Nitrosyl Complexes of Rhenium

By **Robert W. Adams, Joseph Chatt, Norman E. Hooper,** and **G. Jeffery Leigh,** A.R.C. Unit of Nitrogen Fixation and School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The complex [ReCl$_2$(N$_2$COPh)(PPh$_3$)$_2$] (I) reacts with nitrogen oxide to give the five-co-ordinate paramagnetic complex [ReCl$_2$(NO)(PPh$_3$)$_2$] (II) which adds other ligands, L, to form six-co-ordinate diamagnetic complexes [ReCl$_2$(NO)(PPh$_3$)$_2$L] (III). Generally tertiary phosphines (PR$_3$) displace triphenylphosphine from (II) to give either [ReCl$_2$(NO)(PR$_3$)$_2$] or [ReCl$_2$(NO)(PR$_3$)$_3$], analogous to (II) and (III) respectively, depending on the bulk of the phosphine PR$_3$, but dimethylphenylphosphine tends to give [ReCl$_2$(NO)(PMe$_2$Ph)$_2$(PPh$_3$)]. The nitrogen oxide in the above complexes is inert to attack by either electrophilic or nucleophilic reagents.

WE have recently reported [1] a range of dinitrogen complexes of rhenium(I) in some of which the dinitrogen undergoes electrophilic attack, but these reactions appear to be restricted to the formation of acyl- and aroyl-azo complexes [2] and the addition of electron acceptor molecules or groups to the terminal nitrogen atom.[3] Dinitrogen is isoelectronic with NO$^+$, and co-ordinated nitrogen oxide can react with either nucleophiles or electrophiles, depending upon its co-ordination site.[4] Nitrogen oxide has often been regarded as a ' dinitrogen analogue,' and we originally hoped that a study of rhenium nitrosyl complexes might give us some guide as to how the reactivity of ligating dinitrogen might be increased. At the commencement of this work few appropriate rhenium nitrosyl complexes were known, and here we report the synthesis and properties of a range of them.

The rhenium nitrosyls reported to date are of various kinds, and are produced by different methods. Those containing metal, halogen, nitrogen oxide, and tertiary phosphine only are: [ReX$_2$(NO)$_2$(PPh$_3$)$_2$] (X = Cl, Br, or I), which are obtained from [Re(NO$_3$)$_2$(NO)$_2$(PPh$_3$)$_2$], itself prepared from [ReH$_5$(PPh$_3$)$_3$] and nitric acid; [5] [ReX(NO)$_2$(PPh$_3$)$_2$] (X = Cl or Br), obtained by the action of nitrogen oxide and ethanolic [ReH$_3$(PPh$_3$)$_4$] in the presence of tetra-alkylammonium halide.[6] Rhenium carbonyl nitrosyl complexes are also known. Thus [Re$_2$Cl$_2$(CO)$_8$] and nitrogen oxide give [Re$_2$Cl$_3$(CO)$_5$NO], which can be converted into [Re$_2$Cl$_4$(CO)$_4$(NO)$_2$], [ReI$_3$(CO)$_3$(NO)]$^-$, and [Re$_2$(OEt)$_3$(CO)$_5$(NO)].[7] Nitrogen oxide plus hydrogen halide [8] or nitrosyl halide [9] react with [Re$_2$X$_2$(CO)$_8$] to give [Re$_2$X$_4$(CO)$_4$(NO)$_2$] (X = Cl, Br, or I), and the halogen bridge is cleaved by neutral ligands, L, such as tri-n-butylphosphine or pyridines, yielding [ReX$_2$(CO)$_2$(NO)L].[8-10] Cyclo-octene cannot split this bridge, but reacts to form [Re$_2$Cl$_4$(CO)-(NO)(C$_8$H$_{14}$)L] and then [ReCl$_2$(CO)(NO)L$_2$].[11] Acetylacetone and other β-diketones also split the bridge, to

give [ReCl(acac)(CO)$_2$(NO)].[11] Finally, in this group, [(π-C$_5$H$_5$)Re(CO)$_3$] reacts with nitrosyl hydrogen sulphate, forming [(π-C$_5$H$_5$)Re(CO)$_2$(NO)]$^+$.[12]
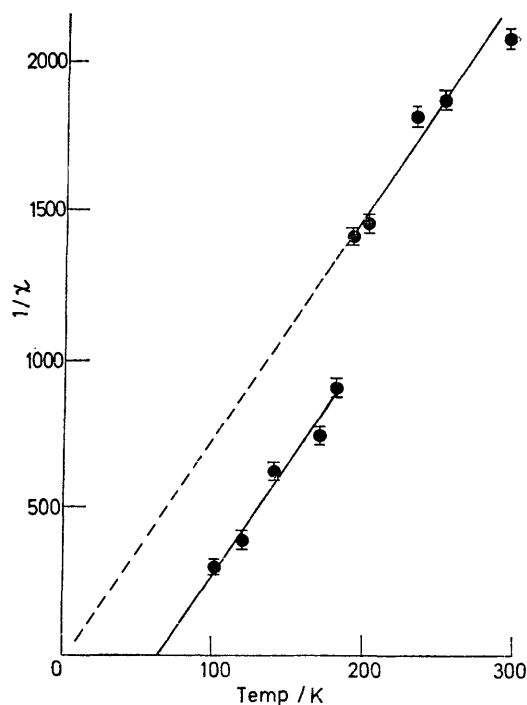
The temperature dependence of the magnetic susceptibility of [ReCl$_2$(NO)(PPh$_3$)$_2$] in the solid state

There is also a small group of nitrosyl halides and related compounds of rhenium. For instance, [ReX$_6$]$^{2-}$ (X = Cl or Br) with nitrogen oxide yield [ReX$_5$-(NO)]$^{2-}$,[6,13,14] and [Re(CN)$_8$]$^{4-}$ and nitric acid produce [Re(CN)$_7$(NO)]$^{3-}$.[15] The pentahalogenonitrosyls can

[1] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

[2] J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organometallic Chem.*, 1973, **57**, C67.

