Nitrosyl Complexes of Molybdenum and Tungsten

By **Fiona King** and **G. Jeffery Leigh,*** School of Molecular Sciences, The University of Sussex, Brighton BN1 9QJ

Molybdenum pentachloride in benzene reacts with nitrogen oxide to form a red nitrosyl from which a series of mononitrosyl complexes of molybdenum can be synthesised, including $[MoCl_4(NO)]^-$, $[MoCl_5(NO)]^{2-}$, $[MoCl_3(NO)L_2]$, $[MoCl_4(NO)L]^-$, $[MoCl_3(NO)L_3]$, $[MoCl_3(NO)L_2]^-$, $[MoCl_2(NO)L_3]$, and $[MoCl(NO)L_4]$ (L = neutral ligand). The co-ordinated NO in these complexes shows no sign of reactivity with nucleophiles or with electrophiles although the original red nitrosyl is apparently converted by some tertiary phosphines into amido- and phosphine-iminido-complexes. Some tungsten analogues are also described.

NITROSYL complexes of molybdenum form a large class of complexes.[1] A large proportion of them are also η-cyclopentadienyl complexes, and there are relatively few which contain only halides and/or tertiary phosphines as ligands in addition to NO. We were initially interested in such complexes because we believed, probably erroneously, that a study of the reactivity of co-ordinated nitrogen oxide might enable us to understand better the synthesis and reactivity of analogous dinitrogen complexes.[2]

However, the synthesis of halido(nitrosyl)(tertiary phosphine) complexes is not easy for the following reasons. Nitrogen oxide is an oxidising agent, and its oxidising power is brought out particularly well by elements such as molybdenum and tungsten which have a high affinity for oxygen, particularly in the higher oxidation states. Thus molybdenum and tungsten complexes often react with NO to form dinitrogen oxide and complexes containing oxido-ligands (see below). Secondly, tertiary phosphines are reducing agents, and NO often converts tertiary phosphines, even when bound, into phosphine oxides. Finally, when nitrosyl complexes are formed there is a tendency to form polynitrosyls, especially dinitrosyls. The purpose of this work was to find simple routes to mononitrosyl complexes of molybdenum and tungsten with only halide and tertiary phosphines as co-ligands. In this we were successful; in our second aim of investigating the reactivity of co-ordinated nitrogen oxide we were not.

The known halidonitrosyl complexes of molybdenum and tungsten are mainly of the types $[\{MX_2(NO)_2\}_n]$ [ν(NO) at *ca.* 1 800 and 1 690 cm^{-1}] and $[MX_2(NO)_2L_2]$ [ν(NO) at *ca.* 1 790 and 1 680 cm^{-1}] (M = Mo or W; X = Cl, Br, or I; L = oxygen, nitrogen, phosphorus, or arsenic donors); [3-7] L_2 may be a bidentate ligand such as ethylenediamine,[8,9] but in only a few cases is L bound to the metal before the nitrogen oxide is introduced.[7,10,11] Useful precursors for dinitrosyls can be obtained from $MoCl_5$ [10-12] or WCl_6 [13] and NO in dichloromethane, but mononitrosyls have hitherto been much rarer. At the time of writing, the known mononitrosyls are $[\{MoCl_3(NO)\}_n]$[ν(NO) at 1 590 cm^{-1}],[14] $[MoCl_3(NO)L_2]$[L_2 = 2,2′-bipyridyl or $(PPh_3O)_2$],[14,15] and $[\{WCl_3(NO)\}_n]$ [14] and $[WCl_3(NO)(PPh_3O)_2]$.[14] The complexes $[MCl_3(NO)L_2]$ have ν(NO) in the range 1 650—1 710 cm^{-1} which is not reliably diagnostic for a straight or bent structure. The eighteen-electron rule is not obeyed by any of these complexes, but linear M–N–O systems (NO as a three-electron donor) seem most appropriate.

RESULTS AND DISCUSSION

Reactions of $[MoCl_4L_2]$ (L = *tertiary phosphine*, PMe_2Ph, $PMePh_2$, $PEtPh_2$, *or* PPh_3) *with Nitrogen Oxide.*—The reactions were carried out at room temperature in benzene, giving greenish yellow crystalline solids which had three bands assigned to ν(NO) at *ca.* 1 660, 1 700, and 1 780 cm^{-1}, three or four bands assignable to ν(P=O) at 1 100–1 200 cm^{-1}, and two strong bands at *ca.* 910 and 950 cm^{-1}. This is consistent with the solids being mixtures of three known kinds of complex, $[MoCl_3(NO)(\text{phosphine oxide})_2]$ [14] [ν(NO) at *ca.* 1 700 cm^{-1}], $[MoCl_2(NO)_2(\text{phosphine oxide})_2]$ [5] [ν(NO) at *ca.* 1 780 and 1 660 cm^{-1}], and $[MoCl_2O_2(\text{phosphine oxide})_2]$ [16] [ν(Mo=O) at *ca.* 910 and 950 cm^{-1}]. The components of these mixtures were usually inseparable by crystallisation and chromatography, but by choice of phosphine L and by varying reaction conditions it was possible to isolate specific products.

The reaction of $[MoCl_4(PEtPh_2)_2]$ with NO in benzene at room temperature for 15 min gave a yellow solution from which pure $[MoCl_2(NO)_2(PEtPh_2O)_2]$ was isolated. After 2 min of such a reaction in tetrahydrofuran (thf), $[MoCl_3(NO)(PEtPh_2O)_2]$ contaminated with dinitrosyl was isolated, but there was no indication of a dioxo-complex. In benzene at reflux after 1 h, pure $[MoCl_2O_2(PEtPh_2O)_2]$ was isolated. These results suggest that the mononitrosyl, dinitrosyl, and dioxo-complexes are formed in successive steps. It is unlikely that oxidation of tertiary phosphine to tertiary phosphine oxide occurs as

---

[1] There are many reviews of metal nitrosyls: see, for example, N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, **6**, 47.

[2] J. H. Enemark and R. D. Feltham, *Co-ordination Chem. Rev.*, 1974, **13**, 339.

[3] B. F. G. Johnson and F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 1609.

[4] B. F. G. Johnson, *J. Chem. Soc.* (*A*), 1967, 475.

[5] F. Canziani, U. Sartorelli, and F. Cariati, *Ann. Chim.* (*Italy*), 1964, **54**, 1354.

[6] U. Sartorelli, F. Zingales, and F. Canziani, *Chim. Ind.* (*Milan*), 1967, **49**, 751.

[7] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1149.

[8] J. A. Bowden, R. Colton, and C. J. Commons, *Austral. J. Chem.*, 1972, **25**, 1393.

[9] R. D. Feltham, W. Silverthorn, and G. McPherson, *Inorg. Chem.*, 1969, **8**, 344.

[10] R. Taube and K. Seyferth, *Z. Chem.*, 1973, **13**, 300.

[11] L. Bencze, *J. Organometallic Chem.*, 1973, **56**, 303.

[12] W. B. Hughes and E. A. Zuech, *Inorg. Chem.*, 1973, **12**, 471.

[13] J. Kohan, S. Vaslag, and L. Bencze, *Inorg. Chim. Acta*, 1975, **14**, L1.

[14] R. Davis, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 508.

[15] L. Bencze, J. Kohan, B. Mohai, and L. Marko, *J. Organometallic Chem.*, 1974, **70**, 421.

[16] M. L. Larson and F. W. Moore, *Inorg. Chem.*, 1966, **5**, 801.

an initial step because $[MoCl_4(PMePh_2O)_2]$ does not react with NO at room temperature, and in benzene at reflux the conversion into $[MoCl_2O_2(PMe_2PhO)_2]$ takes *ca.* 5 h. This ligand oxidation which is so ready in Group 6 is not unknown for the later transition elements, for example, the *only* product formed from an excess of NO and $[NiCl_2(PEt_3)_2]$ is $[NiCl_2(PEt_3O)_2]$.[17]

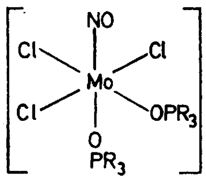
The tungsten complex $[WCl_4(PEtPh_2)_2]$ gave $[WCl_2O_2(PEtPh_2O)_2]$ after 10 min at room temperature. No intermediate nitrosyls were isolated. Nitrogen oxide reacted slowly with $[MoCl_4(py)_2]$ (py = pyridine) in refluxing benzene to give an inseparable mixture apparently containing both dinitrosyl and dioxo-species. It reacts with $[MoCl_4(NCEt)_2]$ in refluxing benzene to give $[MoCl_2(NO)_2(NCEt)_2]$ after 2 h.[10] No other products were detected.

