Mono- and Di-carbonyl Complexes of Molybdenum(II) with Mixed Bidentate Ligands. *X*-Ray Crystal Structure of $[MoBr_2(CO)(bipy)(Ph_2PCH_2PPh_2)]$ (bipy = 2,2'-bipyridine):† a Novel Type of [M(bidentate)$_2$(unidentate)$_3$] Structure

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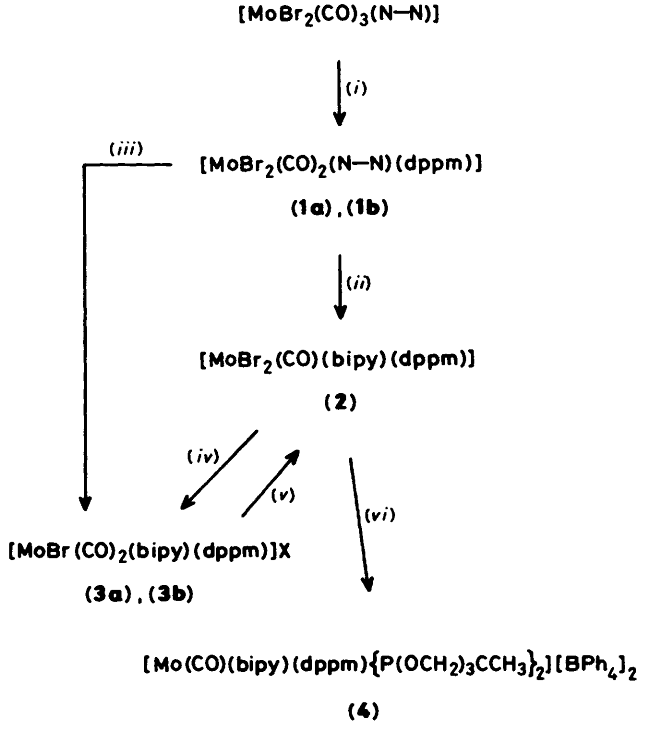
The diphosphine $Ph_2PCH_2PPh_2$ (dppm) reacts with $[MoBr_2(CO)_3(bipy)]$ (bipy = 2,2'-bipyridine) or $[MoBr_2(CO)_3(phen)]$ (phen = 1,10-phenanthroline) to give the seven-co-ordinate complexes $[MoBr_2(CO)_2(bipy)(dppm)]$ (**1a**) and $[MoBr_2(CO)_2(phen)(dppm)]$ (**1b**) respectively. Sunlight irradiation of (**1a**) in dichloromethane solution leads to the mixed bidentate monocarbonyl complex $[MoBr_2(CO)(bipy)(dppm)]$ (**2**) which has been characterized by *X*-ray crystallography. Crystals are orthorhombic, space group *Pbca*, with a = 18.440(7), b = 19.997(6), c = 17.900(9) Å, and Z = 8. The structure has been refined to R = 0.072 and R' = 0.059 from 2 078 reflections with $F > 3\sigma(F)$. The Mo co-ordination sphere is a distorted pentagonal bipyramid with carbonyl and one bipyridine nitrogen atom in the axial positions. Compound (**2**) reacts with ligands L, giving cationic species $[MoBr(CO)(bipy)(dppm)L]^+$ [L = CO, PH_3, $P(OMe)_3$, $P(OPr^i)_3$, or $P(OPh)_3$] and $[Mo(CO)(bipy)(dppm)L_2]^{2+}$ when L = $P(OCH_2)_3CCH_3$.

Although seven-co-ordinate Mo^{II} and W^{II} compounds of the form [M(bidentate)$_2$(unidentate)$_3$] have been described,[1,2] there are no references to complexes in which both bidentate ligands are different. In addition, the scarceness of seven-co-ordinate Mo^{II} mononuclear monocarbonyl complexes justifies the structural interest in these compounds. In an attempt to investigate further the stereochemical implications of the presence of two different chelating ligands in seven-co-ordinate Mo^{II} compounds, we have explored the reaction of the ligand dppm [dppm = bis(diphenylphosphino)methane] with $[MoBr_2(CO)_3(bipy)]$ (bipy = 2,2'-bipyridine) since we had previously found that compounds $[MoX_2(CO)_3(N{-}N)]$[N-N = bipy or phen (1,10-phenanthroline), X = Cl or Br] react with many P-donor ligands (L) replacing one carbonyl ligand and leading to complexes of stoicheiometry $[MoX_2(CO)_2(N{-}N)L]$.[3] This led us to the preparation of the dicarbonyl $[MoBr_2(CO)_2(bipy)(dppm)]$ (**1a**) and from this to the monocarbonyl $[MoBr_2(CO)(bipy)(dppm)]$ (**2**) which are both seven-co-ordinate Mo^{II} complexes. Moreover the reactivity of (**2**) has yielded cationic species of Mo^{II} as discussed below.