[3] J. Chatt, R. H. Crabtree, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 534; J. Chatt, R. C. Fay, and R. L. Richards, *J. Chem. Soc. (A)*, 1971, 702, and references therein.

[4] J. Masek, *Inorg. Chim. Acta Rev.*, 1969, **3**, 99.

[5] M. Freni, D. Giusto, and V. Valenti, *Gazzetta*, 1964, **94**, 797.

[6] D. Giusto and G. Cova, *Gazzetta*, 1972, **102**, 265.

[7] J. R. Norton and G. Dolcetti, *Inorg. Chem.*, 1973, **12**, 485.

[8] F. Zingales, A. Trovati, F. Cariati, and P. Uguagliati, *Inorg. Chem.*, 1971, **10**, 507.

[9] F. Zingales, A. Trovati, and F. Cariati, *Proc. XIth I.C.C.C.*, 1968, 248.

[10] F. Zingales, A. Trovati, and P. Uguagliati, *Inorg. Chem.*, 1971, **10**, 510.

[11] A. Trovati, P. Uguagliati, and F. Zingales, *Inorg. Chem.*, 1971, **10**, 851.

[12] E. O. Fischer and H. Strametz, *Z. Naturforsch.*, 1968, **23B**, 278.

[13] B. K. Sen, P. Bandyopadhyay, and P. B. Sarkar, *J. Ind. Chem. Soc.*, 1967, **44**, 227.

[14] S. Rakshit and P. Bandyopadhyay, *J. Ind. Chem. Soc.*, 1970, **47**, 1205.

[15] R. Colton, R. D. Peacock, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1374.

also be synthesised from [ReCl$_3$(NO)] [12] and [ReBr$_3$-(NO)].[14]

We have discovered that nitrogen oxide with benzoyl-hydrazido(3—)-(*ON'*)dichlorobis(triphenylphosphine)-rhenium(v) [16] (the 'green chelate') (I) gives a five-co-ordinate compound, [ReCl$_2$(NO)(PPh$_3$)$_2$] (II), which is the parent compound of a large series of nitrosyl complexes.

RESULTS AND DISCUSSION

Nitrogen oxide reacts with the 'green chelate' in benzene–methanol during 1 h at room temperature to yield the orange-brown paramagnetic complex [ReCl$_2$-(NO)(PPh$_3$)$_2$] (II). This substance is monomeric in solution in 1,2-dichloroethane, and a nonconductor in nitrobenzene solution. The formulation is unequivocally determined by the analysis, and the compound is presumably five-co-ordinate. An X-ray structural analysis at present in progress should confirm this. The rhenium is formally in oxidation state +II * but electronically it corresponds to +III or +I, depending upon whether the nitrogen oxide co-ordinates as a one- or a three-electron donor. The i.r. stretching frequency [ν(NO) = 1725 cm^{-1}, chloroform] is in a region which makes the assignment difficult, but is possibly associated with a three-electron donor. Rhenium(I) (d^6) would be expected to be diamagnetic, and rhenium(III) (d^4), which can show temperature-independent paramagnetism in octahedral complexes,[17] can be either paramagnetic or diamagnetic when five-co-ordinate. Our samples of [ReCl$_2$(NO)(PPh$_3$)$_2$] were always paramagnetic (μ_{eff} = 1·7 B.M.), however often recrystallised, and from whichever solvent. This is considerably less than the 'spin-only' value for two unpaired electrons, but the moments of five-co-ordinate complexes are very dependent upon structure, and change considerably for small distortions.[18]

Because nitrosyl complexes have occasionally been found to show persistent paramagnetism due to impurities [19] when diamagnetism would be expected, we have satisfied ourselves that the paramagnetism is an inherent property of this complex. The temperature variation of the paramagnetism in the solid state is of the normal Curie–Weiss form, but with a reversible and reproducible break at 180—190 K. Above the break, θ is 4 K, and below it θ is 66 K. This behaviour is not consistent with T.I.P. (see Figure 1). The susceptibility was measured as a function of field strength at three different temperatures (140, 190, and 230 K), and was found to be essentially independent of field strength. This excludes ferro- or antiferro-magnetism. Paramagnetism thus appears to be an inherent property of the solid state. The complexes [ReCl$_2$(NO)(PMePh$_2$)$_2$]

(IV) and [ReCl$_2$(NO)(PCy$_3$)$_2$] (X) (cy = cyclohexyl) (see below) also have Curie–Weiss paramagnetism, but without a break.

The solutions of complex (II) would also be expected to be paramagnetic and the ^{1}H n.m.r. spectrum in dry deoxygenated deuteriobenzene showed no resonances in the region τ 0—10. The substance gives an e.s.r. signal both in the solid state and in benzene solution. The solution spectrum has six lines, which are not symmetrical, and is not easy to interpret. The compound is not associated in solution, and the i.r. spectrum of a Nujol mull, ν(NO) at 1710, 1725 cm^{-1}, shows no significant change from that of a solution. The diffuse reflectance spectrum is very similar to that of a solution in dry, deoxygenated chloroform. The magnetic moment of [ReCl$_2$(NO)(PEtPh$_2$)$_2$] in solution in 1,1,2,2-tetrachloroethane was measured by Evans' method [20] and found to be 1·5 B.M.