Reactions of $[MoCl_3L_3]$ (L = thf *or* PMe_2Ph) *with Nitrogen Oxide.*—At room temperature in thf or benzene, these reactions gave inseparable mixtures of mono- and di-nitrosyls.

Nitrosation of Molybdenum Pentachloride and Tungsten Hexachloride.—As discussed above, molybdenum pentachloride reacts with NO in dichloromethane to give dark green $[\{MoCl_2(NO)_2\}_n]$.[10-12] However, in benzene, a dark red solid was precipitated. This decomposes in air, and in thf, hexane, methanol, acetone, and diethyl ether, but is stable under dinitrogen and in dichloromethane and benzene. The i.r. spectrum has weak bands at 1 700 and 1 815 cm^{-1} which may be due to trace amounts of $[\{MoCl_3(NO)_2\}_n]$ and a third very strong band at 2 000 cm^{-1} which is characteristic of the new red nitrosyl. The frequency is too low to suggest a nitrosonium salt [ν(NO) in the range 2 150—2 400 cm^{-1}], but is rather high for a co-ordinated nitrogen oxide unless it be in a complex of very high oxidation state, *e.g.* $[MoCl_5(NO)]$, but no satisfactory analyses were obtained for this solid.

One molar equivalent of tetraethylammonium chloride reacted with the red nitrosyl in dichloromethane to give an immediate yellow precipitate of $[NEt_4][MoCl_4(NO)]$, which can be obtained pure and can also be completely characterised. It has ν(NO) at 1 715 cm^{-1}, which is probably consistent with a linear M–N–O system, and it reacts with tertiary phosphines to form a series of mononitrosyls as discussed below. An excess of $[NEt_4]Cl$ converted the red nitrosyl into $[NEt_4]_2[MoCl_5(NO)]$. This has ν(NO) at 1 670 cm^{-1}, but is remarkably unreactive and is apparently not of great value for further synthetic work.

Products derived from the Red Nitrosyl, ($MoCl_5$ + NO).—(a) *Reaction with phosphine oxides.* The red nitrosyl ($MoCl_5$ + NO) reacted with tertiary phosphine oxides (PR_3O) to give greenish yellow crystalline solids $[MoCl_3(NO)(PR_3O)_2]$ (PR_3O = $PMePh_2O$, $PEtPh_2O$, or PPh_3O). These complexes are diamagnetic, monomeric in solution, and non-conductors in nitromethane solution. The i.r. spectra each showed a strong band at *ca.* 1 700 cm^{-1} [ν(NO)] and two bands in the region 1 120—1 170 cm^{-1} [ν(PO)]. The i.r. and ^1H n.m.r. spectra are consistent with the following structure.



(b) *Reactions with tertiary phosphines.* The reactions of the red nitrosyl with phosphines are more complex, and depend on the particular phosphine.

(i) *Triphenylphosphine.* The red nitrosyl reacted with triphenylphosphine to give $[MoCl_3(NO)(PPh_3O)_2]$, and in less yield than obtained with the phosphine oxide direct, but free from dioxo-species.

(ii) *Alkyldiphenylphosphines.* The reactions of the red nitrosyl with alkyldiphenylphosphines are very complex and give mixtures of products, containing, in addition to nitrosyls, phosphineimine and amido-complexes. The reactions of $PMePh_2$ were best characterised and allowed easiest separation of the three products, $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ [ν(NO) at 1 585 cm^{-1}], $[MoCl_4(NPMePh_2)(PMePh_2O)]$ [ν(P=N) at 1 125 cm^{-1}], and $[MoCl_3(NH_2)(PMePh_2O)]Cl$ [ν(NH) at 3 210 and 3 300 cm^{-1}]. The mechanism of formation of these complexes will be discussed below. Fewer complexes could be isolated from other reaction mixtures, but $[MoCl_2(NO)(PPr^nPh_2)_2(PPr^nPh_2O)]$, $[MoCl_4(NPPr^nPh_2)(PPr^nPh_2O)]$, and $[MoCl_3(NH_2)(PEtPh_2O)_2]Cl$ were obtained from the appropriate reaction mixtures.

The complexes $[MoCl_2(NO)(PRPh_2)_2(PRPh_2O)]$ (R = Me or Pr^n) are green, needle-shaped, crystalline solids which decompose slowly in air. They are paramagnetic ($\mu_{eff.}$ *ca.* 1.9 B.M. in the solid state).* The methyldiphenylphosphine derivative reacted with $[NEt_4]Cl$ to yield $[NEt_4][MoCl_3(NO)(PMePh_2)_2]$. This reaction tends to confirm the presence of both methyldiphenylphosphine and its oxide in the original derivative. With 1,2-bis(diphenylphosphino)ethane (dppe), $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ forms $[MoCl(NO)(dppe)_2]$ and $[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]$. The complex $[MoCl(NO)(dppe)_2]$, which has also been synthesised from $[MoCl(NNH)(dppe)_2]$ and nitrogen oxide,[18] is monomeric and diamagnetic in solution and a non-conductor in nitromethane. A band at 1 545 cm^{-1} is assigned to ν(NO), but the M–N–O system is presumably linear. The complex $[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]$ has been formulated only on the basis of analytical and i.r. data, but it is too insoluble for any solution measurements. A dimeric structure with a bridging diphosphine conforms with the 18-electron rule. Finally, $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ reacts with trimethylsilyl diethyldithiocarbamate to yield the known complex $[Mo(NO)(S_2CNEt_2)_3]$.[19]

---

* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2; 1 mmHg $\approx 13.6 \times 9.8$ Pa.

[17] G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099.

[18] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1976, 1520.

[19] B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc.* (*A*), 1969, 1668.

(*iii*) *Diphenylphosphine*. The red nitrosyl reacted with diphenylphosphine to yield $[MoCl_2(NO)(PPh_2H)_3]$, which, like its alkyldiphenylphosphine analogues, is a monomeric paramagnetic ($\mu_{eff.}$ 1.76 B.M.) solid, a non-conductor in solution, and unstable in air; ν(NO) is at 1 628 cm^{-1}, some 40 cm^{-1} higher than in the alkyldiphenylphosphine analogues. The far-i.r. spectrum has two bands assignable to ν(Mo–Cl), which implies that $[MoCl_2(NO)(PRPh_2)_2(PRPh_2O)]$ ($R = Me$ or Pr^n), which show only one band assignable to ν(Mo–Cl), are not isostructural with $[MoCl_2(NO)(PPh_2H)_3]$.

(*iv*) *Dimethylphenylphosphine*. The red nitrosyl reacted with dimethylphenylphosphine to yield an oily mixture from which $[MoCl_3(NO)(PMe_2Ph)_3]$ was isolated in poor yield. This monomeric diamagnetic species has ν(NO) at 1 630 cm^{-1}. The ^1H n.m.r. spectrum in CD_2Cl_2 does not change significantly between -20 and 50 °C, and the phosphorus methyl protons appear as a triplet with a very broad and intense central resonance and sharp, relatively minor, side components. Apparently this indicates a *meridional* configuration for the phosphines with the doublet arising from the methyl protons of the unique phosphine coincident with the central peak of the *trans*-phosphine triplet.

(v) 1,2-*Bis*(*diphenylphosphino*)*ethane*. This diphosphine reacted with the red nitrosyl to yield a complex mixture from which we were able to isolate $[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]$, identical with the material prepared by an alternative route (see above).

Products derived from $[NEt_4][MoCl_4(NO)]$.—This complex reacted with neutral ligands L ($L = PPh_3$, $PMePh_2$, $PMePh_2O$, or $PEtPh_2O$) to form anionic diamagnetic complexes $[NEt_4][MoCl_4(NO)L]$ which have ν(NO) at *ca.* 1 700 cm^{-1} for L = phosphine oxide and *ca.* 1 675 cm^{-1} for L = phosphine. The far-i.r. spectra give no firm indication of structure because the three bands assignable to ν(Mo–Cl) are equivocal. With PMe_2Ph and dppe, disproportionation reactions occurred, producing $[MoCl_3(NO)(PMe_2Ph)_3]$ or $[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]$ respectively, and $[NEt_4]_2[MoCl_5(NO)]$. This last complex is totally unreactive towards neutral ligands, except in refluxing thf in the presence of magnesium when intractable mixtures were generally formed. The only exception was the reduction reaction with PPh_2H, which allowed the isolation of $[MoCl(NO)(PPh_2H)_4]$.

