Preparation and Reactions of Nitrosyl Complexes of Molybdenum and Tungsten; *X*-Ray Structure of *trans*-[Mo(OH)(NO)($Ph_2PCH_2CH_2PPh_2$)$_2$]·$2C_4H_8O$ †

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The nitrosyl complexes *trans*-[MX(NO)(dppe)$_2$] (1; X = NCO, H, or OH; dppe = $Ph_2PCH_2CH_2PPh_2$; M = Mo or W) have been prepared by treating *trans*-[M(N_2)$_2$(dppe)$_2$] with MeN(NO)C(O)NH_2 in tetrahydrofuran (thf) (X = NCO), Et_2NNO in thf or thf–MeOH (X = H), or Et_2NNO in thf–K_2[CO_3] (X = OH). The crystal structure of *trans*-[Mo(OH)(NO)(dppe)$_2$]·2thf shows the *trans* geometry and a linear Mo–N–O system apparently with a rather long Mo–N distance [1.985(7) Å] and rather short Mo–OH distance [1.922(8) Å]. A series of analogues (1; X = N_3, Cl, Br, I, or NCS) has been prepared by metathesis. Chemical oxidation of these compounds gives the complexes [MI(NO)(dppe)$_2$][I_3] (from I_2), [MX(NO)(dppe)$_2$]Y (Y = $FeCl_4$, $CuCl_2$, or BF_4), [Mo(NO)(NCR)(dppe)$_2$][BF_4], and [Mo(NO)(NCR)(dppe)$_2$][BF_4]$_2$ (Ag[BF_4] in RCN, R = Me or Ph). Halogen (Cl_2 or Br_2) oxidation of (1; X = Cl or Br) gives the compounds [MCl_2(dppe)$_2$] and [MBr_2(dppe)$_2$]Br. These reactions and other physical properties of the complexes are discussed in terms of their structural and electrochemical data and possible mechanisms for the formation of (1; X = OH or H) are considered.

FOR some years we have investigated the reactions of dinitrogen complexes particularly with the aim in mind of reducing ligating dinitrogen [1] and of replacing dinitrogen by analogous ligands such as RNC [2] and RCN,[3] so that the effect of ligation at an electron-rich centre upon the properties of these ligands could be studied. During the course of this work we treated the dinitrogen complexes *trans*-[M(N_2)$_2$(dppe)$_2$] (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) with nitrogen oxide, hoping to produce [M(NO)$_2$(dppe)$_2$] which should have one linear and one bent nitrosyl groups to confer an 18-electron environment upon the metal. Such complexes could not be obtained in a pure state, however (see Experimental section), so that the reactions of NO precursors MeN(NO)-C(O)NH_2 and Et_2NNO were studied. These reactions gave the mononitrosyl complexes which are described below.

RESULTS AND DISCUSSION

Preparation of Nitrosyl Complexes trans-[MX(NO)-(dppe)$_2$] (1; X = H, OH, NCO, NCS, N_3, F, Cl, Br, *or* I).—Some members of this series (1; X = F, Cl, or Br) have already been prepared by treatment of the complexes [MX(N_2H)(dppe)$_2$] {prepared indirectly from *trans*-[M(N_2)$_2$(dppe)$_2$]} with NO.[4] Here we report the preparation of their analogues directly from *trans*-[M(N_2)$_2$(dppe)$_2$] according to reactions (1) and (2) (thf = tetrahydrofuran).

$$trans\text{-}[\mathrm{M(N_2)_2(dppe)_2}] + \mathrm{MeN(NO)C(O)NH_2} \xrightarrow[\text{heat}]{\text{thf}} trans\text{-}[\mathrm{M(NCO)(NO)(dppe)_2}] + 2\mathrm{N_2} + \mathrm{NH_2Me} \qquad (1)$$

$$\begin{array}{l} trans\text{-}[\mathrm{M(N_2)_2(dppe)_2}] + \mathrm{Et_2NNO} \xrightarrow[h\nu]{\text{thf–MeOH}} trans\text{-}[\mathrm{MH(NO)(dppe)_2}] + 2\mathrm{N_2} + \mathrm{NH_2Et} + \mathrm{C_2H_4} \\ \qquad\qquad \text{thf–K}_2[\mathrm{CO_3}]\cdot n\mathrm{H_2O} \Big\downarrow \text{heat, } h\nu \\ \qquad\qquad trans\text{-}[\mathrm{M(OH)(NO)(dppe)_2}] \end{array} \qquad (2)$$

The formulation of (1; X = NCO) follows from its analytical and spectroscopic properties (Table 1). The formulation of (1; X = H) is less straightforward. Their analytical and i.r. spectroscopic properties are so similar to the other members of the (1) series that (1; X = H) are presumed to contain an anionic ligand in addition to the nitrosyl group. Moreover, they can be converted into other analogues by metathesis and formed from them by treatment with Na[BH_4] (see later). Since they are monomeric complexes with intact *trans*-dppe ligands (Table 1) the hydride formulation seems the most likely one although we have no ***direct*** evidence for the presence of this ligand.

A similar difficulty arose during the characterisation of (1; X = OH). Their spectroscopic data clearly distinguished them from (1; X = H) (Table 1) but their other properties were rather similar and therefore we determined the crystal structure of *trans*-[Mo(OH)(NO)-(dppe)$_2$] which is shown in the Figure. It confirms the *trans* stereochemistry [expected on the basis of ^{31}P spectra (Table 1)] and the presence of an OH group. This grouping is particularly difficult to detect in these complexes since the OH i.r. band is extremely weak, perhaps because of hydrogen-bonding effects and analytical data are not reliably diagnostic. Presumably the source of this group is adventitious moisture. This probably arises from the K_2[CO_3], which was originally added to the reaction mixture to maintain basic conditions, which were at the time considered necessary to promote the reaction. Interestingly, the ν(NO) value of

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† *trans*-Bis[1,2-bis(diphenylphosphino)ethane]hydroxo-(nitrosyl)molybdenum–tetrahydrofuran (1/2).

Table 1

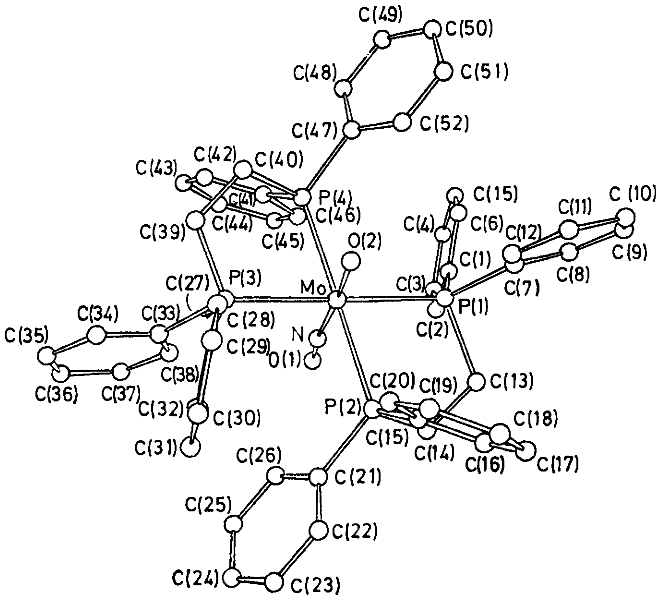
Physical properties of nitrosyl complexes