We are not able to assign a definite structure to complex (II) or its homologues (Table 1) on the basis of available data. There are two bands in the i.r. spectrum, at 283 and 297 cm^{-1}, assignable to ν(ReCl), which indicate that the Cl–Re–Cl system is probably not linear. These bands are not found in the spectrum of the paramagnetic bromo-analogue (III) (synthesised in similar fashion from the 'bromo-green chelate').

The compound [ReCl$_2$(NO)(PPh$_3$)$_2$] (II) adds a variety of unidentate ligands, L, to give six-co-ordinate complexes, [ReCl$_2$(NO)(PPh$_3$)$_2$L], but, especially where L is a tertiary phosphine, replacement of triphenylphosphine often occurs. No characterisable products were obtained using diphosphines. For ease of discussion, the six-co-ordinate adducts are considered in two groups, first those where L is not a tertiary phosphine, and secondly those where it is.

The complexes [ReCl$_2$(NO)(PPh$_3$)$_2$L] (see Table 1) are diamagnetic solids, monomeric in 1,2-dichloroethane solution, and nonconductors in nitrobenzene solution. Usually there are two bands in the far-i.r. spectrum assignable to ν(ReCl) so that the halogens are probably cis, but the complexes are generally too insoluble for ^{1}H n.m.r. measurements. However, the ^{1}H n.m.r. spectrum of [ReCl$_2$(NO)(CO)(PMePh$_2$)$_2$] (XXIV) shows that the tertiary phosphines are *trans*. There is no obvious correlation of ν(NO), which is in the region of 1700 cm^{-1}, with L, but the range is not great. The value of ν(NO) suggests that the NO is co-ordinating as a three-electron donor, which is consistent with the eighteen-electron rule. The reaction of [ReCl$_2$(NO)-(PPh$_3$)$_2$] (II) with ethyleneimine gives an unstable adduct which degrades slowly, even *in vacuo*, and satisfactory analyses were never obtained. This adduct reacts with methanol to give the corresponding adduct of 2-methoxyethylamine, which was later obtained directly from the amine and the parent nitrosyl. No

---

* According to IUPAC Inorganic Nomenclature, NO is to be regarded formally as a 2-electron donor.

[16] J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, *J. Chem. Soc. (A)*, 1971, 2631.

[17] H. P. Gunz and G. J. Leigh, *J. Chem. Soc. (A)*, 1971, 2229.

[18] M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc. (A)*, 1970, 3283.

[19] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1972, 1.

[20] D. F. Evans, *J. Chem. Soc.*, 1959, 2003; K. D. Bartle, D. W. Jones, and S. Maričic, *Croat. Chem. Acta*, 1968, **40**, 227.

adducts were obtained for L = water, dioxygen, dinitrogen, or ethylene.

In general, the more aliphatic tertiary phosphines displace triphenylphosphine completely from the parent complex. Tertiary phosphines $PRPh_2$ (R = Me, Et, Pr^n, or Bu^n), PR_2Ph (R = Pr^n or Bu^n), and P(cyclohexyl)$_3$ produce paramagnetic five-co-ordinate complexes with properties essentially similar to those of the parent

was formed. The complex $[ReCl_2(NO)(PMe_2Ph)_3]$ was eventually synthesised by an alternative route (see Experimental section). Methyldiphenylphosphine, di-n-propylphenylphosphine, and probably di-n-butylphenylphosphine, also give rise to six-co-ordinate complexes in addition to those five-co-ordinate complexes mentioned above. All these complexes are, as expected, diamagnetic, and all have only two bands assignable to