Tungsten hexachloride (and also the pentachloride) reacted with NO in benzene to form a red air-sensitive solid with a strong broad i.r. band at *ca.* 2 000 cm^{-1}. This red solid reacted with tertiary phosphines PR_3 ($PR_3 = PPh_3$, $PMePh_2$, or $PEtPh_2$) to form $[WCl_3(NO)(PR_3O)_2]$, and by careful choice of reaction conditions $[WCl_3(NO)(PR_3)_2]$ ($PR_3 = PMePh_2$ or $PEtPh_2$) were also isolated. Direct reaction with phosphine oxides yielded tungsten oxo-species. The band assigned to ν(NO) in these complexes is some 20 cm^{-1} lower than in the molybdenum analogues. Niobium and tantalum pentachlorides also reacted with NO in benzene to yield red materials with ν(NO) at *ca.* 2 000 cm^{-1}. However, on further reaction with tertiary phosphines, tertiary phosphine oxides, or with $[NEt_4]Cl$, the co-ordinated nitrogen oxide was lost and only oxo-species were formed.

The general classes of molybdenum nitrosyl complexes isolated (see Table 2) in this work, together with the approximate values assigned to ν(NO), are detailed below (Table 1). These complexes represent the first general series of mononitrosyl complexes of molybdenum. The observed ν(NO) range from values which can only be reconciled with the nitrogen oxide behaving as a three-electron donor (linear M–N–O) to values which could possibly arise from a one-electron (bent M–N–O) donor.[20] The 18-electron rule is not necessarily obeyed in complexes to the left-hand end of the transition series, so that $[MoCl(NO)L_4]$ may possibly contain a bent M–N–O system, giving the molybdenum valence shell 16 electrons only.

TABLE 1

Classes of molybdenum nitrosyl isolated

Formal oxidation state of metal	Complex type	$\bar{\nu}(NO)/cm^{-1}$ (Nujol)
V	$(MoCl_5 + NO)$	2 000
III	$[MoCl_4(BO)]^-$	1 715
III	$[MoCl_3(NO)L_2]$	1 700
III	$[MoCl_4(NO)L]^-$	1 685
III	$[MoCl_5(NO)]^{2-}$	1 670
III	$[MoCl_3(NO)L_3]$	1 630
II	$[MoCl_3(NO)L_2]^-$	1 600
II	$[MoCl_2(NO)L_3]$	1 600
I	$[MoCl(NO)L_4]$	1 540

We have also tried to investigate the reactivity of co-ordinated nitrogen oxide in these complexes. The red nitrosyl ($MoCl_5 + NO$) contains nitrogen oxide which should be susceptible to nucleophilic attack.[21] Assuming that the base strengths of the ligands L parallels their nucleophilicity, then the observed reactions of ($MoCl_5 + NO$) may be rationalised in terms of the base strengths of ligands L:[22,23] $PPh_3O < PRPh_2O < PPh_2H < PPh_3 < PRPh_2 < PR_2Ph$ ($R = alkyl$). Phosphine oxides are very weak bases, and hence react with ($MoCl_5 + NO$) to give simple mononitrosyls. Similarly, the more basic PPh_2H and PPh_3 also do this, but in lower yield. However, PR_2Ph and $PRPh_2$, in addition to ligating, also attack the nitrogen oxides probably as nucleophiles, and at the oxygen, yielding phosphineiminido- and amido-complexes. Whether all the ligands L also reduce ($MoCl_5 + NO$) (from Mo^V to Mo^{III}) cannot be ascertained without clarification of the nature of the red nitrosyl.

The phosphineiminido-complexes $[MoCl_4(NPRPh_2)(PRPh_2O)]$ ($R = Me$ or Pr^n) are yellow, crystalline, paramagnetic solids, whose solutions are both air and moisture sensitive. The complex with $R = Pr^n$ is identical with that formed from toluene-*p*-sulphonyl azide and $[MoCl_4(PPr^nPh_2)_2]$, which has been characterised by i.r.,

---

[20] B. A. Frenz and J. A. Ibers, *M.T.P. Internat. Rev. Sci. Phys. Chem. Ser.* 1, 1972, **11**, 33.

[21] F. Bottomley, W. V. F. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919.

[22] C. A. Streuli, *Analyt. Chem.*, 1960, **32**, 985.

[23] S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.

e.s.r., and mass-spectral measurements.[24] Its formation in this system may arise from nucleophilic attack of phosphine on co-ordinated nitrogen oxide, thus weakening the N–O bond and facilitating the removal of the oxygen by a further phosphine molecule.

TABLE 2

Nitrosyl complexes of molybdenum and tungsten

Complex	Colour	M.p. (θ_c/°C)[a]	Analysis[b] (%)				M[b]	μ/B.M.	Λ[c]/S cm^2 mol^{-1}	I.r. spectrum (cm^{-1})[d]				
			C	H	N	Cl				ν(NO)	ν(PO)		ν(M–Cl)	
$(MoCl_5 + NO)$	Dark red									2 000vs, br		360vs, br	300m, br	
$[NEt_4][MoCl_4(NO)]$	Yellow		24.8 (24.2)	5.5 (5.1)	7.5 (7.1)			*e*	93.4	1 715vs, br		340vs, br	310m	
$[NEt_4][MoCl_4(NO)(PMe_2Ph)]$	Orange	157	42.4 (42.2)	5.6 (5.6)	4.8 (4.7)	24.1 (23.7)			100	1 675vs		332s	321s	308s
$[NEt_4][MoCl_4(NO)(PPh_3)]$	Orange	176—182	46.8 (47.3)	5.6 (5.3)	3.8 (4.2)	21.9 (21.5)		*e*		1 675 vs (sh)		318vs		
$[NEt_4][MoCl_4(NO)(PMePh_2O)]$	Greenish yellow	170—173	41.4 (41.1)	5.5 (5.4)	4.3 (4.6)	23.2 (23.1)		*e*	83.7	1 700vs	1 160vs, br	320vs, br		
$[NEt_4][MoCl_4(NO)(PEtPh_2O)]$	Greenish yellow	162—166	42.1 (42.1)	6.0 (5.6)	4.2 (4.5)	22.9 (22.6)		*e*	72.7	1 681vs	1 160vs, br	316vs, br		
$[MoCl_3(NO)(PMePh_2O)_2]\cdot C_6H_6$	Greenish yellow	102—104	50.0 (50.5)	4.1 (4.3)	1.7 (1.9)	14.1 (14.3)		*e*	*f*	1 695s	1 150vs 1 128vs	350vs	325vs	
$[MoCl_3(NO)(PEtPh_2O)_2]$	Yellowish green	158	49.0 (48.5)	4.4 (4.4)	1.7 (2.0)	15.3 (15.4)	651 (693)[g]	*e*	*f*	1 701vs	1 169vs 1 127vs	330vs, br		
$[NEt_4]_2[MoCl_5(NO)]$	Greenish yellow		34.5 (34.1)	7.2 (7.2)	7.1 (7.5)	31.7 (31.4)		*e*	157	1 670vs		310vs, br		
$[MoCl_3(NO)(PMe_2Ph)_3]\cdot 0.33C_6H_6$	Yellow	113—116	46.7 (46.4)	5.5 (5.2)	2.4 (2.1)	16.1 (15.8)	650 (673)[g]	*e*	*f*	1 630vs (sh)		280m	270s	
$[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]\cdot CH_2Cl_2$	Yellow	178	54.2 (54.4)	4.4 (4.3)	1.7 (1.6)	16.2 (16.1)		*e*	*f*	1 660vs		310m	295w	
$[NEt_4][MoCl_3(NO)(PMePh_2)_2]$	Green	119 (decomp.)	53.7 (53.5)	6.2 (6.1)	3.4 (3.7)	14.1 (13.9)		1.89	101	1 610vs 1 585vs		310m	298s	285m
$[MoCl_2(NO)(PMe_2Ph)_2(PMePh_2O)]$	Green	156 (decomp.)	57.6 (57.6)	5.0 (4.8)	1.8 (1.7)	9.0 (8.7)		1.91	*f*	1 585vs	1 160vs	310m		
$[MoCl_2(NO)(PPr^nPh_2)_2(PPr^nPh_2O)]$	Pale green	102—105 (decomp.)	59.8 (60.2)	5.7 (5.7)	1.5 (1.6)	8.1 (7.9)		1.93	*f*	1 600vs	1 145s	315m		
$[MoCl_2(NO)(PPh_2H)_3]$	Yellow	134—135	56.9 (57.2)	4.4 (4.4)	2.0 (1.9)	9.7 (9.4)		1.76	*f*	1 628vs		310s	270m	
$[MoCl(NO)(PPh_2H)_4]$	Yellow	135—140	63.9 (63.6)	5.2 (4.9)	1.6 (1.5)	4.1 (3.9)	910 (906)[g]	*e*	*f*	1 542vs		245w		
$[MoCl(NO)(dppe)_2]$	Yellow	215—220	65.5 (65.2)	5.3 (5.0)	1.5 (1.5)	4.0 (3.7)	941,[g] 959 ±1[h] (960)	*e*		1 542vs		245w		
$(WCl_n + NO)$ (n = 5 or 6)	Dark red									2 000vs, br		360m	325s	
$[WCl_3(NO)(PMePh_2)_2]\cdot CH_2Cl_2$	Pale greenish yellow	140—141	40.8 (41.0)	3.7 (3.6)	1.9 (1.8)		*i*			1 618vs		305s	300vs	283m
$[WCl_3(NO)(PEtPh_2)_2]\cdot CH_2Cl_2$	Pale yellow	134—135	43.0 (42.7)	4.1 (3.9)	1.9 (1.7)	22.1 (21.7)	748 (749)[h]			1 605vs, br		306s	301vs	281m
$[WCl_3(NO)(PMePh_2O)_2]$	Green	122—126	41.1 (41.6)	3.5 (3.5)	2.1 (1.9)	13.7 (14.2)	*j*			1 635vs	1 151vs 1 130vs	330m	302s	
$[WCl_3(NO)(PMePh_2O)_2]$	Green	*k*	44.1 (42.7)	4.4 (3.8)	1.8 (1.8)	14.4 (13.5)	*j*			1 637vs, br	1 161vs, br 1 123vs	305vs		
$[WCl_3(NO)(PPh_3O)_2]$	Green		49.3 (49.3)	3.5 (3.5)	1.6 (1.6)	12.4 (12.1)	*i*			1 640vs	1 172vs 1 130vs, br	334m	318s	301s
$[WCl_3(NO)(py)_2]$	Buff		25.1 (25.1)	2.4 (2.1)	8.3 (8.7)	22.8 (22.3)	*i*			1 640vs, br		346m	327s	312vs

