$), ω-scan technique, scan width 1°, scan speed 0·03° s^{-1}; 2724 independent reflections with $\theta \leq 30°$; 2698 with $I \geq 2{\cdot}5\sigma(I)$; $hkl = -16$ to 16, 0 to 13, and 0 to 13. Three standard reflections ($2\bar{3}1$, $\bar{1}\bar{3}2$ and $\bar{2}\bar{3}2$) measured every two hours, no significant variations; Lp correction, absorption ignored. Mn atom from Patterson map (*SHELX76*; Sheldrick, 1976). Remaining non-hydrogen atoms from weighted Fourier synthesis. Full-matrix least-squares refinement (*SHELX76*), $\sum w||F_o|-|F_c||^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}0015 \times |F_o|^2]^{-1}$; f, f' and f'' from *International Tables for X-ray Crystallography* (1974); number of refined parameters 205. $\Delta\rho$ map at $R = 0{\cdot}12$ revealed double peaks for oxygen atoms of perchlorate ion; disorder was assumed with occupancy factor 0·5 for each oxygen position; 16 H from $\Delta\rho$ map, remaining H atoms in calculated positions, all H refined with overall isotropic temperature factor; final $R = 0{\cdot}054$ ($wR = 0{\cdot}061$) for all observed reflections; max. $\Delta/\sigma = 1{\cdot}6$ in U_{11} of O(Cl2) (−0·8 in z coordinate of Mn for non-disordered atom); max. and min. peaks in final $\Delta\rho$ map 0·4 and −0·2 e Å^{-3}. IBM-4341 computer.

* This paper forms part of the work by this author for a PhD.

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