Results and Discussion

Stirring a mixture of $[MoBr_2(CO)_3(N{-}N)]$ (N-N = bipy or phen) and dppm in dichloromethane at room temperature in the absence of light afforded the orange crystalline light-sensitive compounds $[MoBr_2(CO)_2(N{-}N)(dppm)]$ (**1a**, N-N = bipy; **1b**, N-N = phen) [reaction (*i*), Scheme]. By monitoring the reaction by i.r. spectroscopy (CH_2Cl_2 solution) in the ν(CO) region a change from three to two bands was observed.



Scheme. All reactions in CH_2Cl_2: (*i*) dppm; (*ii*) sunlight irradiation; (*iii*) $NaBPh_4$; (*iv*) CO (1 atm); (*v*) spontaneously only for (**3a**); (*vi*) $P(OCH_2)_3CCH_3$ and $NaBPh_4$

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**1a**) in $CDCl_3$ at room temperature showed two absorptions centred at +36 (d, $^2J_{PP}$ = 24 Hz) and −24 p.p.m. (br), which are very similar to the chemical shifts observed for the dppm attached to Mo *via* only one phosphorus ligand.[4] The conductivity and

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† 2,2'-Bipyridine[bis(diphenylphosphino)methane]dibromo(carbonyl)-molybdenum(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm ≃ 101 325 N m^{-2}.

Table 1. Melting points, conductivity, and analytical data for the complexes prepared

Compound	M.p. (°C)[a]	Λ_M[b]	Analysis[c] C	N	H
(**1a**) $[MoBr_2(CO)_2(bipy)(dppm)]$	136	5.5[d]	51.85 (52.15)	3.15 (3.30)	3.80 (3.55)
(**1b**) $[MoBr_2(CO)_2(phen)(dppm)]$	187	3.8[d]	52.85 (53.35)	3.05 (3.20)	3.65 (3.40)
(**2**) $[MoBr_2(CO)(bipy)(dppm)]$	203	4.0[d]	52.40 (52.45)	3.35 (3.40)	3.75 (3.65)
(**3b**) $[MoBr(CO)_2(bipy)(dppm)]BPh_4$	174	25[e]	68.60 (67.10)	2.60 (2.55)	4.85 (4.60)
(**4**) $[Mo(CO)(bipy)(dppm)\{P(OCH_2)_3CCH_3\}_2][BPh_4]_2$	185	54[e]	69.80 (70.60)	1.70 (1.75)	5.70 (5.55)

[a] All melted with decomposition. [b] Molar conductivity (S cm^2 mol^{-1}) of *ca.* 5 × 10^{-4} mol dm^{-3} solutions at 25 °C. [c] Calculated values given in parentheses. [d] In acetone solution. [e] In nitrobenzene solution.

Table 2. Infrared data[a]

Compound	$\nu(CO)/cm^{-1}$
(**1a**) $[MoBr_2(CO)_2(bipy)(dppm)]$	1 942, 1 860
(**1b**) $[MoBr_2(CO)_2(phen)(dppm)]$	1 948, 1 865
(**2**) $[MoBr_2(CO)(bipy)(dppm)]$	1 790
(**3b**) $[MoBr(CO)_2(bipy)(dppm)]BPh_4$	1 962, 1 900
$[MoBr(CO)(bipy)(dppm)(PH_3)]BPh_4$[b]	1 820
$[MoBr(CO)(bipy)(dppm)\{P(OMe)_3\}]BPh_4$[b]	1 820
$[MoBr(CO)(bipy)(dppm)\{P(OPr^i)_3\}]BPh_4$[b]	1 810
$[MoBr(CO)(bipy)(dppm)\{P(OPh)_3\}]BPh_4$[b]	1 825
(**4**) $[Mo(CO)(bipy)(dppm)\{P(OCH_2)_3CCH_3\}_2][BPh_4]_2$	1 872

[a] The i.r. spectra were recorded in CH_2Cl_2 solution; all bands are strong. [b] Not isolated.

analytical data (Table 1) for the complexes (**1a**) and (**1b**) were in accord with the proposed formulae.