[a] In air. [b] Calculated values are in parentheses. [c] In nitromethane (1 : 1 electrolytes give values in the range 75—95 S cm^2 mol^{-1}, 2 : 1 electrolytes in the range 150—180 S cm^2 mol^{-1}) (W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81). [d] Nujol mulls. [e] Diamagnetic. [f] Non-conductor. [g] In 1,2-dichloroethane. [h] Parent ion in mass spectrum. [i] Too insoluble. [j] Too unstable. [k] Too impure.

TABLE 3

Phosphineiminido- and amido-complexes of molybdenum

Complex	Colour	M.p.[a] (θ_c/°C)	Analysis[b] (%)				M[b,c]	Λ[d]/S cm^2 mol^{-1}	μ/B.M.	I.r. spectrum (cm^{-1})[e]				
			C	H	N	Cl				ν(NH)		ν(PO)		ν(PN)
$[MoCl_4(NPMe_2Ph)(PMe_2PhO)]$	Yellow	143	46.8 (46.7)	4.0 (3.9)	2.1 (2.1)	21.1 (20.8)	*f*	*g*	1.51			1 085vs, br		1 125vs
$[MoCl_4(NPPr^nPh_2)(PPr^nPh_2O)]$	Yellow	134—140	49.2 (49.8)	4.5 (4.7)	1.6 (1.9)	20.1 (19.6)	713 (725)	*g*	1.64			1 093vs, br		1 128vs
$[MoCl_3(NH_2)(PMePh_2O)_2]Cl$	Pale yellow	*ca.* 155 (decomp.)	45.8 (45.6)	4.3 (4.1)	2.1 (2.0)	20.3 (20.6)		66	1.62	3 300w (2 490)[h]	3 245w (2 400)[h]	1 140vs, br	1 125vs	
$[MoCl_3(NH_2)(PEtPh_2O)_2]Cl$	Pale yellow	*ca.* 150 (decomp.)	47.0 (47.1)	4.5 (4.5)	1.6 (2.0)	20.1 (19.8)		70	1.66	3 300w	3 210w	1 142vs	1 127s	

[a] In air. [b] Calculated values are in parentheses. [c] In 1,2-dichloroethane. [d] In nitromethane. [e] Nujol mulls. [f] Too insoluble. [g] Non-conductor. [h] ν(ND).

The amido-complexes $[MoCl_3(NH_2)(PRPh_2O)_2]Cl$ (R = Me or Et) are yellow crystalline solids which are reasonably air-stable in the solid state. Their magnetic moments in the solid state are 1.6 B.M. There are two bands in the i.r. spectrum assigned to ν(NH) at 3 300 and 3 210 cm^{-1}, which show the appropriate shift to lower frequencies on deuteriation (see Table 3). The complex with R = Me reacted with hydrogen chloride to yield 0.95 mole of ammonia per atom of molybdenum. The complex could not be deprotonated with bases such as pyridine to give characterisable complexes. A very insoluble complex with one nitrogen and one phosphine oxide per molybdenum was obtained using both triethylamine and pyridine but this was not $[MoCl_3(NH)(PMePh_2O)_2]$ or $[MoCl(N)(PMePh_2O)_2]$. We also attempted to prepare amido-complexes by protonation of nitrido-complexes $[MoCl_2(N)L_2]$, but only succeeded in obtaining intermediates containing N–H groups and 1.5 phosphines per molybdenum. These were certainly not our amido-complexes, and since terminal (as opposed to bridging) amido-complexes are rather rare[25] our formulation should be treated with a little caution.

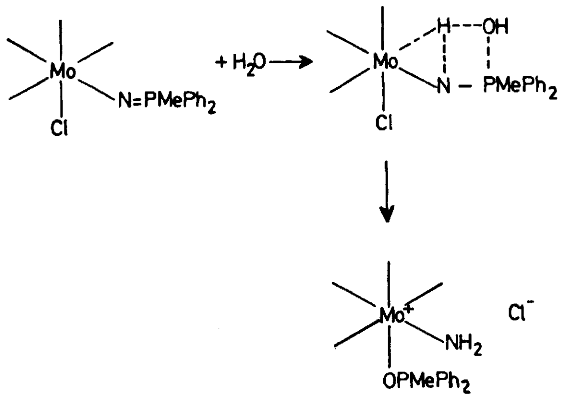
The formation of the amido-complexes can be rationa-

---

[24] D. Scott and A. G. Wedd, *J.C.S. Chem. Comm.*, 1974, 527.

[25] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

lised on the basis of nucleophilic attack by phosphine on nitrogen, and subsequently oxygen of co-ordinated nitrogen oxide yielding what has been termed a co-ordinated nitrene rather than a phosphineimine. This seems rather unlikely. In fact when the preparative reaction was carried out in benzene which had been distilled from Li[AlH$_4$] in a vacuum system no amido-complex was obtained, but the yield of phosphineiminido-complex was increased. When water was deliberately added to the preparative reaction, [PMePh$_2$H][MoCl$_4$(PMePh$_2$O)] was the major product isolated. We thus prefer the following genesis for the amido-complex.



Analogous reactions have been reported,[26] but we were unable to confirm this by reaction of the phosphineiminido-complex with water in dichloromethane. The only isolable product was [PMePh$_2$H][MoCl$_4$(PMePh$_2$O)].

We also investigated the reactions of the red nitrosyl with other nucleophiles. Phenylhydrazine formed intensely coloured maroon solids, but the only product isolated with certainty was phenylhydrazine hydrochloride. Aniline yielded uncharacterisable mixtures. Trimethylsilyl azide (tmsa) reacted vigorously with the red nitrosyl in dichloromethane solution to evolve gas, and, after addition of triphenylphosphine, [MoCl$_2$(N)(PPh$_3$)$_2$] [27] was isolated in good yield. The fate of the nitrogen oxide was not determined.

Several of the nitrosyls have very low ν(NO), and the co-ordinated nitrogen oxide in them should be susceptible to electrophilic attack, for which low ν(NO), but not necessarily a bent M–N–O system, is required. The reactions of [MoCl$_2$(NO)(PMePh$_2$)$_2$(PMePh$_2$O)], [MoCl$_3$(NO)(PPh$_2$H)$_3$], [MoCl(NO)(dppe)$_2$], and [NEt$_4$][MoCl$_3$(NO)(PMePh$_2$)$_2$] with 1, 2, and 3 moles of hydrogen chloride were investigated. In each case, starting material was recovered essentially quantitatively. The complex [MoCl(NO)(dppe)$_2$] did not react even with an excess of hydrogen chloride, and the other three complexes yielded mixtures of nitrosyls of higher oxidation states. There was no evidence of attack on co-ordinated nitrogen oxide, nor of hydride formation. Thus, a low value for ν(NO) is not a sufficient condition for reactivity with electrophiles. It may be that co-ordination unsaturation is also necessary, allowing attack of a further ligand on the metal, thus providing extra electron density at the nitrogen in a manner reminiscent of, but not necessarily similar to, the theory of 'stereochemical control of valence'.[2,28] None of the complexes we investigated seems likely to become seven-co-ordinate.