Analyses and physical data for the new nitrosyl complexes

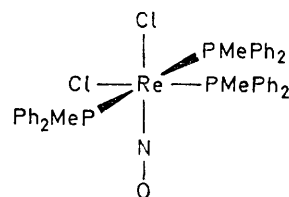| Compound	Colour	M.p. (t/°C) (decomp.)	Analyses a C	H	N	Cl or Br	M	Effective magnetic moment (B.M.) c	ν(NO) cm⁻¹ Nujol	ν(NO) cm⁻¹ Chloroform	Metal–halogen stretch region cm⁻¹
(II) $[ReCl_2(NO)(PPh_3)_2]$	Brown	250—253	52·9 (53·3)	3·9 (3·7)	1·8 (1·7)	8·7 (8·8)	788 (811)	1·7	1710, 1725	1725	283s, 297s
(III) $[ReBr_2(NO)(PPh_3)_2]$	Brown	228—233	47·5 (48·0)	3·6 (3·4)	1·6 (1·6)	17·8 (17·7)	944 (900)	1·8	1710, 1740sh	1720	192s, 204s
(IV) $[ReCl_2(NO)(PMePh_2)_2]$	Brown	159—162	45·6 (45·4)	4·2 (3·8)	2·0 (2·0)	9·9 (10·3)	724 (687)	1·8	1710	1725	281s, 293s, 318w
(V) $[ReCl_2(NO)(PEtPh_2)_2]$	Brown	167—170	46·5 (47·0)	4·7 (4·2)	2·0 (2·0)	9·9 (9·9)	796 (715)	1·8	1720, 1735	1725	284s, 297s, 317m
(VI) $[ReCl_2(NO)(PPr^nPh_2)_2]$	Brown	177—182	48·9 (48·5)	5·0 (4·6)	1·8 (1·9)	9·8 (9·6)	820 (743)	1·7	1705, 1730	1730	280s, 296s, 321m
(VII) $[ReCl_2(NO)(PBu^nPh_2)_2]$	Brown	131—134	49·7 (49·8)	5·2 (5·0)	1·8 (1·8)	9·3 (9·2)	850 (771)	1·7	1730	1730	283s, 299s, 317m
(VIII) $[ReCl_2(NO)(PPr^n_2Ph)_2]$	Brown	118—123	43·0 (42·7)	5·9 (5·7)	2·1 (2·1)	9·8 (10·5)	752 (675)	1·8	1710	1720	284s, 304s, 319s
(IX) $[ReCl_2(NO)(PBu^n_2Ph)_2]$	Brown	106—110	45·4 (46·0)	6·7 (6·4)	1·9 (1·9)	9·4 (9·7)	724 (731)	1·8	1710	1720	283s, 298s, 313s
(X) $[ReCl_2(NO)(PCy_3)_2]$	Brown	270—280	51·3 (51·0)	7·8 (7·9)	1·7 (1·7)	8·7 (8·4)	840 (847)	1·7	1700, 1730	Insol.	287m, 305m, 320s
(XI) $[ReBr_2(NO)(PCy_3)_2]$	Red-brown	255—260	46·0 (46·1)	6·9 (7·1)	1·5 (1·5)	17·8 (17·1)	1000 (936)	—	1705, 1730	Insol.	below 225
(XII) $[ReCl_2(NO)(CO)(PPh_3)_2]$	Yellow-brown	>300	52·9 (52·9)	3·9 (3·6)	1·9 (1·7)	8·7 (8·5)	827 (841)	D	1720, 1725	1720	286s, 311s
(XIII) $[ReCl_2(NO)(NH_3)(PPh_3)_2]$	Brown	280—285	52·6 (52·2)	4·3 (4·0)	3·4 (3·4)	8·6 (8·6)	862 (828)	D	1640, 1670, 1690	Insol.	277s, 310s
(XIV) $[ReCl_2(NO)(SO_2)(PPh_3)_2]$	Brown	163—167	49·7 (49·4)	3·5 (3·5)	1·8 (1·6)	8·0 (8·1)	897 (875)	D	1730, 1770	1765	306s, 325s
(XV) $[ReCl_2(NO)(CH_3CN)(PPh_3)_2]$	Yellow	300—304	52·8 (53·5)	3·9 (3·9)	3·5 (3·3)	9·2 (8·4)	883 (852)	D	1670, 1690	1690	280s, 304s
(XVI) $[ReBr_2(NO)(CH_3CN)(PPh_3)_2]$	Yellow	289—293	47·8 (48·4)	3·6 (3·5)	3·0 (3·0)	16·4 (16·5)	943 (941)	D	1680, 1700	1700	below 200
(XVII) $[ReCl_2(NO)(C_6H_5CN)(PPh_3)_2]$	Brown	255—264	55·3 (55·4)	4·0 (3·9)	3·1 (3·1)	7·8 (7·8)	978 (914)	D	1665, 1695	1700	279m, 302s
(XVIII) $[ReCl_2(NO)(C_5H_5NC)(PPh_3)_2]$	Khaki	260—262	55·4 (55·4)	3·9 (3·9)	3·3 (3·1)	8·3 (7·8)	928 (914)	D	1680, 1720	1710	276s, 295s
(XIX) $[ReCl_2(NO)(py)(PPh_3)_2]$	Yellow	277—280	54·6 (55·2)	4·1 (4·0)	3·2 (3·2)	8·2 (8·0)	940 (890)	D	1670	1680	278s, 300s
(XX) $[ReCl_2(NO)(CH_3NH \cdot NH_2)(PPh_3)_2]$	Orange	180—190	51·9 (51·8)	4·4 (4·2)	4·6 (4·9)	9·0 (8·3)	Decomp. (851)	D	1680	Decomp.	287s, 302m, 310m
(XXI) $[ReCl_2(NO)(NH_2CH_2CH_2OCH_3)(PPh_3)_2]$	Orange	201—203	53·1 (52·8)	4·2 (4·5)	3·4 (3·2)	8·5 (8·0)	922 (886)	D	1645, 1665	1670	275s, 295s
(XXII) $[ReCl_2(NO)(tcne)(PPh_3)_2]$	Blue	215—221	54·2 (53·8)	3·1 (3·2)	7·5 (7·5)	8·3 (7·6)	978 (939)	D	1720, 1730	1750	276m, 318s
(XXIII) $[ReCl_2(NO)(py)_2(PPh_3)]$	Orange-red	222—227	47·5 (47·1)	3·8 (3·5)	5·9 (5·9)	10·4 (10·0)	707 (714)	D	1675	1680	282s, 303s
(XXIV) $[ReCl_2(NO)(CO)(PMePh_2)_2]$	Brown	166—170	45·5 (45·3)	4·0 (3·7)	2·2 (2·0)	10·2 (9·9)	751 (715)	D	1710, 1730	1725	278s, 298s
(XXV) $[ReCl_2(NO)(PEt_3)_2(PPh_3)]$	Yellow	134—136	45·9 (45·9)	5·8 (5·8)	1·9 (1·8)	8·6 (9·0)	753 (785)	D	1665, 1680	1685	265s, 295s
(XXVI) $[ReCl_2(NO)(PMe_2Ph)_2(PPh_3)]$ b	Yellow	200—204	49·5 (49·8)	4·5 (4·6)	1·9 (1·7)	9·1 (8·6)	879 (825)	D	1695	1695	260s, 285s
(XXVII) $[ReCl_2(NO)(PMe_2Ph)_3]$	Yellow	175—178	41·8 (41·2)	4·8 (4·9)	2·0 (2·0)	10·1 (10·0)	750 (701)	D	1665	1680	260s, 290s
(XXVIII) $[ReCl_2(NO)(PEt_2Ph)_3]$	Yellow	224—226	45·8 (45·5)	5·9 (5·8)	1·9 (1·8)	9·9 (9·1)	789 (785)	D	1660, 1680	1660	257s, 294s
(XXIX) $[ReCl_2(NO)(PMePh_2)_3]$	Yellow	181—184	52·9 (52·8)	4·7 (4·4)	1·6 (1·6)	8·7 (8·0)	892 (887)	D	1670, 1690	1690	265s, 290s
(XXX) $[ReCl_2(NO)(PPr^n_2Ph)_3]$	Yellow	167—170	49·8 (49·7)	6·6 (6·6)	1·7 (1·6)	9·2 (8·2)	825 (869)	D	1675	1630	255s, 288s
(XXXI) $[ReCl_3(NO)(PPh_3)_2]$	Red-purple	256—261	51·3 (51·0)	3·6 (3·6)	1·9 (1·7)	13·1 (12·6)	900 (847)	1·9	1730	1735	295m, 321s, 335m
(XXXII) $[ReCl_3(NO)(PEt_2Ph)_2]$	Purple	155—158	37·2 (36·7)	4·8 (4·6)	2·3 (2·1)	16·2 (16·4)	668 (655)	1·9	1735	1735	290s, 317s
(XXXIII) $[ReCl_3(NO)(PMePh_2)_2]$	Purple	180—185	42·7 (43·2)	3·7 (3·6)	2·1 (1·9)	15·4 (14·7)	720 (723)	1·9	1740	1740	293m, 318s
(XXXIV) $[Et_4N][ReCl_3(NO)(PMePh_2)_2]$	Orange	154—168	48·4 (47·9)	5·6 (5·5)	3·2 (3·3)	12·0 (12·5)	622 (853)	D	1660	1670	263m, 282s, 290sh
(XXXV) $[ReCl_4(NO)(PMePh_2)_2]$	Yellow-green	decomp. >35	41·5 (41·2)	3·9 (3·5)	1·8 (1·9)	16·5 (18·7)	729 (758)	D	1750	Decomp.	291s, 322s