Dichloromethane solutions of (**1a**) in a Pyrex flask turned slowly dark green when exposed to sunlight [reaction (*ii*), Scheme]. After irradiation for 30 min, the i.r. showed five $\nu(CO)$ bands, two at 1 942 and 1 860 cm^{-1} due to the unreacted species (**1a**), and three at 1 962, 1 900, and 1 790 cm^{-1}. At the end of the reaction (90 min) only the band at 1 790 cm^{-1} remained. This behaviour could be explained as follows. In a first step reaction [(*ii*), Scheme], the irradiation caused the loss of one CO and the vacant site generated at the Mo atom was occupied by the second unco-ordinated P of the dppm yielding the monocarbonyl $[MoBr_2(CO)(bipy)(dppm)]$ (**2**), characterized by the band at 1 790 cm^{-1}. The CO released can subsequently react with (**2**) [reaction (*iv*), Scheme] giving $[MoBr(CO)_2(bipy)(dppm)]Br$ (**3a**) which shows two bands at 1 962 and 1 900 cm^{-1}. This assumption is supported by the reaction of (**2**) with CO gas (1 atm) which readily afforded (**3a**). However all attempts to isolate (**3a**) were unsuccessful since it easily loses CO to regenerate (**2**) [reaction (*v*), Scheme]. It was remarkable that attempts to prepare (**2**) from (**1a**) by thermal as well as by photochemical u.v. treatment failed.

The reactions (*iv*) and (*v*) constitute one example for a reversible CO carrier system like others well known in the literature.[5,6] Nevertheless the known systems generally undergo reversible CO dissociation reactions (from seven-co-ordinate 18-electron to six-co-ordinate 16-electron complexes). In our case a ligand-replacement (Br^- or CO) system was found. The loss of CO from (**3a**) could be inhibited if the bromide anion was changed for another non-co-ordinating anion. Thus, bubbling CO gas (1 atm) through (**2**) in dichloromethane at room temperature in the presence of $NaBPh_4$ allowed us to isolate the salt $[MoBr(CO)_2(bipy)(dppm)]BPh_4$ (**3b**) which does not lose CO. Furthermore, the reaction of (**1a**) with $NaBPh_4$ [reaction (*iii*), Scheme] led directly to the formation of (**3b**).

The reactions of (**2**) with CO to give (**3a**) or (**3b**) suggested the possibility that other different ligands could behave in the same way. We have found that the behaviour of various P-donor ligands depended upon steric and electronic factors. Thus, for PPh_3, which exhibits the greatest cone angle of the ligands employed, no reaction was observed, even if $NaBPh_4$ is simultaneously added. For $P(OPh)_3$ and $P(OPr^i)_3$, equilibria were produced which were shifted towards the cationic species $[MoBr(CO)(bipy)(dppm)L]BPh_4$ [L = $P(OPh)_3$ or $P(OPr^i)_3$] in the presence of $NaBPh_4$. For $P(OMe)_3$ the species $[MoBr(CO)(bipy)(dppm)\{P(OMe)_3\}]Br$ was formed as evidenced by its $\nu(CO)$ absorption in the i.r. spectrum, but this complex loses $P(OMe)_3$ *in vacuo* to yield (**2**), though the reverse reaction was inhibited when $NaBPh_4$ was added. For PH_3, which has the lowest cone angle, no reaction was observed although it could be promoted by adding $NaBPh_4$. Unfortunately, the complexes $[MoBr(CO)(bipy)(dppm)L]BPh_4$ [L = $P(OPh)_3$, $P(OPr^i)_3$, $P(OMe)_3$, or PH_3] have been identified only in solution since oily products were always formed.

Use of the ligand $P(OCH_2)_3CCH_3$ has allowed isolation of $[Mo(CO)(bipy)(dppm)\{P(OCH_2)_3CCH_3\}_2][BPh_4]_2$ (**4**) by its reaction with (**2**) [reaction (*vi*), Scheme] in a molar ratio (**2**): $P(OCH_2)_3CCH_3$ of 1:2 with $NaBPh_4$ present. If an equimolar ratio (1:1) was used, unreacted (**2**) was observed together with the formation of (**4**); no monocationic species, analogous to those obtained with all other P-donor ligands, have been formed for this ligand.

Melting points, conductivity, and analytical data for the prepared compounds are given in Table 1; $\nu(CO)$ frequencies for the compounds are in Table 2.

Structural Study of $[MoBr_2(CO)(bipy)(dppm)]$.—In order to check the seven-co-ordinate structure of (**2**) and in order to have a better insight of its stereochemistry, the structure determination of $[MoBr_2(CO)(bipy)(dppm)]$ was undertaken.

Final positional parameters are given in Table 3. Bond distances and angles are listed in Tables 4—6. The molecular geometry and the atom numbering are shown in Figure 1; a projection of the co-ordination sphere onto the equatorial plane is shown in Figure 2.