EXPERIMENTAL

Infrared spectra were recorded as Nujol mulls on Unicam SP 1200 (400—4 000 cm^{-1}), and on Perkin-Elmer 457 (250—4 000 cm^{-1}) and 557 (200—4 000 cm^{-1}) spectrometers, using KBr (400—4 000 cm^{-1}) or CsI (200—4 000 cm^{-1}) plates. The spectra were calibrated with polystyrene film. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates T60 and HA 100 spectrometers at *ca.* 30 °C unless otherwise stated, with SiMe$_4$ or CH$_2$Cl$_2$ as internal standards. Mass spectra were obtained on an A.E.I. MS9 spectrometer. Magnetic moments were measured on a Faraday balance calibrated against Hg[Co(SCN)$_4$]. Molecular weights were determined by vapour-pressure osmometry in 1,2-dichloroethane solution using an Hitachi–Perkin-Elmer, model 116, osmometer. Conductivities were measured in nitromethane solution using a Portland Electronics series 300 conductivity bridge. Melting points were determined in air on a Kofler block. Elemental microanalyses were by the Microanalytical Laboratories of the School of Molecular Sciences, University of Sussex.

Molybdenum pentachloride and tungsten hexachloride were obtained from Koch–Light Laboratories. Triphenylphosphine and triphenylphosphine oxide were obtained commercially and other phosphine and phosphine oxide ligands were prepared by standard literature methods, as was trimethylsilyl diethyldithiocarbamate.[29] Nitrogen oxide (Matheson) was used as received. Tetraethylammonium chloride was dried at 120 °C (0.01 mmHg) for 6 h before use. All the reactions and manipulations were carried out in an atmosphere of pure dry dinitrogen using Schlenk-tube techniques. Solvents were dried by standard procedures. Before analysing, complexes were dried at room temperature and 0.01 mmHg for 6 h unless otherwise stated. The complexes [MoCl$_4$L$_2$] (L = EtCN, PMePh$_2$, PEtPh$_2$, or py),[30,31] [WCl$_4$(PEtPh$_2$)$_2$],[32] [MoCl$_3$(thf)$_3$],[33] and [MoCl$_3$(PMe$_2$Ph)$_3$] were prepared by standard literature methods.

Reaction of Nitrogen Oxide with Tetrachlorobis(methyldiphenylphosphine)molybdenum(IV).—Nitrogen oxide was passed through a suspension of tetrachlorobis(methyldiphenylphosphine)molybdenum(IV) (0.50 g) in benzene (30 cm^3), stirred at room temperature. A greenish yellow crystalline precipitate was slowly formed and when the red colour of the starting material had completely disappeared (*ca.* 1 h) the product was filtered off and washed with hexane (3 × 10 cm^3), yield 0.24 g. The i.r. spectrum of the product

---

[26] G. Singh and H. Zimmer, *Organometallic Chem. Rev.*, 1967, **2**, 279.

[27] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 517.

[28] J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *Inorg. Chem.*, 1975, **14**, 624.

[29] H. Breederveld, *Rec. Trav. chim.*, 1960, **79**, 1126; 1962, **81**, 276.

[30] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531.

[31] E. A. Allen, K. Feenan, and G. W. A. Fowles, *J. Chem. Soc.*, 1965, 1636.

[32] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J.C.S. Dalton*, 1972, 1064.

[33] M. W. Anker, J. Chatt, G. J. Leigh, and A. G. Wedd, *J.C.S. Dalton*, 1975, 2639.

indicated that it was a mixture of three complexes, $[MoCl_3(NO)(PMePh_2O)_2]$ [ν(NO) at 1 700s cm^{-1}], $[MoCl_2(NO)_2(PMePh_2O)_2]$ [ν(NO) at 1 780s and 1 660s cm^{-1}], and $[MoCl_2O_2(PMePh_2O)_2]$ [ν(Mo=O) at 942s and 904s cm^{-1}]. No change in the composition of the mixture was observed on recrystallisation from dichloromethane–hexane.

The corresponding triphenylphosphine complex reacted similarly.

Reactions of Nitrogen Oxide with Tetrachlorobis(ethyldiphenylphosphine)molybdenum(IV).—(i) Dichlorobis(ethyldiphenylphosphine oxide)dinitrosylmolybdenum. Tetrachlorobis(ethyldiphenylphosphine)molybdenum(IV) (0.30 g) was dissolved in benzene (25 cm^3). Nitrogen oxide was passed through the solution, which was stirred at room temperature, for 15 min. The resulting green solution was evaporated to 10 cm^3 at 0.1 mmHg and refrigerated, yielding a yellow-green solid which on recrystallisation from benzene–hexane afforded the pure *complex* (0.17 g, 58%) (Found: C, 50.4; H, 4.7; Cl, 10.6; N, 4.0. $C_{28}H_{30}Cl_2MoN_2O_4P_2$ requires C, 48.9; H, 4.4; Cl, 10.3; N, 4.1%). The i.r. spectrum shows ν(NO) at 1 780vs and 1 660vs cm^{-1}.

(ii) *Trichlorobis(ethyldiphenylphosphine oxide)nitrosylmolybdenum*(III). Tetrachlorobis(ethyldiphenylphosphine)molybdenum(IV) (0.30 g) was dissolved in thf (20 cm^3). Nitrogen oxide was passed through the solution, which was stirred at room temperature, for 2 min. The resulting yellow-green solution was evaporated to dryness under reduced pressure and the oily solid extracted with benzene (10 cm^3) to give a yellow-green powder (0.21 g), a mixture consisting mainly of the mononitrosyl complex [ν(NO) at 1 700 cm^{-1}]. Even after repeated recrystallisation from dichloromethane–hexane, the dinitrosyl complex could not be completely removed.

(iii) *Dichlorobis(ethyldiphenylphosphine oxide)dioxomolybdenum*(VI).[16] Tetrachlorobis(ethyldiphenylphosphine)molybdenum(IV) (0.30 g) was dissolved in benzene (25 cm^3). Nitrogen oxide was passed through the stirred solution which was heated under reflux for 1 h. The resulting greenish yellow solution was evaporated at 0.1 mmHg to 10 cm^3 and addition of hexane (10 cm^3) afforded the *complex* as a pale yellow solid which was recrystallised from dichloromethane–hexane (0.22 g, 72%) (Found: C, 50.9; H, 4.7; Cl, 11.0; N, 0. $C_{28}H_{30}Cl_2MoO_4P_2$ requires C, 51.0; H, 4.6; Cl, 10.7%). The i.r. spectrum shows ν(Mo=O) at 947vs and 904vs cm^{-1}. The same complex was obtained in toluene at -30°C, after passing NO for 2 h.

The corresponding triphenylphosphine oxide, methyldiphenylphosphine oxide, and dimethylphenylphosphine oxide complexes were prepared similarly by the reaction of nitrogen oxide with the appropriate tetrachlorobis(phosphine)- or tetrachlorobis(phosphine oxide)-molybdenum(IV) complexes.

Dichlorobis(ethyldiphenylphosphine oxide)dioxotungsten(VI).[16]— Tetrachlorobis(ethyldiphenylphosphine)tungsten(IV) (0.30 g) was dissolved in benzene (25 cm^3). Nitrogen oxide was passed through the solution, stirred at room temperature, for 10 min. The resulting yellow solution was evaporated to 10 cm^3 at 0.1 mmHg, and refrigerated. The complex crystallised as a buff solid which was filtered off and washed with hexane (0.16 g, 54%) (Found: C, 44.5; H, 4.1; Cl, 9.6; N, 0. $C_{28}H_{30}Cl_2O_4P_2W$ requires C, 45.0; H, 4.1; Cl, 9.5%). The i.r. spectrum shows ν(W=O) at 960s and 906s cm^{-1}.

Reaction of Nitrogen Oxide with Tetrachlorobis(pyridine)molybdenum(IV).—Nitrogen oxide was passed for 4 h through a suspension of tetrachlorobis(pyridine)molybdenum(IV) (0.30 g) in benzene (20 cm^3), heated under reflux. The resulting buff precipitate was filtered off and washed with hexane (3 × 10 cm^3), yield 0.24 g. The i.r. spectrum of the *product* exhibits strong bands assignable to both ν(NO) at 1 630 cm^{-1} and to ν(Mo=O) at 905, 925, 945, and 958 cm^{-1}, indicative of a mixture of complexes; the insolubility of the product mixture precluded recrystallisation.