Compound	Colour	M.p. (θ_c/°C) (decomp.)	Analysis [a] (%)			M [a]	μ/B.M.	Λ [b]/S cm^2 mol^{-1}	$\tilde{\nu}$(NO) [c]/ cm^{-1} (obs.)	$\tilde{\nu}$(NO) [d]/ cm^{-1} (corr.)
			C	H	N					
$[MoH(NO)(dppe)_2]$ [e]	Yellow	222	67.3	5.4	1.5	950			1 545	1 725
			(67.7)	(5.3)	(1.5)	(923.8)				
$[Mo(OH)(NO)(dppe)_2]\cdot 2thf$ [f]	Yellow	210	67.0	5.4	1.4				1 510	1 670
			(66.9)	(5.5)	(1.3)					
$[Mo(NCO)(NO)(dppe)_2]\cdot 2thf$	Yellow	230	65.9	5.2	2.8				1 550	1 710
			(66.0)	(5.3)	(2.9)				2 200 [g]	
$[Mo(SCN)(NO)(dppe)_2]\cdot \frac{1}{2}CH_2Cl_2$	Yellow	210	62.9	5.0	2.7	1 003			1 560	1 720
			(62.8)	(4.8)	(2.7)	(982)			2 080 [h]	
$[Mo(N_3)(NO)(dppe)_2]$	Yellow	264	64.7	5.6	5.4	951			1 530	1 690
			(64.7)	(5.0)	(5.8)	(966)			2 060 [i]	
$[Mo(NO)(NCMe)(dppe)_2][BF_4]$	Orange-yellow	200	59.8	4.9	2.6			50.1 [j]	1 595	1 655
			(60.1)	(4.7)	(2.7)				2 270 [k]	
$[Mo(NO)(NCMe)(dppe)_2][BF_4]_2$	Purple		56.8	4.8	2.4		2.2	198.4 [l]	1 685	
			(57.0)	(4.5)	(2.5)				2 275 [k]	
$[Mo(NO)(NCPh)(dppe)_2][BF_4]$	Orange		64.1	4.5	2.7			49.7 [h]	1 595	1 685
			(64.6)	(4.9)	(2.6)				2 270 [k]	
$[Mo(NO)(NCPh)(dppe)_2][BF_4]_2$	Purple		59.5	4.7	2.1		2.1	210.3 [l]	1 700	
			(59.9)	(4.5)	(2.5)				2 275 [k]	
$[MoI(NO)(dppe)_2][I_3]$	Brown		43.7	3.6	1.0		2.1	43.5 [i]	1 645	
			(43.7)	(3.4)	(1.0)					
$[MoI(NO)(dppe)_2][BPh_4]$	Brown		66.5	5.0	1.1		2.0	42.5 [j]	1 645	
			(66.7)	(5.0)	(1.0)					
$[MoI(NO)(dppe)_2][FeCl_4]$	Violet		51.0	3.7	1.0			102.1 [l]	1 650	
			(50.4)	(3.9)	(1.1)				390 [m]	
$[MoI(NO)(dppe)_2][CuCl_2]$	Violet		51.0	3.7	1.0		1.9	106.5 [l]	1 645	
			(50.4)	(3.9)	(1.1)				410 [n]	
$[MoCl(NO)(dppe)_2][BPh_4]$	Brown		68.1	5.5	0.9		1.91	85.8 [j]	1 645	
			(67.9)	(5.1)	(1.0)					
$[MoCl(NO)(dppe)_2][FeCl_4]$	Violet	221	54.1	4.4	1.1			105.5 [l]	1 650	
			(54.0)	(4.2)	(1.2)				390 [m]	
$[MoCl(NO)(dppe)_2][CuCl_2]$	Violet	215	57.2	4.3	1.1		2.02	103.1 [l]	1 645	
			(57.2)	(4.4)	(1.3)				410 [n]	
$[MoCl(NO)(dppe)_2][I_3]$	Brown		47.9	3.2	1.0		1.98	98.5 [l]	1 645	
			(46.7)	(3.6)	(1.0)					
$[WH(NO)(dppe)_2]$	Yellow	283	62.3	5.2	1.4	1 045			1 535	1 725
			(61.9)	(4.8)	(1.4)	(1 012)				
$[W(OH)(NO)(dppe)_2]\cdot 2thf$	Yellow	273	62.0	5.0	2.3				1 505	1 675
			(61.7)	(5.7)	(1.2)					
$[W(N_3)(NO)(dppe)_2]$	Yellow	288	59.5	4.9	4.7				1 525	1 695
			(59.3)	(4.6)	(4.6)				2 030 [i]	
$[WI(NO)(dppe)_2][I_3]$	Brown		43.7	3.6	1.0		1.97	64.1 [j]	1 625	
			(43.7)	(3.7)	(1.1)					
$[WI(NO)(dppe)_2][BPh_4]$	Brown		62.4	4.9	1.1		1.89	58.6 [j]	1 625	
			(62.7)	(4.7)	(1.0)					
$[WI(NO)(dppe)_2][FeCl_4]$	Violet		46.5	3.5	1.0			60.3 [j]	1 615	
			(46.7)	(3.6)	(1.0)				390 [m]	
$[WI(NO)(dppe)_2][CuCl_2]$	Violet		48.7	3.6	1.0		2.11	96.7 [l]	1 610	
			(49.1)	(3.8)	(1.1)				410 [n]	
$[WCl(NO)(dppe)_2][I_3]$	Brown		42.3	3.9	1.0		2.01	89.9 [l]	1 625	
			(42.5)	(3.4)	(1.0)					
$[WCl(NO)(dppe)_2][BPh_4]$	Brown		66.5	5.0	0.9		2.05	60.0 [j]	1 620	
			(66.9)	(5.0)	(1.0)					
$[WCl(NO)(dppe)_2][FeCl_4]$	Violet		50.0	4.3	1.2			66.7 [j]	1 610	
			(50.2)	(3.9)	(1.1)				390 [m]	
$[WCl(NO)(dppe)_2][CuCl_2]$	Violet	219	51.5	4.1	1.1		1.99	95.6 [l]	1 620	
			(51.4)	(4.0)	(1.2)				410 [n]	

[a] Calculated values are given in parentheses. [b] In *ca.* 10^{-3} mol dm^{-3} solution. [c] Nujol mulls. [d] Some examples of values corrected according to Ibers (see text). [e] $\delta(^{31}P) = -85.44$ in thf relative to $P(OMe)_3$. [f] $\delta(^{31}P) = -87.13$ in thf relative to $P(OMe)_3$. [g] ν(NCO). [h] ν(SCN). [i] $\nu(N_3)$. [j] In $C_2H_4Cl_2$ solution. [k] ν(CN). [l] In $MeNO_2$ solution. [m] ν(Fe–Cl). [n] ν(Cu–Cl).

trans-$[Mo(OH)(NO)(dppe)_2]$ (1 510 cm^{-1}) is the same as the compound formulated [5] $[\{Mo(NO)(dppe)_2\}_2]$, prepared from $[Mo(CO)_3(NO)(dppe)_2][PF_6]$ by treatment with dppe, followed by chromatography of the products on alumina. This compound is diamagnetic and was formulated as a dimer to give an 18-electron count to molybdenum. Its properties and mode of preparation strongly suggest that is in fact *trans*-$[Mo(OH)(NO)(dppe)_2]$.

Some interesting points emerge from the structure of (1; M = Mo, X = OH) the details of which are given in the Experimental section. The linearity of the M–N–O system confirms that the NO group is acting as a three-electron donor despite its low stretching frequency (see later). In Table 2 the *X*-ray parameters of some other molybdenum nitrosyl complexes whose structures have been determined and of the oxo-analogue *trans*-$[Mo(OH)O(dppe)_2]$ are grouped for comparison. All the nitrosyl complexes have linear NO groups. A problem arises when we attempt to discuss bond distances because (1;



Molecular structure of *trans*-[Mo(OH)(NO)(dppe)$_2$]

M = Mo, X = OH) has a pseudo-centre of symmetry at the Mo atom, causing the space group to be very nearly $P2_1/c$. Thus the atom parameters are highly correlated in the least-squares refinement and all positional estimated standard deviations (e.s.d.s) are probably underestimates. Thus the Mo–P distances vary from 2.435 to 2.499 Å although the nominal e.s.d.s are 0.003 Å. Nevertheless, the bond-length data of Table 2 appear to indicate that the M–N distance [1.985(7) Å], while shorter than the calculated distance from covalent radii[6] [1.58 (Mo) + 0.65 (N) = 2.23 Å], is rather longer than that observed in other nitrosyl complexes. In addition, the Mo–OH distance [1.922(8) Å] appears to be somewhat shorter than both the distance calculated from covalent radii[6] [1.58 (Mo) + 0.60 (O) = 2.18 Å] and the reported range of Mo–OH distances [1.96(1)—2.181(3) Å, ref. 7 and Table 2]. Of the compounds quoted in Table 2, *trans*-[Mo(OH)(O)(dppe)$_2$][BF$_4$] is particularly interesting since it was formed (in the presence of [CPh$_3$][BF$_4$]) by an adventitious reaction of air with [MoH$_4$(dppe)$_2$], the hydride analogue of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] which we have used as starting material. Although discussion of the bond distances of the ONMo-OH system must be tentative for the reasons noted above, nevertheless the apparent shortening of the Mo–OH distance can be rationalised by suggesting that OH acts as a strong π-releasing ligand, behaviour consistent with the particularly low oxidation potential of (1; X = OH) compared to their analogues (Table 3).[8] The long *trans*-Mo–NO distance is perhaps induced by competition with OH for available π orbitals although there is still strong π release to NO from the metal, resulting in the low ν(NO) value (Table 1). It may well be that in the analogue *trans*-[Mo(OH)(O)(dppe)$_2$]$^+$ the somewhat longer Mo–OH distance[7] is caused by superior electron