The molybdenum atom is seven-co-ordinate with pentagonal-bipyramidal geometry; the compound is monomeric. In the basal plane are found both bromine atoms, both dppm phosphorus atoms, and one bipyridine nitrogen atom. Axial positions are occupied by the carbonyl and the other bipyridine nitrogen atom. The molecule has a pseudo-mirror plane containing molybdenum, bipyridine, CO, and dppm CH_2; it is thus perpendicular to the pentagonal basal plane. The five basal plane atoms together with molybdenum were taken to define a basal plane by least-squares calculations; the largest deviation corresponds to Br(2) with −0.074 Å. The bond angles in this plane are shown on Figure 2; their sum is equal to 360.0(6)°. This supports the surrounding description as a pentagonal bipyramid.

Table 3. Fractional atomic co-ordinates with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo	−0.056 47(8)	0.548 94(9)	0.274 05(7)	C(2)	0.156(1)	0.611(1)	0.388(1)
Br(1)	−0.081 7(1)	0.677 1(1)	0.307 8(1)	C(3)	0.134(1)	0.625 1(9)	0.460(1)
Br(2)	−0.051 1(1)	0.421 1(1)	0.318 3(1)	C(4)	0.064(1)	0.611 7(9)	0.480 6(9)
P(1)	−0.014 9(3)	0.615 2(2)	0.164 8(3)	C(5)	0.018(1)	0.584 3(9)	0.428 2(9)
P(2)	−0.005 6(2)	0.480 8(2)	0.171 6(3)	N(2)	−0.1027(8)	0.546 1(8)	0.388 7(7)
C(11)	−0.148 1(9)	0.536(1)	0.222 6(9)	C(6)	−0.062(1)	0.565 1(8)	0.447 5(9)
O(11)	−0.203 7(6)	0.530 5(7)	0.195 7(8)	C(7)	−0.087(1)	0.570(1)	0.521(1)
C(12)	−0.001 2(9)	0.544(1)	0.097 9(8)	C(8)	−0.157(1)	0.550(1)	0.532(1)
N(1)	0.037 2(7)	0.570 0(7)	0.357 8(8)	C(9)	−0.201(1)	0.528 7(9)	0.477(1)
C(1)	0.105 2(9)	0.584 0(9)	0.338(1)	C(10)	−0.170 6(9)	0.528 5(9)	0.404(1)

Table 4. Bond lengths (Å) involving Mo

Mo–Br(1)	2.673(3)	Mo–N(2)	2.22(1)
Mo–Br(2)	2.678(3)	Mo–P(1)	2.483(5)
Mo–C(11)	1.94(2)	Mo–P(2)	2.471(5)
Mo–N(1)	2.33(1)		

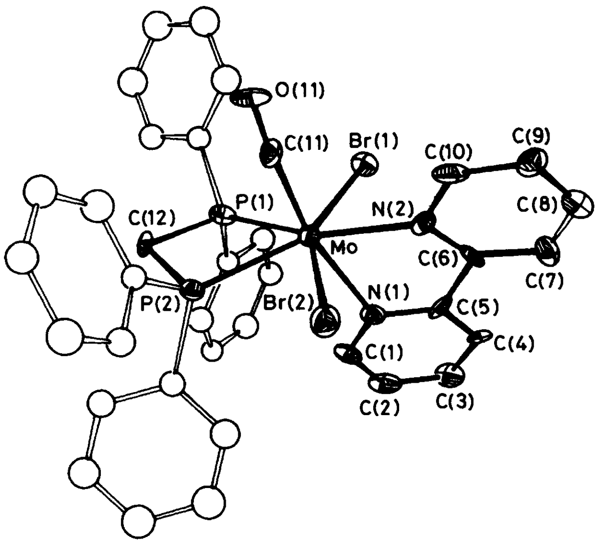

Figure 1. Molecular geometry and atom labelling

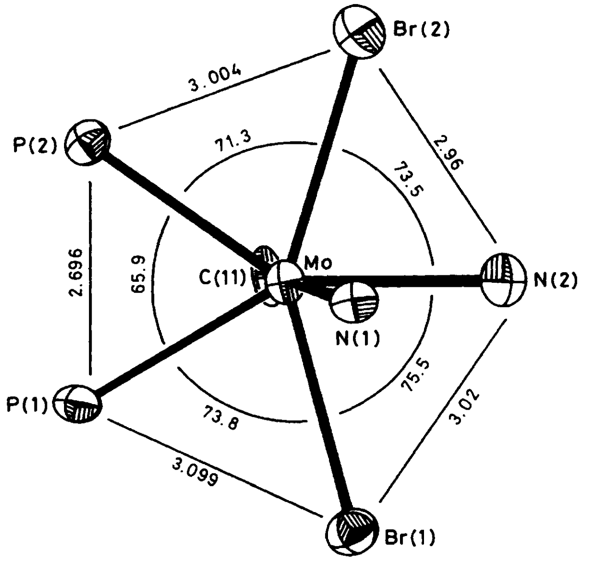

Figure 2. Projection of the co-ordination sphere onto the equatorial plane with angles (°) around molybdenum and intramolecular distances (Å) between ligating atoms attached to molybdenum

The title compound, which is diamagnetic, involves a d^4 molybdenum central atom. In a review, Kepert[7] discussed the various geometries corresponding to a complex of general formula [M(bidentate)$_2$(unidentate)$_3$]. This is similar to the present case except that the bidentate ligands are different. This geometry is rare; indeed Kepert pointed out that the repulsion energy calculations show that this stereochemistry is not normally expected. We therefore discuss in some detail the bonding inside the molecule.