Dichlorobis(ethyl cyanide)dinitrosylmolybdenum(II).[10]—A suspension of tetrachlorobis(ethyl cyanide)molybdenum(IV) (0.50 g) in benzene (60 cm^3) was brought to reflux temperature. Nitrogen oxide was passed through the stirred solution which was maintained under reflux for 2 h. The resulting green solution was cooled and filtered. Evaporation at 0.1 mmHg to *ca.* 10 cm^3 and subsequent refrigeration yielded the complex as a green microcrystalline powder (0.35 g, 73%) (Found: C, 21.4; H, 3.2; Cl, 21.6; N, 16.2. $C_6H_{10}Cl_2MoN_4O_2$ requires C, 21.4; H, 3.0; Cl, 21.1; N, 16.6%). The i.r. spectrum shows ν(NO) at 1 800vs and 1 680vs cm^{-1}.

Dichlorodinitrosylbis(triphenylphosphine)molybdenum(II).[3]—A suspension of dichlorobis(ethyl cyanide)dinitrosylmolybdenum(II) (0.20 g) and triphenylphosphine (0.80 g, 5.1 mol) was heated under reflux in benzene (30 cm^3) for 2 h. The resulting green solution was filtered hot and evaporated under reduced pressure to give the complex as a yellow-green solid which was recrystallised from dichloromethane–diethyl ether, m.p. 246 °C (lit.,[3] 247 °C) (0.31 g, 70%) (Found: C, 57.5; H, 4.3; Cl, 9.1; N, 3.9. $C_{36}H_{30}Cl_2MoN_2O_2$ requires C, 57.5; H, 4.0; Cl, 9.4; N, 3.7%); the i.r. spectrum shows ν(NO) at 1 790vs and 1 670vs cm^{-1}.

Reaction of Nitrogen Oxide with Molybdenum Pentachloride.—Molybdenum pentachloride (4.0 g) was dissolved in benzene (150 cm^3). Nitrogen oxide was passed through the solution (magnetically stirred at room temperature) for 8 min. The excess of nitrogen oxide was then removed *in vacuo* and the extremely air-sensitive *product* was filtered off, washed with benzene, and dried at 0.01 mmHg (4.0 g). In order to obtain a clean product, the reaction conditions described must be strictly adhered to and, in addition, efficient stirring is essential throughout. The nitrogen oxide–molybdenum pentachloride product is subsequently referred to as the red nitrosyl ($MoCl_5 + NO$); percentage yields of products are calculated on the formulation as a 1 : 1 adduct.

Tetraethylammonium Tetrachloromononitrosylmolybdenum(III).—The red nitrosyl (4.0 g) was dissolved in dichloromethane (150 cm^3) and the dark red solution was filtered in order to remove impurities. Tetraethylammonium chloride was added in small portions to the stirred solution until the red colour was just discharged (this requires *ca.* 1.5 of g $[NEt_4]Cl$) and a yellow solid was precipitated. The *complex* was filtered off immediately and washed with dichloromethane (3 × 20 cm^3), yield 3.5 g (63%).

Bis(tetraethylammonium) Pentachloromononitrosylmolybdenum(III).—The red nitrosyl (4.0 g) was dissolved in dichloromethane (150 cm^3) and the solution was filtered to remove impurities. Addition of $[NEt_4]Cl$ (4.0 g, *ca.* 3 mol) resulted in precipitation of a greenish yellow solid. After stirring the mixture at room temperature for 20 min, the *complex* was filtered off and washed with dichloromethane (3 × 20 cm^3), yield 5.6 g (68%).

Trichlorobis(methyldiphenylphosphine oxide)mononitrosylmolybdenum(III).—To a suspension of the red nitrosyl (0.5 g) in benzene (20 cm^3) was added methyldiphenylphosphine oxide (1.1 g) and the mixture was stirred at room temperature for 1 h. A yellowish green crystalline complex and a sticky black solid precipitated from the reaction mixture. The *complex* was purified by recrystallisation from 1,2-dichloroethane–diethyl ether and retains 1 mol of benzene of crystallisation, yield 0.8 g (62%). Hydrogen-1 n.m.r. spectrum (in deuteriodichloromethane):

τ	Multiplicity	Relative integration	Assignment
2.6	Complex	21.0	Ph protons of phosphine
2.70	Singlet	6.4	protons of benzene of crystallisation
7.76	Doublet	2.9	CH_3 of phosphine split by ^{31}P
7.88	Doublet	3.1	CH_3 of phosphine split by ^{31}P

Trichloromononitrosylbis(triphenylphosphine oxide)molybdenum.—This complex was prepared similarly to the corresponding methyldiphenylphosphine oxide complex using the red nitrosyl and triphenylphosphine oxide. The *product* contained some $[MoCl_2O_2(PPh_3O)_2]$ (5—10%) which could not be removed by recrystallisation.

Trichlorobis(ethyldiphenylphosphine oxide)mononitrosylmolybdenum(III).—To a suspension of the red nitrosyl (0.5 g) in benzene (30 cm^3) was added ethyldiphenylphosphine oxide (1.2 g) and the mixture was stirred at room temperature for 30 min. The resulting yellow-green solution was filtered to remove some sticky black solid and on refrigeration yielded yellowish green crystals of the *complex* (0.83 g, 65%).

Trichlorotris(dimethylphenylphosphine)mononitrosylmolybdenum(III).—(i) To a suspension of the red nitrosyl (0.5 g) in benzene (20 cm^3) was added dimethylphenylphosphine (1.0 g) and the mixture was stirred at room temperature for 1 h and then filtered. The sticky black solid was extracted with dichloromethane but gave no characterisable product. The filtrate, a green solution, was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (50 cm^3) to give a green solid, which on recrystallisation from dichloromethane–hexane gave the *complex*, containing 0.5 mol of CH_2Cl_2 of crystallisation, in very low yield (0.09 g, 7%).

(ii) Tetraethylammonium tetrachloromononitrosylmolybdenum(III) (0.35 g) and PMe_2Ph (0.5 g, 4.1 mol) were suspended in dichloromethane (20 cm^3) and the mixture was stirred at room temperature for 2 h. The resulting green solution was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (2 × 50 cm^3) to give a yellow-green solid consisting of a mixture of products. Separation of the mixture was effected by addition of benzene (20 cm^3), which dissolved the major fraction leaving yellow $[NEt_4]_2[MoCl_5(NO)]$ (0.22 g, 45%) which was removed by filtration. The yellow-green filtrate, on addition of hexane (30 cm^3), afforded yellow crystals of the *complex* containing 0.33 mol of benzene of crystallisation, yield 0.24 g (41%). Hydrogen-1 n.m.r. spectrum (in deuteriodichloromethane):

τ	Multiplicity	Relative integration	Assignment
2.4	Complex	6.3	*o*-protons of Ph of phosphines
2.64	Singlet	11.1	*m*- and *p*-protons of Ph of phosphines
2.70	Singlet		C_6H_6 of crystallisation (0.33 mol)
9.0	Complex	18.0	Me protons of phosphine

No spectral change was observed in the range −20 to 50 °C.

(iii) A solution of trichlorobis(methyldiphenylphosphine oxide)mononitrosylmolybdenum(III) (0.3 g) and PMe_2Ph (0.2 g, 3.3 mol) in dichloromethane (20 cm^3) was stirred at room temperature for 30 min. The resulting red solution was evaporated to 5 cm^3 at 0.1 mmHg, and on addition of hexane (40 cm^3) the *complex* was precipitated as a yellow solid and was recrystallised from benzene–hexane as yellow prisms containing 0.33 mol of C_6H_6 of crystallisation, yield 0.24 g (79%).

Tris[1,2-bis(diphenylphosphino)ethane]hexachlorodinitrosyldimolybdenum(III).—(i) To a suspension of the red nitrosyl (0.5 g) in benzene (30 cm^3) was added 1,2-bis(diphenylphosphino)ethane (1.0 g) and immediate precipitation of a brown solid was observed. After stirring at room temperature for *ca.* 30 min, the mixture was filtered giving a brown uncharacterisable solid and an orange-yellow solution. The filtrate was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with diethyl ether (40 cm^3). The *complex* was obtained in very poor yield and was recrystallised from dichloromethane–diethyl ether as a yellow microcrystalline powder containing 1 mol of CH_2Cl_2 of crystallisation, yield 0.11 g (6%).