TABLE 2

Structural parameters of molybdenum nitrosyl and related complexes

Compounds	M–N/Å	N–O/Å	M–N–O/°
[MoCl$_2$(NO)$_2$(PPh$_3$)$_2$] [a]	1.818	1.223	163.1
	1.905	1.159	160.4
[PPh$_4$]$_2$[Mo(NCS)$_4$(NO)(OCNMe$_2$)] [b]	1.767	1.179	
[Mo(OPr^i)$_6$(NO)$_2$] [c]	1.749	1.205	178
[{Mo(η-C$_5$H$_5$)I(NO)}$_2$(μ-NNMe)] [d]	1.701	1.184	177
trans-[Mo(OH)(NO)(dppe)$_2$]·2thf	1.985(7)	1.060(11)	173.8
trans-[Mo(OH)(O)(dppe)$_2$][BF$_4$]	1.833 [e,f]	1.952 [e,g]	

[a] M. O. Visscher and K. G. Caulton, *J. Am. Chem. Soc.*, 1972, **94**, 5293. [b] A. Muller, U. Seyer, and W. Ellzner, *Inorg. Chim. Acta*, 1979, **32**, L65. [c] M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, 1978, **100**, 3354. [d] W. G. Kita, A. J. McCleverty, B. E. Mann, and D. Seddon, *J. Chem. Soc., Chem. Commun.*, 1974, 132. [e] Ref. 7. [f] Mo=O. [g] Mo–OH.

TABLE 3

Oxidation potentials for some nitrosyl complexes of molybdenum and tungsten at $V = 0.3$ V s^{-1} [a]

Compound	$E_{\frac{1}{2}}^{\text{ox}}$	E_{p}^{ox}	$E_{\text{p}}^{\text{red}}$	$\lvert E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}}\rvert$
	V			
trans-[Mo(OH)(NO)(dppe)$_2$]	0.12	0.16	0.08	0.08
trans-[Mo(N$_3$)(NO)(dppe)$_2$]	0.27	0.31	0.23	0.08
trans-[MoI(NO)(dppe)$_2$]	0.28	0.34	0.22	0.12
trans-[MoH(NO)(dppe)$_2$]	0.29	0.31	0.26	0.05
trans-[Mo(NCO)(NO)(dppe)$_2$]	0.32	0.34	0.30	0.04
trans-[Mo(SCN)(NO)(dppe)$_2$]	0.50	0.55	0.45	0.11
trans-[Mo(NO)(NCMe)(dppe)$_2$][BF$_4$]	0.53	0.56 (0.37) [b]	0.50	0.06
trans-[Mo(NO)(NCPh)(dppe)$_2$][BF$_4$]	0.64	0.68	0.60	0.08
trans-[Mo(NO)(CO)(dppe)$_2$][BF$_4$]	0.91	0.95	0.87	0.08
cis-[Mo(NO)(CO)(dppe)$_2$][BF$_4$]	1.30 (irreversible)			
trans-[W(OH)(NO)(dppe)$_2$]	0.08	0.11	0.05	0.06
trans-[WI(NO)(dppe)$_2$]	0.25	0.29	0.21	0.08
trans-[WH(NO)(dppe)$_2$]	0.29	0.32	0.26	0.06

[a] Symbols have their usual meanings,[8] measurements in thf, 0.1 mol dm^{-3} in [NBu$^t{}_4$][BF$_4$], internal reference *trans*-[Mo(N$_2$)$_2$-(dppe)$_2$] in thf, $E_{\frac{1}{2}}^{\text{ox}} = -0.16$ V *versus* calomel–thf. Under these conditions the oxidation potential of the couple [Fe(η-C$_5$H$_5$)$_2$]–[Fe(η-C$_5$H$_5$)$_2$]$^+$ is 0.55 V, and 0.36 V in CH$_2$Cl$_2$. $\lvert E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}}\rvert$ *ca.* 0.08 V. [b] Corrected to CH$_2$Cl$_2$, *cf.* 0.35 V given in ref. 13.

release/overlap of the *trans*-oxide ligand compared to NO.

The Mo–P distances and bond angles involving the phosphine ligands (Table 4) are unexceptional and are similar to those observed in related compounds such as *trans*-$[Mo(N_2)_2(dppe)_2]$,[9] *trans*-$[Mo(CO)(N_2)(dppe)_2]$,[10] and *trans*-$[Mo(OH)(O)(dppe)_2][BF_4]$.[7]

TABLE 4

Intramolecular distances and angles with estimated standard deviations in parentheses

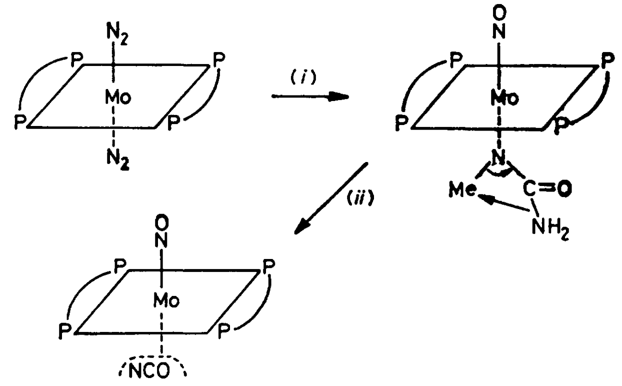
(*a*) Bonds (Å)

Mo–P(1)	2.484(3)	P(3)–C(33)	1.819(7)
Mo–P(2)	2.499(3)	P(4)–C(40)	1.856(10)
Mo–N	1.985(7)	P(4)–C(41)	1.834(6)
Mo–P(3)	2.478(3)	P(4)–C(47)	1.847(6)
Mo–P(4)	2.435(3)	C(39)–C(40)	1.479(15)
Mo–O(2)	1.922(8)	C(53)–O(4)	1.493(28)
P(1)–C(13)	1.987(10)	C(53)–C(54)	1.647(45)
P(1)–C(1)	1.774(6)	C(54)–C(55)	1.677(47)
P(1)–C(7)	1.846(6)	C(55)–C(56)	1.486(38)
P(2)–C(14)	1.837(12)	C(56)–O(4)	1.485(23)
P(2)–C(15)	1.815(6)	O(3)–C(57)	1.658(28)
P(2)–C(21)	1.826(6)	O(3)–C(59)	1.523(27)
N–O(1)	1.060(11)	C(57)–C(58)	1.443(39)
C(13)–C(14)	1.552(15)	C(58)–C(60)	1.493(42)
P(3)–C(39)	1.760(10)	C(59)–C(60)	1.357(35)
P(3)–C(27)	1.882(6)		

(*b*) Angles (°)