The dppm ligand chelated to one central atom usually leads to a fairly closed angle on the metal atom. For example, Drew *et al.*[8] studied the structure of [MoCl$_2$(CO)$_2$(dppm)$_2$], another seven-co-ordinate d^4 molybdenum complex with two dppm ligands. It differs from the title compound by its geometry which is a capped octahedron and only having one bidentate ligand (dppm). The angles of the Mo–P–C–P ring follow the sequence 63.5, 94, 90, and 99° starting with the P–Mo–P angle.[7] In our case, they are 65.9, 97.9, 93.3, and 100.0°. It is clear that 65.9° for P–Mo–P is closer to angles normally found in a pentagonal basal plane rather than to the angle corresponding to one axial P and one equatorial P (Table 6).

In his paper, Kepert[7] mentioned that the unexpected pentagonal-bipyramidal stereochemistry might be stabilized by two strongly bonded bidentate and three weakly bonded unidentate ligands. Although CO cannot be considered as weakly bonded, such a stabilization can be explained as follows. According to a discussion by Hoffmann *et al.*[9] on seven-co-ordination, it would be anticipated that better σ donors should preferably enter the equatorial sites for d^0—d^4 metal atoms in a pentagonal-bipyramidal environment for which the example of [OsH$_4$(PMe$_2$Ph)$_3$] is given.[10] This is also true in the present case. Both bromine atoms are in the equatorial plane and CO is in an axial position. The Mo–CO bond length and the CO stretching frequency (1 790 cm^{-1}) are in agreement with the usual back-bonding.

A detailed analysis of the bonding of bipy provides more insight into the electronic structure of this complex. In his review, Drew[1] wrote: 'In most examples with equivalent atoms in both sites the M–L$_{ax}$ bonds are shorter than the M–L$_{eq}$ bonds by approximately 0.05 Å.' We found the opposite. The axial Mo–N length is much longer than the equatorial Mo–N length: 2.33(1) Å *versus* 2.22(1) Å. 2,2′-Bipyridine has been presented on several occasions as an acceptor by its π* orbitals;[11–13] back-bonding towards bipy should shorten the metal–nitrogen bond length. The longer axial bond length is obviously derived from the *trans* influence of CO. Indeed the π acidity of bipy is lower

Table 5. Bond lengths (Å) and angles (°) for the ligands in [$MoBr_2(CO)(bipy)(dppm)$]

C(11)–O(11)	1.14(2)	P(2)–C(211)	1.84(1)	C(3)–C(4)	1.38(3)	C(6)–C(7)	1.40(2)
P(1)–C(12)	1.88(2)	P(2)–C(221)	1.85(1)	C(4)–C(5)	1.37(2)	C(7)–C(8)	1.37(3)
P(1)–C(111)	1.83(1)	N(1)–C(1)	1.33(2)	C(5)–N(1)	1.34(2)	C(8)–C(9)	1.35(3)
P(1)–C(121)	1.83(1)	C(1)–C(2)	1.41(3)	C(5)–C(6)	1.57(3)	C(9)–C(10)	1.43(3)
P(2)–C(12)	1.82(2)	C(2)–C(3)	1.39(3)	N(2)–C(6)	1.35(2)	C(10)–N(2)	1.33(2)
Mo–C(11)–O(11)	176.0(2)	Mo–P(2)–C(12)	100.0(6)	C(1)–C(2)–C(3)	118(2)	C(7)–C(6)–C(5)	120(2)
Mo–P(1)–C(12)	97.9(5)	Mo–P(2)–C(211)	124.6(4)	C(2)–C(3)–C(4)	119(2)	C(10)–N(2)–C(6)	116(1)
Mo–P(1)–C(111)	119.3(4)	Mo–P(2)–C(221)	121.0(4)	C(3)–C(4)–C(5)	118(2)	N(2)–C(6)–C(7)	125(2)
Mo–P(1)–C(121)	124.6(4)	C(12)–P(2)–C(211)	102.8(6)	C(4)–C(5)–N(1)	125(2)	C(6)–C(7)–C(8)	115(2)
C(12)–P(1)–C(111)	105.1(6)	C(12)–P(2)–C(221)	105.1(7)	N(1)–C(5)–C(6)	114(1)	C(7)–C(8)–C(9)	123(2)
C(12)–P(1)–C(121)	103.5(7)	C(211)–P(2)–C(221)	100.5(5)	C(4)–C(5)–C(6)	122(1)	C(8)–C(9)–C(10)	116(2)
C(111)–P(1)–C(121)	103.3(6)	C(5)–N(1)–C(1)	117(1)	N(2)–C(6)–C(5)	115(1)	C(9)–C(10)–N(2)	124(2)
P(1)–C(12)–P(2)	93.3(7)	N(1)–C(1)–C(2)	123(2)				