(ii) Tetraethylammonium tetrachloromononitrosylmolybdenum(III) (0.3 g) was suspended in a solution of dppe (0.7 g, 2.3 mol) in dichloromethane (40 cm^3) and the mixture was stirred at room temperature for 18 h. The yellow precipitate was filtered and characterised as $[NEt_4]_2[MoCl_5(NO)]$ by comparison with an authentic sample (0.18 g, 42%). The orange filtrate was evaporated to dryness under reduced pressure and the unchanged phosphine extracted with diethyl ether (60 cm^3). The resulting yellow solid was recrystallised from dichloromethane–diethyl ether as a microcrystalline powder. A second recrystallisation was necessary to give the pure *complex*, containing 1 mol of CH_2Cl_2 of crystallisation, yield 0.22 g (34%).

Tetraethylammonium Tetrachloromononitrosyl(triphenylphosphine)molybdenum(III).—A suspension of $[NEt_4][MoCl_4(NO)]$ (0.2 g) and PPh_3 (0.5 g, 3.8 mol) in dichloromethane (20 cm^3) was stirred at room temperature for 5 h. The resulting orange solution was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (50 cm^3). Because of the oily nature of the product, recrystallisation from dichloromethane–hexane was difficult, but afforded orange crystals of the *complex* in low yield (0.07 g, 21%).

Tetraethylammonium Tetrachloro(methyldiphenylphosphine)mononitrosylmolybdenum(III).—This complex was prepared similarly to the corresponding triphenylphosphine complex using $[NEt_4][MoCl_4(NO)]$ (0.2 g) and methyldiphenylphosphine (0.4 g, 4.0 mol). The *complex* was recrystallised from dichloromethane–hexane as an orange microcrystalline powder (0.18 g, 61%). Hydrogen-1 n.m.r. spectrum (in deuteriodichloromethane):

τ	Multiplicity	Relative integration	Assignment
2.5	Complex	12.3	Ph protons of phosphine
6.76	Complex	8.0	CH_2 protons of $[NEt_4]^+$ split by CH_3
7.86	Doublet (1 : 1)	2.9	CH_3 protons of phosphine split by ^{31}P
8.71	Complex	12.0	CH_3 protons of $[NEt_4]^+$ split by CH_2

Tetraethylammonium Tetrachloro(methyldiphenylphosphine oxide)mononitrosylmolybdenum(III).—A suspension of

$[NEt_4][MoCl_4(NO)]$ (0.2 g) and $PMePh_2$ (0.4 g, 3.7 mol) in dichloromethane (20 cm^3) was stirred at room temperature for 5 h. The resulting yellow-green solution was evaporated to dryness and the unchanged phosphine was extracted with benzene (50 cm^3). Subsequent recrystallisation of the product from dichloromethane–hexane afforded the *complex* as greenish yellow prisms (0.22 g, 72%).

Tetraethylammonium Tetrachloro(ethyldiphenylphosphine oxide)mononitrosylmolybdenum(III).—This complex was prepared similarly to the corresponding methyldiphenylphosphine oxide complex using $[NEt_4][MoCl_4(NO)]$ (0.20 g) and ethyldiphenylphosphine oxide (0.45 g, 3.9 mol). The *complex* was isolated as greenish yellow prisms (0.22 g, 69%).

Reactions of the Red Nitrosyl.—With methyldiphenylphosphine.—To a suspension of the nitrosyl (1.0 g) in benzene (40 cm^3) was added $PMePh_2$ (2.1 g). Immediately, a yellow-brown solution was formed and a black sticky solid precipitated. After stirring at room temperature for 30 min, the mixture was filtered.

(i) The solid was extracted with dichloromethane (30 cm^3) to give a yellow solution which was filtered and evaporated to 15 cm^3 at 0.1 mmHg. Slow addition of hexane (5 cm^3) to the solution gave the complex *tetrachloro(methyldiphenylphosphineiminido)(methyldiphenylphosphine oxide)molybdenum*(V), $[MoCl_4(NPMePh_2)(PMePh_2O)]$, as a yellow microcrystalline solid (0.24 g, 10%).

(ii) The filtrate was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (60 cm^3). The resulting yellow solid consisted of a mixture of products, which on fractional recrystallisation from dichloromethane–hexane gave initially the pale yellow complex *amidotrichlorobis(methyldiphenylphosphine oxide)molybdenum*(V) *chloride*, $[MoCl_3(NH_2)(PMePh_2O)_2]Cl$ (0.12 g, 5%); further addition of hexane to the mother liquor afforded green needle-shaped crystals of the nitrosyl complex, $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$. The *complex* was contaminated with a yellow-brown oil, but this was readily removed by washing with small aliquot portions of acetone, yield 0.6 g (20%).

The same reaction in benzene more rigorously dried by distillation from $Li[AlH_4]$ afforded only the phosphineiminido- and nitrosyl complexes in yields of 15 and 20% respectively.

With ethyldiphenylphosphine. The same procedure was followed as for the corresponding reaction with $PMePh_2$, using the nitrosyl (1.0 g) and $PEtPh_2$ (2.2 g). No characterisable product could be isolated from the solid fraction, and the filtrate afforded only the pale yellow complex, *amidotrichlorobis(ethyldiphenylphosphine oxide)molybdenum*(V) *chloride*, $[MoCl_3(NH_2)(PEtPh_2O)_2]Cl$ in very poor yield (0.07 g, 3%). Attempted separation of the product mixture by chromatography on a silica gel column eluted with dichloromethane was unsuccessful, the mixture decomposing on the column without any separation being achieved.

With diphenyl-n-propylphosphine. The same procedure was followed as for the corresponding reactions with $PMePh_2$ and $PEtPh_2$, using the nitrosyl (1.0 g) and PPr^nPh_2 (2.5 g). No characterisable product could be isolated from the solid fraction, but the product mixture obtained from the filtrate afforded both the yellow complex *tetrachloro(diphenyl-n-propylphosphineiminido)(diphenyl-n-propylphosphine oxide)molybdenum*(V), $[MoCl_4(NPPr^nPh_2)(PPr^nPh_2O)]$ (0.08 g, 3%), and the green complex $[MoCl_2(NO)(PPr^nPh_2)_2(PPr^nPh_2O)]$ (0.15 g, 5%), on fractional crystallisation from dichloromethane–hexane.

Dichlorotris(diphenylphosphine)mononitrosylmolybdenum(II).—To a suspension of the red nitrosyl (1.0 g) in benzene (30 cm^3) was added PPh_2H (2.0 g). After stirring at room temperature for 1 h the mixture was filtered. The filtrate, a yellow-brown solution, was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (60 cm^3) to give the *complex* as a yellow oily solid which was recrystallised from dichloromethane–hexane as yellow prisms (0.93 g, 35%).

Tetraethylammonium Trichlorobis(methyldiphenylphosphine)mononitrosylmolybdenum(III).—Tetraethylammonium chloride (0.08 g, 2 mol) was added to a stirred solution of $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ (0.2 g) in dichloromethane (15 cm^3). After stirring at room temperature for 1 h the solution was evaporated to 2 cm^3 at 0.1 mmHg and benzene (10 cm^3) was added, precipitating a green solid which was filtered off, washed with water to remove unchanged $[NEt_4]Cl$, dried *in vacuo* and recrystallised from dichloromethane–hexane, yield 0.13 g (81%).

Tris(diethyldithiocarbamato)mononitrosylmolybdenum(III).[19]—A suspension of $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ (0.2 g) and trimethylsilyl diethyldithiocarbamate (0.13 cm^3, 2—3 mol) in benzene (15 cm^3) was stirred at room temperature for 2 h. The resulting brown solution was evaporated to dryness under reduced pressure and the solid residue extracted with methanol (10 cm^3) and diethyl ether (20 cm^3) to give the complex as a brown solid which was recrystallised from dichloromethane–hexane as yellow crystals, m.p. 204 °C (0.06 g, 43%) (Found: C, 32.0; H, 5.8; N, 9.6. $C_{15}H_{30}MoN_4OS_6$ requires C, 31.5; H, 5.3; N, 9.8%). The i.r. spectrum showed $\nu(NO)$ at 1 630s cm^{-1} (lit.,[19] 1 630 cm^{-1}).