a Required values in parentheses.　b Phosphorus analysis 10·8 (11·3)%.　c D = Diamagnetic.

triphenylphosphine complex. They all have three bands in the region of the i.r. spectrum in which ν(ReCl) is generally found, and therefore at least one of these is a phosphine ligand band. The position of ν(NO) (chloroform) is very close to that in the parent complex, indicating that NO probably behaves as a three-electron donor, and essentially independent of the phosphine.

Phosphines PR_2Ph (R = Me or Et), generally less sterically demanding than those cited above, react with $[ReCl_2(NO)(PPh_3)_2]$ to produce six-co-ordinate nitrosyl complexes, e.g., $[ReCl_2(NO)(PEt_2Ph)_3]$ (XXVIII) but triethylphosphine apparently can replace only one of the two triphenylphosphines, and on one occasion only were we able to obtain $[ReCl_2(NO)(PMe_2Ph)_3]$ (XXVII), for on all other occasions $[ReCl_2(NO)(PMe_2Ph)_2(PPh_3)]$ (XXVI)

²¹ K. W. Muir, L. Manojlovic-Muir, and R. Herak, personal communication.

ν(ReCl) in their far-i.r. spectra. The ¹H n.m.r. spectra are consistent with a *meridional* arrangement of tertiary phosphines. The dipole moments of $[ReCl_2(NO)(PEt_2Ph)_3]$ and $[ReCl_2(NO)(PMe_2Ph)_2(PPh_3)]$ (6·3 D) are also consistent with *meridional* tertiary phosphines. The X-ray analysis [21] of (XXIX) shows the molecular structure below, with Re–N̂–O = 178·8 (1·4)°. Re–N

```
            Cl
            |        PMePh₂
            |      ↗
   Cl ——— Re ——— PMePh₂
          ↗ |
   Ph₂MeP   |
            N
            |
            O
```

= 1·775 (10) Å and N–O = 1·182 (14) Å. This makes it exceedingly likely that all the complexes

discussed so far have essentially linear Re–N–O systems, in which the nitrosyl ligand is a three-electron donor.