Table 6. L–Mo–L bond angles (°), grouped with reference to the pentagonal bipyramid[a]

[$MoBr_2(CO)(bipy)(dppm)$]		Ideal value[b]
C(11)–Mo–N(1)	167.6(6)	180
Br(1)–Mo–Br(2)	148.70(8)	144
Br(2)–Mo–P(1)	136.9(1)	144
N(2)–Mo–P(1)	149.2(4)	144
Br(1)–Mo–P(2)	139.7(1)	144
N(2)–Mo–P(2)	144.8(4)	144
C(11)–Mo–Br(1)	95.0(6)	90
C(11)–Mo–N(2)	95.8(6)	90
C(11)–Mo–Br(2)	92.4(6)	90
C(11)–Mo–P(2)	84.4(5)	90
C(11)–Mo–P(1)	88.2(5)	90
N(1)–Mo–Br(1)	79.1(3)	90
N(1)–Mo–N(2)	72.2(5)	90
N(1)–Mo–Br(2)	87.4(3)	90
N(1)–Mo–P(2)	107.2(3)	90
N(1)–Mo–P(1)	100.5(3)	90
Br(2)–Mo–N(2)	73.5(4)	72
Br(2)–Mo–P(2)	71.3(1)	72
Br(1)–Mo–N(2)	75.5(4)	72
Br(1)–Mo–P(1)	73.8(1)	72
P(1)–Mo–P(2)	65.9(2)	72

[a] Average deviation from the pentagonal bipyramid is 0.062 Å. [b] Ideal value (°) for a pentagonal bipyramid.

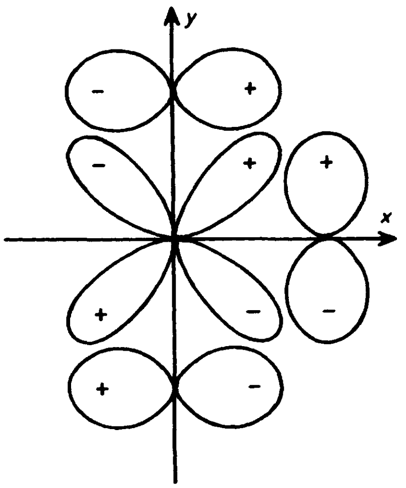

Figure 3. Diagram showing orbital overlap between the equatorial molybdenum *d* orbital and the corresponding orbitals of the bromine and nitrogen atoms

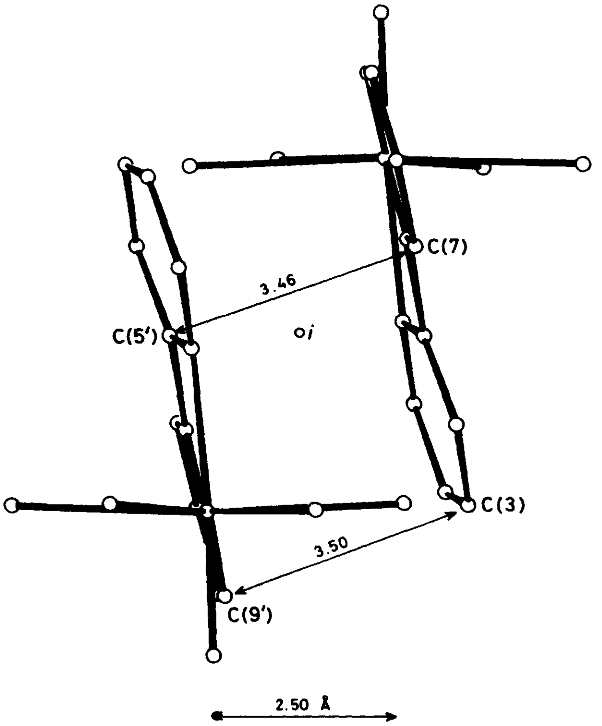

Figure 4. Packing of two [$MoBr_2(CO)(bipy)(dppm)$] molecules, related by inversion, displaying bipy plane distortion (*i* = inversion centre)