Bis[1,2-bis(diphenylphosphino)ethane]chloromononitrosylmolybdenum(I).—A suspension of $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$ (0.3 g) in benzene (15 cm^3) and dppe (0.44 g, 3.0 mol) was stirred at room temperature for 3 h. The *complex* was precipitated as a yellow microcrystalline solid which was filtered off and washed with benzene (5 cm^3) and hexane (2 × 5 cm^3), yield 0.14 g (40%). Addition of hexane (30 cm^3) to the filtrate precipitated a second yellow complex, $[\{MoCl_3(NO)(dppe)_{\frac{3}{2}}\}_2]$, which was filtered off, washed with benzene–methanol (1 : 1) (3 × 10 cm^3), and recrystallised from dichloromethane–hexane, yield 0.11 g (34%).

Chlorotetrakis(diphenylphosphine)mononitrosylmolybdenum(I).—Bis(tetraethylammonium) pentachloromononitrosylmolybdenum (0.3 g), magnesium turnings (flame dried *in vacuo*) (*ca*. 2 g), and PPh_2H (1.5 g, 15 mol) were suspended in thf (30 cm^3). The mixture was heated under reflux for 6 h, then cooled and filtered. The filtrate, a greenish yellow solution, was evaporated to dryness under reduced pressure and the unchanged phosphine was extracted with hexane (2 × 60 cm^3), giving a yellow solid which on recrystallisation from benzene–hexane afforded the *complex* in low yield (0.07 g, 14%).

Reactions of Molybdenum Mononitrosyl Complexes with an Excess of Hydrogen Chloride.—Reactions of the following complexes were studied: (i) $[MoCl_2(NO)(PMePh_2)_2(PMePh_2O)]$, (ii) $[MoCl_2(NO)(PPh_2H)_3]$, (iii) $[NEt_4][MoCl_3(NO)(PMePh_2)_2]$, and (iv) $[MoCl(NO)(dppe)_2]$. In each case the same experimental procedure was adopted.

The complex (0.3 g) was dissolved in dichloromethane (20 cm^3). Hydrogen chloride was passed through the solution for 15 min and the reaction mixture was then stirred at room temperature until no further change was observed.

The solvent was removed under reduced pressure and the product was recrystallised from dichloromethane–hexane or benzene–hexane. The results are summarised below:

Complex	$\bar{\nu}$(NO)/cm^{-1}	Reaction time (t/h)	$\bar{\nu}$(NO)/cm^{-1} of product mixture
(i)	1 585	0.25	1 605s, br, 1 640vs, 1 700m
(ii)	1 628	5	1 605m, 1 637vs, 1 660br
(iii)	1 610vs, 1 585vs	0.25	1 638vs, 1 595s, br
(iv)	1 542	5	1 542vs

With the exception of complex (iv) which did not react, inseparable mixtures of nitrosyl complexes were formed in each case.

Reaction of Nitrogen Oxide with Tungsten Hexachloride or Pentachloride.—Tungsten hexachloride or pentachloride (2.0 g) was dissolved in benzene (70 cm^3). Nitrogen oxide was passed through the solution, magnetically stirred at room temperature, for 6 min. The resulting dark red, extremely air-sensitive, precipitate was filtered off, washed with benzene (3 × 20 cm^3), and dried at 0.01 mmHg (yield *ca.* 2.0 g). The nitrogen oxide adducts of tungsten hexachloride and tungsten pentachloride will in subsequent preparations be referred to as (WCl_6 + NO) and (WCl_5 + NO) respectively, and percentage yields of products obtained from reactions involving these complexes are calculated appropriately.

Trichlorobis(methyldiphenylphosphine oxide)mononitrosyltungsten(III).—(i) To a suspension of (WCl_6 + NO) (0.5 g) in benzene (30 cm^3) was added $PMePh_2$ (1.1 g). An immediate reaction occurred resulting in formation of a green solution from which a green oil separated. The mixture was decanted and the oil extracted with hexane (60 cm^3) to give the *complex* as a green powder. Attempted recrystallisation from dichloromethane–diethyl ether was unsuccessful, but the crude product was reasonably pure (0.64 g, 68%).

(ii) Repeated as method (i), using (WCl_5 + NO). Recrystallisation of the product mixture from dichloromethane–hexane afforded both [$WCl_3(NO)(PMePh_2)_2$], as a greenish yellow microcrystalline solid (0.08 g, 8%), and the *complex* [$WCl_3(NO)(PMePh_2O)_2$] as a green microcrystalline solid (0.6 g, 65%).

Trichlorobis(ethyldiphenylphosphine oxide)mononitrosyltungsten(III).—This complex was prepared similarly to the corresponding $PMePh_2O$ complex, using either (WCl_6 + NO) or (WCl_5 + NO) (0.5 g) and $PEtPh_2$ (1.2 g). In both reactions the *complex* could not be recrystallised but separated as an oil which was converted into a powder on extraction with hexane, yield *ca.* 0.66 g (67%). In the reaction involving (WCl_5 + NO), the *complex* [$WCl_3(NO)(PEtPh_2)_2$] was also isolated in low yield as a greenish yellow microcrystalline solid (0.07 g, 7%).

Trichloromononitrosylbis(triphenylphosphine oxide)tungsten(III).[14]—This complex was prepared similarly to the corresponding $PMePh_2O$ complex using (WCl_6 + NO) (0.5 g) and PPh_3 (1.5 g). The complex was recrystallised from dichloromethane–hexane, yield 0.38 g (35%).

Trichloromononitrosylbis(pyridine)tungsten(III).—To a suspension of (WCl_6 + NO) (0.5 g) in benzene (30 cm^3) was added pyridine (0.5 cm^3). After stirring at room temperature for a few minutes, an orange solution was formed from which the *complex* slowly precipitated as a buff solid. The *complex*, which was too insoluble for recrystallisation, was filtered off and washed with dichloromethane (2 × 10 cm^3) and hexane (2 × 10 cm^3), yield 0.4 g (66%).

Reaction of Nitrogen Oxide with Niobium Pentachloride.—Niobium pentachloride (2.0 g) was suspended in benzene (100 cm^3) and, after stirring the mixture at room temperature for *ca.* 10 min to aid dissolution, undissolved complex was removed by filtration. Nitrogen oxide was passed through the filtrate, which was magnetically stirred at room temperature, for 8 min. A dark red solid was precipitated which was filtered off, washed with benzene, and dried at 0.01 mmHg for several hours, yield 2.2 g. The nitrogen oxide adduct of tantalum pentachloride was prepared similarly. The i.r. spectra shows ν(NO) at 1 960vs,br and 1 980vs,br cm^{-1} for the niobium and tantalum complexes respectively. These complexes are referred to as ($NbCl_5$ + NO) and ($TaCl_5$ + NO).

Reaction of ($NbCl_5$ + NO) *with Triphenylphosphine.*—To a suspension of ($NbCl_5$ + NO) (0.3 g) in dichloromethane (30 cm^3), stirred at room temperature, was added PPh_3 (0.8 g). Immediately a dark red solution was formed which slowly deposited a pale pink precipitate. After standing at room temperature for 18 h, the *product* was filtered off and washed with dichloromethane (2 × 10 cm^3) and diethyl ether (10 cm^3), yield 0.42 g (Found: C, 43.2; H, 3.2; N, 0. $C_{18}H_{15}Cl_3NbO_2P$ requires C, 43.7; H, 3.1; N, 0%). The i.r. spectrum shows ν(P=O) at 1 121 cm^{-1}. [No bands assignable to ν(NO) or ν(Nb=O) were present in the spectrum.] The i.r. and analytical data are consistent with the tentative formulation of this complex as [$\{NbCl_3O(PPh_3O)\}_n$] which is probably dimeric with two bridging oxygen atoms.

Reaction of ($NbCl_5$ + NO) *with Triphenylphosphine Oxide.*—To a suspension of ($NbCl_5$ + NO) (0.3 g) in benzene (20 cm^3) was added PPh_3O (0.8 g). A yellow solution was formed immediately from which a pale yellow solid slowly precipitated. After stirring at room temperature for 2 h, the *product* was filtered off and recrystallised from dichloromethane–hexane, yield 0.39 g (Found: C, 55.9; H, 3.9; Cl, 14.0; N, 0. $C_{36}H_{30}Cl_3NbO_3P_2$ requires C, 56.0; H, 3.9; Cl, 13.8; N, 0%). The i.r. spectrum shows ν(P=O) at 1 160vs and 1 120vs,br cm^{-1} and ν(Nb=O) at 940vs cm^{-1}. The i.r. and analytical data are consistent with the formulation of this complex as [$NbCl_3O(PPh_3O)_2$].

The ($TaCl_5$ + NO) complex reacted similarly with PPh_3 and PPh_3O. The products were not fully characterised but they contained no nitrogen.

We thank the S.R.C. for a Postgraduate Studentship (to F. K.).

[6/1032 *Received, 2nd June,* 1976]