P(2)–Mo–P(1)	79.6(1)	C(16)–C(15)–P(2)	119.3(5)
N–Mo–P(1)	85.1(2)	C(22)–C(21)–P(2)	122.3(4)
N–Mo–P(2)	82.7(2)	C(26)–C(21)–P(2)	117.7(4)
P(3)–Mo–P(1)	179.0(1)	C(39)–P(3)–Mo	109.8(4)
P(3)–Mo–P(2)	101.2(1)	C(27)–P(3)–Mo	113.9(2)
P(3)–Mo–N	95.5(2)	C(27)–P(3)–C(39)	108.2(5)
P(4)–Mo–P(1)	100.7(1)	C(33)–P(3)–Mo	126.0(3)
P(4)–Mo–P(2)	179.1(1)	C(33)–P(3)–C(39)	98.5(5)
P(4)–Mo–N	96.4(2)	C(33)–P(3)–C(27)	98.5(3)
P(4)–Mo–P(3)	78.5(1)	C(40)–P(4)–Mo	105.6(3)
O(2)–Mo–P(1)	99.4(2)	C(41)–P(4)–Mo	116.9(2)
O(2)–Mo–P(2)	96.7(2)	C(41)–P(4)–C(40)	105.6(4)
O(2)–Mo–N	175.4(3)	C(47)–P(4)–Mo	124.9(2)
O(2)–Mo–P(3)	80.0(2)	C(47)–P(4)–C(40)	101.0(4)
O(2)–Mo–P(4)	84.1(2)	C(47)–P(4)–C(41)	100.5(3)
C(13)–P(1)–Mo	110.3(3)	C(40)–C(39)–P(3)	117.2(7)
C(1)–P(1)–Mo	114.9(2)	C(39)–C(40)–P(4)	110.8(7)
C(1)–P(1)–C(13)	101.0(4)	C(28)–C(27)–P(3)	121.8(5)
C(7)–P(1)–Mo	123.6(2)	C(32)–C(27)–P(3)	117.9(5)
C(7)–P(1)–C(13)	98.5(4)	C(34)–C(33)–P(3)	119.6(5)
C(7)–P(1)–C(1)	105.1(3)	C(38)–C(33)–P(3)	120.1(5)
C(14)–P(2)–Mo	106.7(4)	C(42)–C(41)–P(4)	127.2(5)
C(15)–P(2)–Mo	114.4(3)	C(46)–C(41)–P(4)	112.6(4)
C(15)–P(2)–C(14)	106.3(5)	C(48)–C(47)–P(4)	122.6(5)
C(21)–P(2)–Mo	122.1(2)	C(52)–C(47)–P(4)	117.4(4)
C(21)–P(2)–C(14)	99.5(4)	C(56)–O(4)–C(53)	104.4(15)
C(21)–P(2)–C(15)	105.9(3)	C(54)–C(53)–O(4)	92.5(18)
O(1)–N–Mo	173.7(7)	C(55)–C(54)–C(53)	81.8(21)
C(14)–C(13)–P(1)	110.3(6)	C(56)–C(55)–C(54)	96.6(23)
C(13)–C(14)–P(2)	115.5(8)	C(55)–C(56)–O(4)	102.1(17)
C(2)–C(1)–P(1)	118.6(5)	C(59)–O(3)–C(57)	101.5(14)
C(6)–C(1)–P(1)	121.1(5)	C(58)–C(57)–O(3)	103.4(19)
C(8)–C(7)–P(1)	122.5(5)	C(60)–C(58)–C(57)	105.8(24)
C(12)–C(7)–P(1)	117.4(5)	C(60)–C(59)–O(3)	109.9(20)
C(20)–C(15)–P(2)	120.7(5)	C(59)–C(60)–C(58)	110.3(24)

Mechanism of Formation of (1; X = NCO, H, *and* OH).—In retrospect, formation of (1; X = NCO) is not particularly surprising since Na[NCO] can be formed from $MeN(NO)C(O)NH_2$ by treatment with Na[OH]. Presumably the mechanism of the formation of the nitrosyl complex involves initial oxidative addition of $MeN(NO)C(O)NH_2$ to *trans*-$[M(N_2)_2(dppe)_2]$ with subsequent elimination of NH_2Me as is shown in Scheme 1. It is not clear from the available data whether the NCO ligand is *N*- or *O*-bonded.



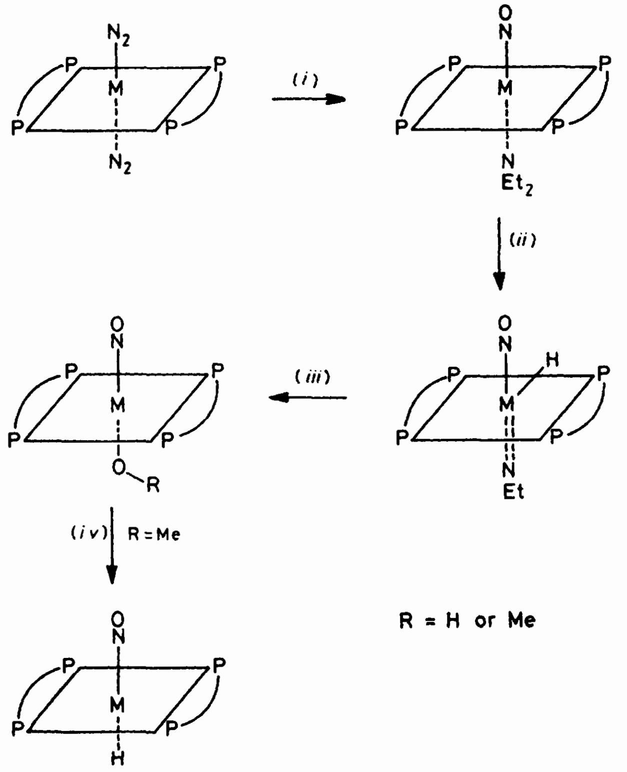
SCHEME 1 (*i*) $MeN(NO)C(O)NH_2$, $-2N_2$; (*ii*) $-NH_2Me$

The reaction of Et_2NNO with *trans*-$[M(N_2)_2(dppe)_2]$ gives (1; X = H or OH) depending upon the conditions [reaction (2)]. From both reactions the expected 2 mol of N_2 are evolved plus *ca.* 0.25 mol equivalents of C_2H_4 and *ca.* 0.75 mol equivalents of NH_2Et (detected by vapour-phase chromatography and mass spectrometry). We also find that (1; X = OH) is converted into (1; X = H) by refluxing in MeOH or MeOH–thf. These observations can be reasonably accommodated by the proposed mechanism of Scheme 2. The first step is again oxidative addition to the dinitrogen complex giving an NO–Mo–NEt_2 intermediate. It is proposed that the NEt_2 group then undergoes β-elimination to produce a hydride and C_2H_4 {as proposed in the formation of $[RhH(PPh_3)_3]$ from $[RhCl(PPh_3)_3]$ and $Li[NR_2]$}.[11] The very reactive hydride intermediate then solvolyses (trace H_2O or MeOH) to eliminate NH_2Et and produce (1) (X = OH or OMe) which is converted into (1; X = H). The latter conversion is presumed to proceed by elimination of CH_2O. Although this product was not detected, the reaction appears to be established, *e.g.* in the formation of $[PtH_2(PPr^i_3)_2]$ from $[Pt(PPr^i_3)_3]$ and MeOH.[12] Although we have attempted to isolate intermediates such as the proposed hydride ethylamide we have been frustrated by their extreme hydrolytic/thermal instability.

Redox Properties and Reactions of Nitrosyl Complexes.—Because complexes (1) are in a low-valent state (formal oxidation state could be M^0 or M^{II}) they are relatively easily oxidised. We give the measured $E_{\frac{1}{2}}^{ox}$ values for the one-electron oxidation of (1) in Table 3; the variation of $E_{\frac{1}{2}}^{ox}$ with ligand *trans* to the NO group has already been discussed elsewhere [8] and the high electron-releasing properties of the OH group have been demonstrated. We have used the oxidation reactions of complexes (1) to prepare new nitrosyl complexes and we have also extended the range of ligands in the (1) series by metathetical reactions. Scheme (3) (M = Mo or W; X = Cl or I; R = Me or Ph; Z = SCN, NCO, or N_3) summarises our discoveries.

The physical properties of all new nitrosyl complexes prepared are given in Table 1.

Compounds of the type $[Mo(NO)(NCR)(dppe)_2][BF_4]$ and $[Mo(NO)(NCR)(dppe)_2][BF_4]_2$ (R = Me or Ph) were originally prepared by treatment of (1; X = OH) with $[NO][BF_4]$ in an attempt to prepare a bis(nitrosyl) cation which could be reduced to the neutral bis(nitrosyl) complex. The reaction solvent was, however, RCN which took part in the reaction to give the isolated RCN–nitrosyl complex cations. Since our work was completed, these complex cations have also been prepared (R = Me) from $[Mo(NO)(NCMe)_5]^{2+}$ and dppe.[13] The mono- and di-cationic complexes may be interconverted by heating the dication or oxidising the monocation with $[NO][BF_4]$ or $Ag[BF_4]$ as shown in Scheme 3. They may also be prepared from (1; X = OH) using $Ag[BF_4]$ in RCN.