than that of CO. This result was emphasized by Chisholm *et al.*[13] who reported the structure of [$Mo(CO)_2(bipy)_2$]. However in the title compound molybdenum has four *d* electrons in the low-lying e_1 (d_{xz} and d_{yz}) orbitals following the familiar pattern.[9] There are enough electrons on molybdenum to fulfil back-bonding towards both CO and axial N, which does not occur. This means that electrons expected to be used with this axial nitrogen are used for something else. It may be noted that, on coupling CO with d_{xz}, for instance, the symmetry of d_{yz} is such that overlap is possible with *d* orbitals of both dppm phosphorus atoms. Although such an overlap is not so good as with axial N, it is well known that dppm is more π acidic than bipy as pointed out for example by Chisholm *et al.*[13] Discussing [$Mo(CO)_2(bipy)_2$], they found Mo–N 2.155 and 2.143 Å, compared with 2.239 and 2.220 Å when N is *trans* to CO. We found values of 2.22 and 2.33 Å. Both our distances are longer but it is a seven-co-ordinate compound.

Then the shorter equatorial Mo–N length has to be explained. It is possible to consider a π bond coming from both bromine atoms towards the equatorial bipy N atom, 'flowing across' the Mo *d* orbital which stretches in the equatorial plane (Figure 3).

A minor point is that the bipy plane is not quite perpendicular to the equatorial plane. At first glance this may look odd; actually crystal packing puts two bipy planes from two molecules related by inversion in front of each other. The average distance between these planes is 3.46 Å (Figure 4). The 'half-thickness' of an aromatic ring has been reported to be in the range 1.70—1.85 Å.[14]

It has been reported that π* back-bonding to bipy may have some drastic consequences on the ring bonds.[13] We shall not discuss this point because it is difficult to distinguish between the effects of back-bonding and those of packing. Moreover the molybdenum–nitrogen bonds are not identical. Nevertheless it is significant that the C–C inter-ring bipy distances are increased to 1.57 Å in the present complex.

Experimental

All reactions were carried out under dry argon. The ligand $P(OCH_2)_3CCH_3$[15] and the complex $[Mo(CO)_4(bipy)]$[16] were prepared by published methods. I.r. spectra were recorded using a Perkin-Elmer 577 spectrophotometer. $^{31}P-\{^1H\}$ N.m.r. spectra were obtained with a Varian FT80A instrument and were measured in $CDCl_3$ solution at room temperature (δ values, to high frequency of external 85% H_3PO_4).

$[MoBr_2(CO)_2(bipy)(dppm)]$ (**1a**).—To a solution of $[Mo(CO)_4(bipy)]$ (0.1 g, 0.27 mmol) in dichloromethane (20 cm^3) was added a solution of bromine in carbon tetrachloride (0.44 cm^3 of a 1.25 mol dm^{-3} solution) and the mixture was stirred until the formation of $[MoBr_2(CO)_3(bipy)]$ was completed [i.r. ν(CO)]. To the resulting solution, dppm (0.104 g, 0.27 mmol) was added and the mixture stirred for 30 min in the absence of light. The solvent was removed almost to dryness and hexane was added to give the orange solid, (**1a**) (0.18 g, 88%). The product was washed with diethyl ether and recrystallized from dichloromethane–hexane (1:1).

The phen derivative (**1b**) was similarly prepared using $[Mo(CO)_4(phen)]$ as starting material; yield 89%.

$[MoBr_2(CO)(bipy)(dppm)]$ (**2**).—The complex (**1a**) (0.1 g, 0.117 mmol) was dissolved in CH_2Cl_2 (20 cm^3). The orange solution, in a Pyrex flask, was then exposed to sunlight for 1.5 h; the colour changed from orange to dark green. The solvent was removed under reduced pressure to *ca.* 10 cm^3. Addition of hexane led to some red-violet undissolved precipitate. This solid was filtered off and the resulting green solution was concentrated under vacuum yielding 0.08 g (83%) of product. Crystallization was carried out from a dichloromethane–hexane mixture; dark green crystals were obtained and used for the *X*-ray structure determination.

$[MoBr(CO)_2(bipy)(dppm)]BPh_4$ (**3b**).—Complex (**2**) (0.1 g, 0.117 mmol) was dissolved in CH_2Cl_2 (20 cm^3). Carbon monoxide (1 atm) was bubbled into the solution and $NaBPh_4$ (0.1 g, 0.29 mmol) was then added and the mixture stirred for 2 h while bubbling in CO. The solution was filtered and concentrated under vacuum. Hexane (20 cm^3) was added and the precipitate washed with diethyl ether. Yield 0.1 g (78%). Recrystallization was carried out from dichloromethane–hexane giving red crystals.