It is clear that the transition from five- to six-co-ordination has caused considerable electronic rearrangement in these complexes, yet the nitrosyl ligand as judged both by i.r. spectroscopy and by ESCA [22] seems little changed. Recently a mechanism has been suggested whereby nitrogen oxide can change from the straight to the bent configuration, with concomitant activation to electrophilic attack, on increasing the co-ordination number of the metal. This so-called 'stereochemical control of valence' was also suggested to be a mechanism for the activation of ligating dinitrogen.[23] In fact, it is not the change in co-ordination number which causes the M–N–O system to bend, but the change in the electronic requirement of the metal. The metal reaches a stable electronic state in a complex when all its low energy molecular and atomic orbitals are filled, i.e. when it reaches the 'closed shell' state. If it does not quite reach it, or only just reaches it with the nitrosyl ligand as a three-electron donor, the M–N–O system will be essentially linear. However, if the ligands would provide more electrons than needed to fill the low-energy orbitals with nitrosyl as a three-electron donor, the nitrosyl ligand will instead become a one-electron donor and the system will become bent. The reason for the straight-to-bent transition which occurs on the change from five-co-ordinate $[Co(diars)_2(NO)]^{2+}$ to six-co-ordinate $[Co(diars)_2(NO)(NCS)]^+$ quoted in reference 23 is not the change in stereochemistry, but that in the former the cobalt reaches the closed shell 18-electron state when the nitrosyl ligand is a three-electron donor, but in the latter, it reaches it when the ligand is a one-electron donor. This electronic situation does not arise in the change from five-co-ordinate $[ReCl_2(NO)(PR_3)_2]$ (16-electron shell) to six-co-ordinate $[ReCl_2(NO)(PR_3)_3L]$ (18-electron shell) and the nitrosyl ligand would be expected to be similar in both classes of complex.

The lower $\nu(NO)$ in the six-co-ordinate complexes as compared with the five-co-ordinate is the result of the additional electron density put on to the metal by the sixth ligand, so increasing electron release from the metal into the antibonding orbitals of the nitrosyl ligand.

The stoicheiometry of the product from the reaction of tertiary phosphines with $[ReCl_2(NO)(PPh_3)_2]$ depends upon the phosphine in a manner reminiscent of the stoicheiometries of the nitrido-complexes $[ReCl_2N(PR_3)_2]$ and $[ReCl_2N(PR_3)_3]$ (PR_3 = tertiary phosphine). For the nitrido-complexes, PR_2Ph (R = Me, Et, Pr^n, or Bu^n) always yield six-co-ordinate complexes, and $PEtPh_2$ and PPr^nPh_2 give a complex of each kind.[24] In the nitrosyl complexes, $PMePh_2$, PPr^n_2Ph, and possibly PBu^n_2Ph, are capable of forming interconvertible five- and six-co-ordinate complexes. Since the expected paramagnetic to diamagnetic changes also occur, this is

a final proof that paramagnetism is an inherent quality of the five-co-ordinate complexes. Five-co-ordinate complexes only were obtained from $PEtPh_2$, PPr^nPh_2, and PBu^nPh_2, and our synthesis involving PMe_2Ph and PEt_2Ph produced only six-co-ordinate complexes. Although the changeover from five- to six-co-ordination does not coincide with that found in the nitrido-complexes, the differences in behaviour of the various phosphines are probably ascribable to steric requirements.

Representative complexes $[ReCl_3(NO)(PR_3)_2]$ (XXXI)—(XXXIII) (PR_3 = tertiary phosphine) were also prepared. The two synthetic routes used are the action of hydrogen chloride on $[ReCl_2(NO)(PR_3)_2]$, and the action of nitrogen oxide on $[ReCl_3(PR_3)_3]$. These nitrosyl complexes (see Table 2) are also paramagnetic, with $\nu(NO)$ at ca. 1735 cm^{-1}, which is almost the same as for the five-co-ordinate species with rhenium in an oxidation state lower by one unit {e.g. $[ReCl_2(NO)(PMePh_2)_2]$ has $\nu(NO)$ at 1725 cm^{-1} and $[ReCl_3(NO)(PMePh_2)_2]$ has $\nu(NO)$ at 1740 cm^{-1}}. The significance of this will be discussed in a following paper.[22]

We have also prepared other rhenium nitrosyl complexes by applying electrochemical techniques in conjunction with Dr. C. M. Elson. Thus electrochemical reduction of $[ReCl_3(NO)(PMePh_2)_2]$ yields $[ReCl_3(NO)(PMePh_2)_2]^-$, isolated as its tetraethylammonium salt, and with $\nu(NO)$ lowered to 1660 cm^{-1}. Electrolytic oxidation of $[ReCl_2(NO)(PMePh_2)_2]$ in CH_2Cl_2 in the presence of NEt_4Cl yields $[ReCl_4(NO)(PMe_2Ph)_2]$ with $\nu(NO)$ at 1745 cm^{-1}.

We attempted to bring about reaction of the co-ordinated nitrogen oxide in selected complexes with a variety of nucleophiles (e.g. H$^-$, OH$^-$, N$_2$H$_4$, NH$_2$OH, or OMe$^-$) and with an electrophile (H$^+$). In no case were new products isolated, not even from H$^+$ and $[NEt_4][ReCl_3(NO)(PMe_2Ph)_2]$. In fact, a survey of the literature indicates that for attack by nucleophiles, the nitrogen oxide should be in a complex with $\nu(NO)$ higher than ca. 1850 cm^{-1} and which is preferably a cation. For attack on neutral complexes by electrophiles, the M–N–O system should generally be bent, and have $\nu(NO)$ considerably below 1700 cm^{-1} although in anions, e.g. $[Fe(CN)_5(NO)]^{2-}$, a reactive NO may have much higher $\nu(NO)$. None of our complexes fulfils these requirements. However, X-ray-induced photoelectron spectroscopy (ESCA) and redox potential measurements provided valuable information on the electronic condition of the co-ordinated nitrogen oxide, and these will be discussed in a following paper.[22]

EXPERIMENTAL

I.r. spectra were obtained using a Grubb–Parsons DM 4 spectrophotometer (400—200 cm^{-1}) and a Unicam SP 1200 instrument (4000—400 cm^{-1}). Melting points in sealed

[22] J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, unpublished work.