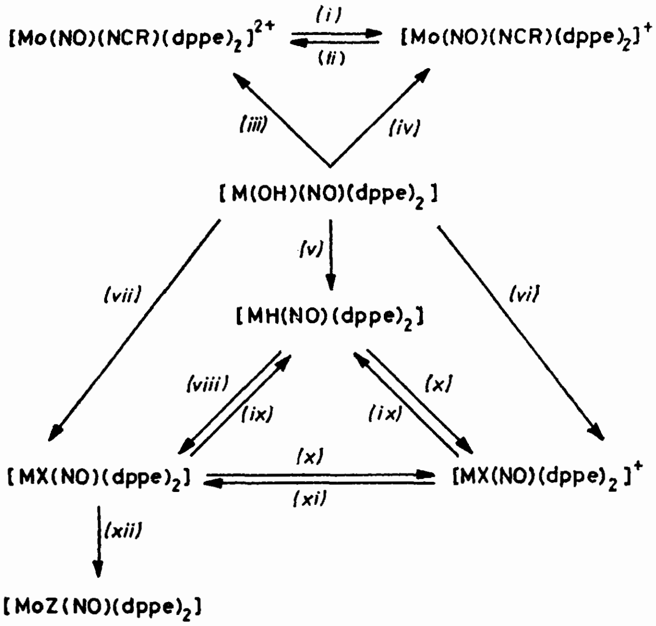
SCHEME 2 (*i*) Et_2NNO, $-2N_2$; (*ii*) $-C_2H_4$; (*iii*) ROH, $-NH_2Et$; (*iv*) $-CH_2O$

Halogens were also used as oxidising agents, thus I_2 gave $[MI(NO)(dppe)_2][I_3]$ from (1; X = OH or H). These cations were reduced on refluxing in thf to $[MI(NO)(dppe)_2]$, which were also prepared from (1; X = OH or H) and $\frac{1}{2}I_2$ (Scheme 3). With the more strongly oxidising halogens Cl_2 and Br_2, oxidation resulted in loss of the nitrosyl group even at −40 °C, to give the halide complexes shown in reactions (3) and (4) (M = Mo or W, X = OH or H).

$$trans\text{-}[MX(NO)(dppe)_2] + Cl_2 \longrightarrow [MCl_2(dppe)_2] \quad (3)$$

$$trans\text{-}[MX(NO)(dppe)_2] + Br_2 \longrightarrow [MBr_2(dppe)_2]Br \quad (4)$$

Oxidation using $FeCl_3$ or $CuCl_2$ in MeOH gave salts of the violet chloride cations $[MCl(NO)(dppe)_2]Y$ (Y = $FeCl_4$ or $CuCl_2$). The complex $[MoCl(NO)(dppe)_2][PF_6]$ has also been obtained from $[MoCl(NO)(dppe)_2]$ and $[N_2C_6H_4F\text{-}p][PF_6]$.[13] These cations could be reduced to the neutral (1; X = Cl) species by Mg or Zn in thf or to (1; X = H) by $Na[BH_4]$.



SCHEME 3 (*i*) Heat; (*ii*) $Ag[BF_4]$ or $[NO][BF_4]$; (*iii*) $Ag[BF_4]$, $[NO][BF_4]$, RCN; (*iv*) $[NO][BF_4]$ or $Ag[BF_4]$, RCN, heat; (*v*) heat, MeOH; (*vi*) I_2, $FeCl_3$ or $CuCl_2$ in MeOH; (*vii*) $\frac{1}{2}I_2$ in thf; (*viii*) $\frac{1}{2}I_2$ in thf, heat; (*ix*) $Na[BH_4]$; (*x*) I_2, $FeCl_3$, or $CuCl_2$; (*xi*) Mg or Zn; (*xii*) NaZ, MeOH–thf. M = Mo or W; X = Cl or I; R = Me or Ph; Z = SCN, NCO, or N_3

Metathetical reactions were also carried out upon (1; X = OH, H, or I) to give (1; X = N_3) from Me_3SiN_3 or $Na[N_3]$ and (1; X = NCO or NCS), from Na[NCO] or Na[NCS]. All the compounds (1) and $[Mo(NO)(NCR)(dppe)_2]^+$ are crystalline, stable, diamagnetic, monomeric, and reasonably stable in air in the solid state but slowly decompose in solution. The cations $[MX(NO)(dppe)_2]^{n+}$ (n = 1 or 2) are paramagnetic, 1 : 1 or 1 : 2 electrolytes (Table 1), and are stable to air in the solid state or in solution.

Complexes (1) have low NO stretching values, in the region 1 510—1 560 cm^{-1}, indicative of strong π release to linear NO from the low-valent metal centre. Such low frequencies are close to the range found for bent NO, acting as a one-electron donor, and might be taken to indicate susceptibility of NO to electrophilic attack. We have no example of such attack however, and correction of the ν(NO) values according to Iber's rules[14] (Table 1) clearly gives a better guide to the linear structure and inert behaviour of NO in this environment. The structures of all the diamagnetic complexes are shown by their singlet ^{31}P n.m.r. spectra and comparison with the structure of (1; M = Mo, X = OH) to have the *trans* arrangement of phosphine ligands.

Conclusions.—The series of low-valent nitrosyl complexes of molybdenum and tungsten has been extended, partly by a fortuitous reaction involving adventitious H_2O, to give [M(OH)(NO)(dppe)$_2$]. This reaction indicates the high affinity of these metals in this environment for oxide and hydroxide ligands which act as strong π-releasing groups, as has also been demonstrated by the preparation and structure of the analogue [Mo(OH)(O)(dppe)$_2$][BF$_4$].[7]

EXPERIMENTAL

Air-sensitive materials were handled by standard dinitrogen-flow or vacuum techniques. Solvents were dried by standard methods and distilled before use. Dinitrogen complex precursors were prepared by published methods.[15] N.m.r. spectra were determined on JEOL PS100 or FX90Q instruments and i.r. spectra with Pye-Unicam SP1200 or SP2000 instruments. Conductivities were determined with a Portland Electronics conductivity bridge and m.p.s with a Kofler hot-stage or electrothermal apparatus. Analyses were by Mr. and Mrs. A. G. Olney of these laboratories.

Crystallography.—*Crystal data*. $C_{52}H_{49}MoNO_2P_4 \cdot 2C_4H_8O$, $M = 1\,084.1$, Monoclinic, $a = 11.434(1)$, $b = 13.541(1)$, $c = 17.510(2)$ Å, $\beta = 95.82(1)°$, $U = 2\,697.0$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}, $F(000) = 1\,132$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 4.08$ cm^{-1}. Space group $P2_1$ from systematic absences of $0k0$ for k odd and successful refinement.

A translucent yellow crystal *ca.* 0.35 × 0.35 × 0.35 mm sealed in a glass capillary tube was used for data collection on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell dimensions were derived from the setting angles for 12 reflections. Intensities for $hk\pm l$ reflections with $2 < \theta < 25°$ were measured by an ω—2θ step scan using Mo-K_α radiation with a graphite-crystal monochromator. The intensities of three standard reflections were monitored every 100 reflections and showed no significant variation. Data were corrected for Lorentz, polarisation, and absorption effects and after averaging any equivalent data, 3 727 reflections with $I > 3\sigma(I)$ based on counting statistics were used in the structure analysis.