$[Mo(CO)(bipy)(dppm)\{P(OCH_2)_3CCH_3\}_2][BPh_4]_2$ (**4**).—Complex (**2**) (0.1 g, 0.117 mmol) was dissolved in CH_2Cl_2 (20 cm^3). $P(OCH_2)_3CCH_3$ (0.036 g, 0.24 mmol) and $NaBPh_4$ (0.1 g, 0.29 mmol) were then added. After stirring for 2 h, the mixture was filtered and the solvent evaporated almost to dryness. Addition of hexane left a red solid precipitate (0.17 g, 87%), which was recrystallized from dichloromethane–hexane.

X-Ray Structure Determination.—Crystal data. $C_{36}H_{30}Br_2MoN_2OP_2$, $M = 824$, orthorhombic, $a = 18.440(7)$, $b = 19.997(6)$, $c = 17.900(9)$ Å, $U = 6\,600(4)$ Å^3 (by least-squares refinement of 9 reflections), $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, space group *Pbca*, $Z = 8$, $D_c = 1.66$ g cm^{-3}, crystal dimensions 0.5 × 0.3 × 0.1 mm, $\mu = 28.6$ cm^{-1}.

Data collection. Automatic three-circle diffractometer; θ–2θ scan with scan speed 1.5° min^{-1} in Bragg angle, scan length $(1.2 + 0.345 \tan\theta)^\circ$; Mo-$K_\alpha$ radiation, 2 825 reflections collected at room temperature up to $2\theta = 40^\circ$; Lorentz, polarization and absorption corrections carried out.[17]

Structure analysis and refinement. 2 078 Independent reflections with $F > 3\sigma(F)$ were used for the refinement. The Mo atom was located from a Patterson map; subsequent Fourier maps enabled the remaining non-hydrogen atoms to be located. Phenyl rings were treated as rigid groups and refined with individual isotropic thermal parameters for carbon atoms; hydrogen atoms were placed in idealized positions [d(C–H) = 1.0 Å]; other atoms were refined anisotropically. Final $R = 0.072$, $R' = 0.059$, goodness of fit = 1.59 [$R = \Sigma|\Delta|/\Sigma|F_o|$ with $\Delta = |F_o| - |F_c|$; $R' = \Sigma|\Delta|w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$ with $w = 1.3156/\sigma^2(F)$, $\sigma(F) = \sigma(I)/2F$, $\sigma(I)$ = error on the integrated intensity]. All refinements were carried out using SHELX 76 programs.[18] Scattering factors were taken from International Tables including $\Delta f'$ and $\Delta f''$ for Mo, Br, and P.

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References

1 M. G. B. Drew, *Prog. Inorg. Chem.*, 1977, **23**, 67 and refs. therein.
2 R. O. Day, W. A. Batschelet, and R. Archer, *Inorg. Chem.*, 1980, **19**, 2113.
3 G. G. Herbosa, Ph.D. Thesis, University of Oviedo, Spain; G. Monzón, M. Perez, and F. J. Arnaiz, *An. Quim. Ser. B*, 1984, **80**, 533.
4 E. E. Isaacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.
5 E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1 and refs. therein.
6 Z. Dori, *Prog. Inorg. Chem.*, 1981, **28**, 239.
7 D. L. Kepert, *Prog. Inorg. Chem.*, 1979, **25**, 41.
8 M. G. B. Drew, A. P. Wolters, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 1977, 974.
9 R. Hoffmann, B. F. Beier, E. L. Muetterties, and A. R. Rossi, *Inorg. Chem.*, 1977, **16**, 511.
10 D. W. Hart, R. Bau, and T. F. Koetzle, *J. Am. Chem. Soc.*, 1977, **99**, 7557.
11 M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress, and W. H. Woodruff, *J. Am. Chem. Soc.*, 1981, **103**, 4945.
12 L. J. Radonowich, M. W. Eyring, T. J. Groshens, and K. J. Klabunde, *J. Am. Chem. Soc.*, 1982, **104**, 2816.
13 M. H. Chisholm, J. A. Connor, J. C. Huffman, E. M. Kober, and C. Overton, *Inorg. Chem.*, 1984, **23**, 2298.
14 M. Van Meerssche and J. Feneau-Dupont, 'Introduction a la Cristallographie et a la Chimie Structurale,' Oyez, Leuven, 1977.
15 J. G. Verkade, *Inorg. Chem.*, 1965, **4**, 83.
16 M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4712.
17 D. J. Wehe, W. R. Busing, and M. A. Levy, ORABS Program, technical report ORNL-TM-229, Oak-Ridge National Laboratory, 1962.
18 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

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