[23] J. H. Enemark and R. D. Feltham, Proc. Nat. Acad. Sci. U.S.A., 1972, 69, 3534.

[24] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, J. Chem. Soc. (A), 1969, 2288.

tubes under dinitrogen were measured using an Electrothermal apparatus. Magnetic measurements were made on a Faraday balance. Microanalyses were by Mr. A. G. Olney of Sussex University. N.m.r. experiments were performed at 100 MHz using a JEOL PS-100 spectrometer. Molecular weights were determined in 1,2-dichloroethane using an Hitachi–Perkin-Elmer Osmometer model 115. Dipole moments were determined in benzene under dinitrogen at 25° by Dr. R. H. Crabtree with a DM 01 Dipolemeter. All experiments were carried out under an atmosphere of dinitrogen and solvents were dried and deoxygenated before use. Data for characterisation of complexes are in the Table.

Dichloronitrosylbis(triphenylphosphine)rhenium(II) (II).—Nitrogen oxide was passed through a suspension of complex (I) (3·0 g) in benzene–methanol (100 ml, 1 : 1) during 1 h. The orange-brown *solid* formed was filtered off, washed with methanol, and finally with ether. The complex was recrystallised from benzene–hexane (yield 2·4 g, 83%).

Dibromonitrosylbis(triphenylphosphine)rhenium(II) (III) was similarly prepared from the bromo-analogue of (I) in 85% yield.

Dichlorobis(methyldiphenylphosphine)nitrosylrhenium(II) (IV).—Complex (II) (0·4 g) and methyldiphenylphosphine (1·8 g) were heated in benzene (40 ml) at reflux for 1·5 h. The solvent was removed at 10^{-3} mmHg. To the resulting oil hexane (15 ml) and methanol (5 ml) were added to give a brown solid. The solid was recrystallised from benzene–hexane to give brown *needles* (0·20 g, 59% yield).

This method was repeated with complex (II) (0·4 g) and other tertiary phosphines as detailed below; with ethyldiphenylphosphine (1·9 g) to give *dichlorobis(ethyldiphenylphosphine)nitrosylrhenium*(II) (V) (0·23 g, 66% yield); diphenyl-n-propylphosphine (1·6 g) to give *dichlorobis-(diphenyl-n-propylphosphine)nitrosylrhenium*(II) (VI) (0·26 g, 72% yield); n-butyldiphenylphosphine (2·0 g) to give *dichlorobis(n-butyldiphenylphosphine)nitrosylrhenium*(II) (VII) (0·15 g, 46% yield); phenyldi-n-propylphosphine (1·9 g) to give *dichloronitrosylbisphenyl-n-propylphosphine)rhenium*(II) (VIII) (0·15 g, 46% yield); di-n-butylphenylphosphine (1·0 g) to give *dichlorobis(di-n-butylphenylphosphine)nitrosylrhenium*(II) (IX) (0·13 g, 37% yield); and tricyclohexylphosphine (1·2 g) to give *dichloronitrosylbis(tricyclohexylphosphine)rhenium*(II) (X) (0·32 g, 77% yield); the bromoanalogue of this last complex was prepared in similar fashion from compound (III) to give *dibromonitrosylbis(tricyclohexylphosphine)rhenium*(II) (XI) (0·37 g, 81% yield).

Carbonyldichloronitrosylbis(triphenylphosphine)rhenium(II) (XII).—Carbon monoxide was passed through a solution of complex (II) (0·3 g) in benzene (50 ml) during 7 h. The brown solution was reduced to 5 ml at 15 mmHg and methanol (10 ml) was added. The yellow-brown *solid* which precipitated was recrystallised from dichloromethane–methanol (yield 0·17 g, 55%). The corresponding ammine (XIII) and sulphur dioxide derivative (XIV) were prepared similarly in 75 and 68% yield, respectively. The carbonyl (XXIV) was prepared from (IV) in 50% yield by an essentially similar method.

Dichloro(methyl cyanide)nitrosylbis(triphenylphosphine)-rhenium(II) (XV).—Methyl cyanide (0·5 ml) was stirred with a solution of (II) (0·4 g) in benzene (50 ml) for 18 h. The volume was reduced to 5 ml at 15 mmHg and methanol (10 ml) was added. A yellow *solid* was precipitated and recrystallised from dichloromethane–methanol as yellow needles (yield 0·32 g, 75%).

Dibromo(methyl cyanide)nitrosylbis(triphenylphosphine)-rhenium(II) (XVI) was prepared in a similar manner in 63% yield using complex (III) as the starting material.

This procedure was also used for the phenyl cyanide (XVII) (63% yield), phenyl isocyanide (XVIII) (59% yield), and mono-pyridine (XIX) (56% yield) complexes. For the tetracyanoethylene (tcne) complex (XXII) (43% yield), 0·27 g of (II) and 0·1 g of tcne were stirred in benzene for 3 h.

Dichloro(methylhydrazine)nitrosylbis(triphenylphosphine)-rhenium(II) (XX).—Complex (II) (0·2 g) and methylhydrazine (4·0 ml in methanol 25 ml) were stirred in benzene (30 ml) for 0·5 h. The solution was reduced to 5 ml at 0·01 mmHg and methanol (20 ml) was added. When the solution was cooled to −18° an orange *solid* was precipitated which was recrystallised from dichloromethane–methanol to give orange crystals (yield 0·07 g, 33%).