Structure solution and refinement. Although the diffraction data of the types $h0l$ for l odd were all very weak, there were 31 of them with $I > 3\sigma(I)$ and the structure was assumed to be $P2_1$ not $P2_1/c$. A Patterson map confirmed the Mo position as one which would be an inversion centre in $P2_1/c$ and therefore the molybdenum-phased map had this symmetry imposed on it. The positions of all the non-hydrogen atoms of the two *trans*-dppe ligands were taken from this Fourier map and in order to break the symmetry two other peaks in one of the remaining co-ordination sites were included, assigned as a nitrosyl group. Least-squares refinement was carried out in two large blocks with the Mo atom and one dppe ligand in one block and the remaining atoms in the other block and refined in alternate cycles. All phenyl rings were refined as idealised rigid bodies (C–C 1.393, C–H 1.08 Å) with H atoms attached. The H atoms were given the $U_{\text{iso.}}$ value of the C atom to which they were attached. A subsequent difference map revealed one atom in the remaining co-ordination site which from its peak height and distance from the Mo atom was assumed to be an oxygen atom of a hydroxyl ligand. Two molecules of tetrahydrofuran (thf) solvate were also located in general positions. Least-squares refinement was continued with anisotropic temperature factors for Mo, N, O, and the C atoms of the methylene groups. Hydrogen-atom positions for the methylene groups were then taken from an angle weight difference map and held fixed with a common $U_{\text{iso.}}$ value of 0.05. No attempt was made to include an H atom for the hydroxyl group or those for the thf molecules. The least-squares weighting scheme was $w = 4.7/[\sigma^2(F) + 0.0005F^2]$ and the refinement converged at $R = 0.058$, $R' = 0.078$, with a maximum shift-to-error ratio of 0.2. An equivalent refinement as the opposite enantiomer converged at exactly the same R and R' values. A final difference map had peaks of up to 0.7 e Å^{-3} in the region of the solvent molecules and also near Mo but was elsewhere featureless.

Scattering factors and dispersion corrections for neutral atoms were taken from ref. 16. The structure solution and refinement was done with the SHELX program system of G. M. Sheldrick. Final atom co-ordinates are listed in Table 5, bond lengths and angles in Table 4. The H-atom parameters, thermal parameters, and structure-factor Tables have been deposited as Supplementary Publication No. SUP 23160 (19 pp.).*

Preparation of Complexes.—trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*cyanato*(*nitrosyl*)*molybdenum*, *trans*-[Mo(NCO)(NO)(dppe)$_2$]. *N*-Methyl-*N*-nitrosourea (0.3 g, 3.8 mmol) was added to a solution of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (1 g, 1 mmol) in thf (100 cm^3). The mixture was heated under reflux under dinitrogen for 3 h when the colour changed from orange to yellow. The mixture was then cooled to room temperature, filtered, and the filtrate concentrated under reduced pressure to *ca.* 20 cm^3. Addition of Et_2O (20 cm^3) gave a yellow solid which was recrystallised from thf–Et_2O as yellow *crystals* (0.6 g, 60%).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydroxo*(*nitrosyl*)*molybdenum*, *trans*-[Mo(OH)(NO)(dppe)$_2$]. Diethyl-*N*-nitrosoamine (0.55 g, 5.4 mmol) and $K_2[CO_3]$ (0.2 g) were added to a solution of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (1 g, 1 mmol) in thf (100 cm^3). The mixture was heated under reflux under dinitrogen with tungsten-light irradiation for 4 h when the colour changed from orange to yellow. The mixture was filtered when hot, then cooled to room temperature to spontaneously produce yellow *crystals* which were recrystallised from thf (0.6 g, 60%).

Measurement of Organic Products in the Reaction of trans-[Mo(N$_2$)$_2$(dppe)$_2$] *with* Et_2NNO.—(*a*) The compound Et_2NNO (0.2 cm^3) was added to a mixture of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (0.55 g, 5.4 mmol) and $K_2[CO_3]$ (0.5 g) in xylene (20 cm^3), the mixture was frozen and then degassed. The flask was sealed and the mixture stirred at 80 °C under tungsten-light irradiation for 4 h. The contents of the flask were then frozen and the evolved gases measured using a Topler pump and identified by mass spectroscopy. The ethylene and amine yields were then determined by mass spectroscopy and gas chromatography.

(*b*) Using MeOH (1 cm^3) instead of $K_2[CO_3]$, all other procedures as method (*a*).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydroxo*(*nitrosyl*)*tungsten*, *trans*-[W(OH)(NO)(dppe)$_2$].—This complex was prepared as its molybdenum analogue with *ca.* 15 h reaction time.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*nitrosyl*)*molybdenum*, *trans*-[MoH(NO)(dppe)$_2$].—(*a*) This com-

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

pound was prepared in a similar way to its hydroxo-analogue using MeOH (0.5 cm^3) instead of K$_2$[CO$_3$] and was recrystallised from thf–Et$_2$O.

TABLE 5

Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	3(1)	5 000(0)	7 501(1)
P(1)	−259(2)	3 898(2)	6 363(1)
P(2)	−1 071(2)	6 132(2)	6 545(1)
P(3)	263(2)	6 076(2)	8 651(1)
P(4)	1 078(2)	3 913(2)	8 433(1)
N	1 397(6)	5 506(5)	7 034(4)
O(1)	2 088(7)	5 763(6)	6 726(5)
O(2)	−1 340(12)	4 604(8)	8 004(5)
C(1)	1 030(5)	3 270(5)	6 150(4)
C(2)	1 827(5)	3 768(5)	5 735(4)
C(3)	2 901(5)	3 332(5)	5 622(4)
C(4)	3 179(5)	2 398(5)	5 923(4)
C(5)	2 382(5)	1 899(5)	6 337(4)
C(6)	1 308(5)	2 335(5)	6 451(4)
C(7)	−1 450(5)	2 976(4)	6 206(4)
C(8)	−1 440(5)	2 225(4)	5 661(4)
C(9)	−2 399(5)	1 588(4)	5 533(4)
C(10)	−3 368(5)	1 703(4)	5 949(4)
C(11)	−3 378(5)	2 454(4)	6 493(4)
C(12)	−2 420(5)	3 091(4)	6 622(4)
C(13)	−629(10)	4 685(8)	5 412(5)
C(14)	−611(12)	5 804(8)	5 602(6)
C(15)	−2 659(4)	6 001(5)	6 463(4)
C(16)	−3 253(4)	5 733(5)	5 758(4)
C(17)	−4 470(4)	5 608(5)	5 689(4)
C(18)	−5 093(4)	5 752(5)	6 325(4)
C(19)	−4 499(4)	6 020(5)	7 030(4)
C(20)	−3 282(4)	6 144(5)	7 099(4)
C(21)	−785(5)	7 458(4)	6 540(4)
C(22)	−1 683(5)	8 152(4)	6 400(4)
C(23)	−1 418(5)	9 158(4)	6 410(4)
C(24)	−255(5)	9 470(4)	6 561(4)
C(25)	644(5)	8 776(4)	6 701(4)
C(26)	378(5)	7 770(4)	6 690(4)
C(27)	−1 077(5)	6 826(4)	8 809(4)
C(28)	−1 989(5)	6 440(4)	9 190(4)
C(29)	−3 015(5)	6 986(4)	9 231(4)
C(30)	−3 130(5)	7 918(4)	8 892(4)
C(31)	−2 218(5)	8 304(4)	8 511(4)
C(32)	−1 191(5)	7 758(4)	8 469(4)
C(33)	1 367(6)	7 037(5)	8 834(4)
C(34)	1 350(6)	7 640(5)	9 478(4)
C(35)	2 260(6)	8 311(5)	9 665(4)
C(36)	3 186(6)	8 380(5)	9 207(4)
C(37)	3 203(6)	7 777(5)	8 562(4)
C(38)	2 293(6)	7 106(5)	8 375(4)
C(39)	634(12)	5 352(8)	9 475(5)
C(40)	605(8)	4 267(7)	9 377(5)
C(41)	2 685(4)	4 020(5)	8 538(4)
C(42)	3 402(4)	4 319(5)	9 190(4)
C(43)	4 606(4)	4 444(5)	9 155(4)
C(44)	5 095(4)	4 269(5)	8 469(4)
C(45)	4 378(4)	3 970(5)	7 818(4)
C(46)	3 173(4)	3 845(5)	7 852(4)
C(47)	907(6)	2 558(4)	8 462(4)
C(48)	1 844(6)	1 925(4)	8 682(4)
C(49)	1 669(6)	905(4)	8 673(4)
C(50)	558(6)	518(4)	8 444(4)
C(51)	−378(6)	1 151(4)	8 224(4)
C(52)	−204(6)	2 171(4)	8 233(4)
O(4)	4 740(12)	4 144(11)	4 197(7)
C(53)	5 767(22)	3 526(18)	4 494(14)
C(54)	6 680(30)	4 176(28)	4 023(21)
C(55)	5 908(28)	3 646(24)	3 267(19)
C(56)	4 778(17)	4 156(15)	3 352(11)
O(3)	6 485(13)	1 709(11)	8 936(8)
C(57)	6 118(21)	894(19)	8 248(13)
C(58)	5 160(25)	358(22)	8 530(16)
C(59)	5 397(19)	1 704(17)	9 370(12)
C(60)	4 589(24)	1 061(22)	9 033(16)

(*b*) The complex *trans*-[Mo(OH)(NO)(dppe)$_2$] (0.5 g, *ca.* 0.5 mmol) was heated under reflux under dinitrogen in MeOH (50 cm^3) for 3 h. The yellow precipitate was filtered off and recrystallised from thf–Et$_2$O as yellow *crystals* (0.4 g, *ca.* 80% yield).

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*hydrido*(*nitrosyl*)*tungsten*, *trans*-[WH(NO)(dppe)$_2$].—This complex was prepared in a similar way to its molybdenum analogue.

trans-*Acetonitrilebis*[1,2-*bis*(*diphenylphosphino*)*ethane*](*nitrosyl*)*molybdenum Tetrafluoroborate*, *trans*-[Mo(NO)(NCMe)(dppe)$_2$][BF$_4$].—(*a*) Nitrosonium tetrafluoroborate (2 molar excess) was added to a suspension of *trans*-[Mo(OH)(NO)(dppe)$_2$] (0.5 g) in MeCN (50 cm^3). The mixture was heated under reflux for 3 h under dinitrogen when the colour changed from yellow to purple and finally to orange. The reaction solution was then concentrated under reduced pressure to *ca.* 10 cm^3 and addition of Et$_2$O (50 cm^3) gave an orange solid which was recrystallised from CH$_2$Cl$_2$–Et$_2$O as orange *crystals* (0.4 g, 70%).

(*b*) As (*a*) but using Ag[BF$_4$] instead of [NO][BF$_4$].

(*c*) The complex [Mo(NO)(NCMe)(dppe)$_2$][BF$_4$]$_2$ (0.3 g) was heated under reflux in thf under dinitrogen for 3 h. The colour of the solution changed from purple to orange and on cooling the reaction mixture to room temperature orange crystals were deposited and shown to be the desired product by spectroscopy (0.2 g, 60%).

Acetonitrilebis[1,2-*bis*(*diphenylphosphino*)*ethane*](*nitrosyl*)*molybdenum Bis*(*tetrafluoroborate*), [Mo(NO)(NCMe)(dppe)$_2$][BF$_4$]$_2$.—(*a*) The compound [NO][BF$_4$] (2 molar excess) was added to a suspension of *trans*-[Mo(OH)(NO)(dppe)$_2$] (0.5 g) in MeCN (50 cm^3). The mixture was stirred at room temperature for 3 h, the colour changed from yellow to purple, and the solution was then concentrated under reduced pressure to *ca.* 10 cm^3. Addition of Et$_2$O (50 cm^3) gave a purple solid which was recrystallised from CH$_2$Cl$_2$–Et$_2$O to give purple *crystals* (0.45 g, 80%).

(*b*) As (*a*) but using Ag[BF$_4$] instead of [NO][BF$_4$].

(*c*) The compound [NO][BF$_4$] (2 mol equivalents) was added to a solution of *trans*-[Mo(NO)(NCMe)(dppe)$_2$][BF$_4$] (0.4 g) in MeCN (50 cm^3). The mixture was stirred under dinitrogen for 2 h when the colour changed from orange to purple. The solution was then concentrated under reduced pressure to *ca.* 10 cm^3 when addition of Et$_2$O gave a purple solid which was recrystallised from CH$_2$Cl$_2$–Et$_2$O as purple *crystals*.

(*d*) As (*c*) but using Ag[BF$_4$] instead of [NO][BF$_4$].

The PhCN analogue was similarly prepared.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*nitrosyl*)*molybdenum*, *trans*-[MoI(NO)(dppe)$_2$].—(*a*) Iodine (0.5 mol equivalents) was added to a solution of *trans*-[MoX(NO)(dppe)$_2$] (X = OH or H) (0.5 g) in thf (50 cm^3). The mixture was heated under reflux under dinitrogen for 3 h when the colour changed from yellow to brown then to yellow again. The solution was then concentrated under reduced pressure to 10 cm^3 then addition of Et$_2$O gave a yellow solid which was recrystallised from CH$_2$Cl$_2$–Et$_2$O as yellow *crystals* (0.45 g, 85%).

(*b*) The complex [MoI(NO)(dppe)$_2$][I$_3$] (0.5 g) was heated under reflux or reduced by Zn or Mg at room temperature under dinitrogen in thf for 3 h. The colour of the solution changed from brown to yellow and further procedure was similar to method (*a*) above.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*nitrosyl*)*molybdenum Tri-iodide*, [MoI(NO)(dppe)$_2$][I$_3$].—Iodine (10 molar excess) was added to a solution of *trans*-[MoX(NO)-

(dppe)$_2$] (X = OH, H, or I) (0.5 g) in thf (50 cm^3). The mixture was stirred for 5 h to give a brown solid then the mixture was concentrated under reduced pressure to *ca.* 20 cm^3. Methanol (*ca.* 10 cm^3) was then added to the mixture which was kept at room temperature for 18 h when brown crystals were deposited (0.6 g, 90%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*nitrosyl*)*molybdenum Tetrachloroferrate*(III), [MoI(NO)(dppe)$_2$][FeCl$_4$].—The compound FeCl$_3$ (10 molar excess) was added to a suspension of *trans*-[MoI(NO)(dppe)$_2$] (0.4 g) in MeOH (30 cm^3) and the mixture stirred for 5 h when the colour changed from yellow to violet. A violet solid precipitated which was recrystallised from CH$_2$Cl$_2$–Et$_2$O as violet *crystals* (0.4 g, 85%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*nitrosyl*)*molybdenum Dichlorocuprate*(I), [MoI(NO)(dppe)$_2$][CuCl$_2$].—This complex was prepared in a similar manner to the [FeCl$_4$]$^-$ salt using CuCl$_2$ instead of FeCl$_3$.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*iodo*(*nitrosyl*)*molybdenum Tetraphenylborate*, [MoI(NO)(dppe)$_2$][BPh$_4$].—The compound Na[BPh$_4$] (1 molar equivalent) was added to a suspension of [MoI(NO)(dppe)$_2$]Y (Y = I$_3$, FeCl$_4$, or CuCl$_2$) (0.5 g) in MeOH (50 cm^3) and the mixture stirred for 1 h to give a brown solid which was filtered off and recrystallised from CH$_2$Cl$_2$–MeOH as brown *crystals* (0.6 g, 90%).

The tungsten analogues of the above cationic complexes were prepared in a similar manner.

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*nitrosyl*)*molybdenum Tetrachloroferrate*(III), [MoCl(NO)(dppe)$_2$][FeCl$_4$].—The compound FeCl$_3$ (10 molar excess) was added to a suspension of *trans*-[MoX(NO)(dppe)$_2$] (X = OH or H) (0.6 g) in MeOH (40 cm^3) and the mixture stirred for 1 h when the colour changed from yellow to violet. The precipitated violet solid was filtered off and recrystallised from CH$_2$Cl$_2$–Et$_2$O as violet *crystals* (0.5 g, 70%).

The analogous complex with [CuCl$_2$]$^-$ as anion was similarly prepared from CuCl$_2$.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*nitrosyl*)*molybdenum*, *trans*-[MoCl(NO)(dppe)$_2$].—The complex [MoCl(NO)(dppe)$_2$]Y (Y = FeCl$_4$ or CuCl$_2$) (0.8 g) was stirred with zinc (1 g) in CH$_2$Cl$_2$ (50 cm^3) under dinitrogen for 2 h when the solution changed from violet to yellow. The mixture was filtered and the filtrate concentrated under reduced pressure to 10 cm^3 when addition of MeOH (20 cm^3) produced yellow crystals, identical with an authentic sample [4] (0.4 g, 50%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*chloro*(*nitrosyl*)*molybdenum Tri-iodide*, [MoCl(NO)(dppe)$_2$][I$_3$].—Iodine (5 molar excess) was added to a solution of *trans*-[MoCl(NO)(dppe)$_2$] (0.4 g) in thf (40 cm^3) and the mixture stirred for 3 h then concentrated under reduced pressure to 10 cm^3 whereupon MeOH (20 cm^3) was added and the mixture kept for 18 h to give a brown solid which was filtered off and recrystallised from CH$_2$Cl$_2$–Et$_2$O as brown *crystals* (0.3 g, 60%).