Dichloro(2-methoxyethylamine)nitrosylbis(triphenylphosphine)rhenium(II) (XXI).—Complex (II) (0·2 g) and ethyleneimine (1 ml) were stirred in benzene (40 ml) for 3 h. The grey solid which precipitated was filtered immediately and washed with methanol. This gave an orange *solid* which was recrystallised from dichloromethane–methanol to give orange crystals (yield 0·12 g, 54%).

Dichloronitrosylbis(pyridine)triphenylphosphinerhenium(II) (XXIII).—Complex (II) (0·3 g) was heated in pyridine (10 ml) at reflux for 2 h. The solution was reduced to 1 ml at 0·01 mmHg and methanol (10 ml) was added. The orange *solid* which precipitated was recrystallised from benzene–hexane to give orange-red crystals (yield 0·17 g, 65%).

Dichlorobis(dimethylphenylphosphine)nitrosyltriphenyl-phosphinerhenium(II) (XXVI).—Complex (II) (0·5 g) and dimethylphenylphosphine (2·0 g) were heated in benzene (40 ml) at reflux for 1 h. All the solvent was removed at 0·01 mmHg and the resulting oil was triturated with methanol–hexane to give a yellow *solid*. The solid recrystallised from dichloromethane–methanol as light yellow needles (yield 0·26 g, 52%).

This preparation was repeated with diethylphenylphosphine (3·5 g) in place of dimethylphenylphosphine to give *dichlorotris(diethylphenylphosphine)nitrosylrhenium*(II) (XXVIII) in 57% yield. With triethylphosphine, (XXV) was obtained in 39% yield.

Dichlorotris(dimethylphenylphosphine)nitrosylrhenium(II) (XXVII).—Compound (I) (1·0 g) and dimethylphenylphosphine (1·4 g) were heated in benzyl alcohol (5 ml) at 190° for 5 min. Nitrogen oxide was immediately passed into the solution until the reaction mixture had cooled to room temperature and then for a further 1 h. Methanol (50 ml) was added and light yellow *crystals* were deposited. The solid was recrystallised from dichloromethane–methanol to give yellow needles (0·3 g, 40% yield).

Dichlorotris(methyldiphenylphosphine)nitrosylrhenium(II) (XXIX).—Compound (IV) (0·3 g) and methyldiphenylphosphine (0·6 g) were heated in benzene (40 ml) at reflux for 6 h. The solvent was removed at 10^{-3} mmHg. Ether-hexane was added to the resulting oil to give a yellow solid. The solid was recrystallised from benzene–methanol to give light yellow *needles* (0·2 g, 51% yield).

Dichlorotris(phenyldi-n-propylphosphine)nitrosylrhenium-(II) (XXX).—Compound (II) (0·4 g) and phenyldi-n-propylphosphine (2·0 g) were heated in benzene (40 ml) at reflux for 8·5 h. The solvent was removed at 10^{-3} mmHg and the resulting oil was shaken with methanol–hexane to

give a yellow solid. The solid was recrystallised from benzene–methanol as yellow *needles* (0·18 g, 43% yield).

Trichloronitrosylbis(triphenylphosphine)rhenium(III) (XXXI).—Complex (II) (0·4 g) was suspended in benzene–methanol (40 ml; 1 : 1) while hydrogen chloride was passed through during 0·2 h. The solution was reduced to 5 ml at 15 mmHg and the dark red *solid* which precipitated was recrystallised from dichloromethane–methanol to give dark red crystals (yield 0·30 g, 71%).

The methyldiphenylphosphine analogue (XXXIII) was synthesised from (IV) in 70% yield in similar fashion.

Trichlorobis(diethylphenylphosphine)nitrosylrhenium(III) (XXXII).— Trichlorotris(diethylphenylphosphine)rhenium (0·3 g) was heated in benzene (50 ml) at reflux while nitrogen oxide was passed through for 1 h. The solution was reduced to 2 ml at 0·01 mmHg and methanol (10 ml) added. The dark purple *solid* which precipitated was recrystallised from dichloromethane–methanol to give purple crystals (yield 0·12 g, 48%).

Tetraethylammonium Trichlorobis(methyldiphenylphosphine)nitrosylrhenate(II) (XXXIV).—Compound (XXXIII) (0·1 g) was reduced electrolytically in a 0·1M-solution of tetraethylammonium tetrafluoroborate, in dichloromethane–methanol (50 ml; 10 : 1), at a controlled potential of $-0·25$ V *vs.* S.C.E. on a platinum gauze electrode under argon at 20°. The electrolysis proceeded smoothly to a negligible background current ($i \leqslant 50$ μA) and an orange solution was obtained. The solvent was removed at 10^{-3} mmHg. The resulting solid was stirred with deoxygenated water to give a pale orange *solid*. This solid was washed three times with water and dried *in vacuo* (yield 0·11 g, 93%).

Tetrachlorobis(methyldiphenylphosphine)nitrosylrhenium-(IV) (XXXV).—Compound (IV) (0·1 g) was oxidised electrolytically at $+0·9$ V *vs.* S.C.E. on a vitreous carbon electrode under argon at 20° in a dichloromethane–methanol solvent (50 ml; 10 : 1) which was 0·1M in tetraethylammonium tetrafluoroborate and 0·01M in tetraethylammonium chloride. The electrolysis was terminated when the current decreased to *ca.* 10% of the initial value. The solvent was removed at 10^{-3} mmHg. The resulting solid was stirred with deoxygenated water and filtered to give a yellow-green *solid*. This solid was washed three times with water and dried *in vacuo* (yield 0·09 g, 84%).