Tungsten analogues of the above chloride complexes were similarly prepared.

trans-*Azidobis*[1,2-*bis*(*diphenylphosphino*)*ethane*](*nitrosyl*)*molybdenum*, *trans*-[Mo(N$_3$)(NO)(dppe)$_2$].—(*a*) The compound Me$_3$SiN$_3$ (5 molar excess) was added to a solution of *trans*-[Mo(OH)(NO)(dppe)$_2$] (0.45 g) in thf (50 cm^3) and the mixture heated under reflux under dinitrogen for 18 h then concentrated under reduced pressure to *ca.* 10 cm^3. Addition of MeOH (25 cm^3) gave yellow *crystals* (0.4 g, 85%).

(*b*) The compound Na[N$_3$] (10 molar excess) was added to a suspension of *trans*-[MoI(NO)(dppe)$_2$] in thf–MeOH (1 : 1, 50 cm^3) and the mixture heated under reflux under dinitrogen for 18 h then filtered and concentrated under reduced pressure to 10 cm^3. Addition of MeOH (30 cm^3) gave a yellow solid which was recrystallised from CH$_2$Cl$_2$–MeOH as yellow *crystals*.

The tungsten analogue was similarly prepared.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*nitrosyl*(*thiocyanato*)*molybdenum*, *trans*-[Mo(SCN)(NO)(dppe)$_2$].—This complex was prepared as its azido-analogue using method (*b*) and Na[SCN].

Reduction of [MX(NO)(dppe)$_2$]$^+$.—Zinc or magnesium (1 g) was added to a thf (30 cm^3) solution of [MX(NO)(dppe)$_2$]Y (X = Cl, I, N$_3$, SCN, or NCO; Y = I$_3$, FeCl$_4$, CuCl$_2$, or BPh$_4$) (0.5 g) and the mixture stirred under dinitrogen for 1 h when the colour changed from brown or violet to yellow. The reaction solution was then filtered, concentrated under reduced pressure to *ca.* 5 cm^3, and MeOH (10 cm^3) added to give the corresponding neutral species *trans*-[MX(NO)(dppe)$_2$].

Reactions of [MX(NO)(dppe)$_2$] *with* Na[BH$_4$].—The compound Na[BH$_4$] (0.5 g) was added to a thf (50 cm^3) solution of [MX(NO)(dppe)$_2$] (X = I, SCN, N$_3$, or NCO) (0.5 g) and the mixture stirred for 3 h then filtered. The filtrate was concentrated under reduced pressure to *ca.* 5 cm^3 then addition of MeOH (10 cm^3) gave a yellow crystalline solid identified by analysis, spectroscopic, and electrochemical properties as *trans*-[MH(NO)(dppe)$_2$].

Reactions of [MX(NO)(dppe)$_2$] *with Dichlorine and Dibromine.*—Two equivalents of Cl$_2$ in CCl$_4$ or of Br$_2$ were added to a toluene solution of [MX(NO)(dppe)$_2$] (X = OH or H) (0.2 g) at −40 °C. For chlorine as reagent, the solution was stirred for 15 min at −40 °C then concentrated under reduced pressure to 5 cm^3 to give a yellow solid identified by elementary analysis and i.r. as [MCl$_2$(dppe)$_2$].[17] For Br$_2$, a red solid was produced from the solution after stirring for 20 min, which was isolated and identified as [MBr$_2$(dppe)$_2$]Br [18] by elementary analysis and conductivity.

Reactions of [M(OH)(NO)(dppe)$_2$] *with* HCl.—One equivalent of HCl gas was added to a thf (30 cm^3) solution of [M(OH)(NO)(dppe)$_2$] (0.3 g) at room temperature and the mixture stirred for 18 h then concentrated under reduced pressure to *ca.* 5 cm^3. Addition of MeOH (*ca.* 20 cm^3) gave a yellow solid identified as [MoCl(NO)(dppe)$_2$] by i.r. and analysis.

Electrochemical Measurements.—Electrochemical experiments employed a three-electrode cell and the experimental conditions have been described elsewhere.[8]

Attempts to prepare Bis(*nitrosyl*) *Complexes of Molybdenum and Tungsten.*—(*a*) Gaseous NO (2 mol equivalents) was condensed *in vacuo* at −196 °C onto a solution of *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W, *ca.* 0.3 g) in thf or benzene (*ca.* 50 cm^3). The reaction mixture was slowly warmed to room temperature, then stirred for 15 h with tungsten-light irradiation. The solution colour changed from orange to yellow. The reaction solution was filtered and concentrated under reduced pressure to 10 cm^3. Addition of Et$_2$O (20 cm^3) gave a mixture of starting material and unidentified products.

(*b*) Gaseous NO was passed through a solution of *trans*-[M(N$_2$)$_2$(dppe)$_2$] (M = Mo or W) in thf for 18 h. An unidentified yellow solid [when M = Mo, ν(NO) at 1 560 cm^{-1}; when M = W, ν(NO) at 1 560, 1 640, and 1 760 cm^{-1}] was produced when the reaction solution was concentrated under reduced pressure to 10 cm^3 followed by addition of Et_2O (20 cm^3).

(*c*) The compound [NO][BF_4] (*ca.* 10 molar excess) was added to a suspension of *trans*-[Mo(N_2)Y(dppe)$_2$] (Y = N_2 or NCMe) (0.3 g) in MeCN (30 cm^3). The reaction mixture was stirred under dinitrogen for 2 h whereupon the colour changed from orange-red to purple and gas was evolved. The reaction mixture was filtered and the filtrate was pumped to dryness, washed with Et_2O (3 × 5 cm^3), and dried to give a purple solid. Repeated recrystallisation from CH_2Cl_2–Et_2O gave purple crystals (0.05 g) whose i.r. spectrum was identified as that of [Mo(NO)(NCMe)(dppe)$_2$][BF_4].

(*d*) The compound [NO][BF_4] (*ca.* 10 molar excess) was added to a solution of *trans*-[Mo(N_2)$_2$(dppe)$_2$] (0.3 g) in thf (50 cm^3). The reaction mixture was stirred for 1 h under dinitrogen whereupon the solution colour changed from orange to green and a gas was evolved. The reaction solution was pumped to dryness, washed with Et_2O (3 × 5 cm^3), and dried to give some green solid. This green solid decomposed during attempted purification in thf.

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REFERENCES

[1] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, 589; J. Chatt and R. L. Richards in ' New Trends in the Chemistry of Nitrogen Fixation,' eds. J. Chatt, L. M. da Câmara Pina, and R. L. Richards, Academic Press, London, 1980.

[2] J. Chatt, C. M. Elson, A. J. L. Pombiero, G. H. D. Royston, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1978, 165; C. J. Pickett, A. J. L. Pombeiro, R. L. Richards, and S. A. Sangokoya, *J. Organomet. Chem.*, 1980, **202**, C15.

[3] T. Tasumi, M. Hidai, and Y. Uchida, *Inorg. Chem.*, 1975, **14**, 2530.

[4] J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1976, 1520.

[5] N. G. Connelly, *J. Chem. Soc., Dalton Trans.*, 1973, 2183.

[6] M. I. Bruce, *Organomet. Chem. Rev. B*, 1972, **9**, 53; J. C. Slater, *J. Chem. Phys.*, 1964, **41**, 3199.

[7] M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1978, **17**, 668.

[8] J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 2032.

[9] T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2883.

[10] M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida, and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 4447.

[11] S. E. Diamond and F. Mares, *J. Organomet. Chem.*, 1977, **142**, C55.

[12] T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, 1977, **99**, 2134.

[13] S. Clamp, N. G. Connelly, G. E. Taylor, and T. S. Louttit, *J. Chem. Soc., Dalton Trans.*, 1980, 2162.

[14] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.

[15] J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, 1980, **20**, 119.

[16] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321; D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1981; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *ibid.*, 1965, **42**, 3175.

[17] M. W. Anker, J. Chatt, G. J. Leigh, and A. G. Wedd, *J. Chem. Soc., Dalton Trans.*, 1975, 2639.

[18] J. Chatt, J. P. Lloyd, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1976, 565.