Nitrido-Complexes of Rhenium which contain Tertiary Phosphines, and Attempts to prepare their Osmium Analogues

By **J. Chatt,* C. D. Falk, G. J. Leigh,** and **Rosemary J. Paske,** A.R.C. Unit of Nitrogen Fixation, The Chemical Laboratory, The University of Sussex, Brighton BN1 9QJ

The preparation of nitrido-complexes of type $[ReNCl_2(PR_3)_n]$ (PR_3 = tertiary phosphine, n = 2 or 3) with azide as a source of nitride ion offers no improvement over the use of hydrazine dihydrochloride, which we use here to prepare a number of new analogues. The value of n appears to depend mainly on the steric requirements of the phosphine. Bond length and i.r. spectra data suggest that the Re≡N bond is weaker than the Re=NR bond, a phenomenon which can be correlated with the increased strength of the C≡N bond upon the co-ordination of organic nitriles. Initial attempts to use the hydrazine dihydrochloride method to prepare nitrido–osmium complexes containing tertiary phosphines have led to the preparation of an ammine $[OsCl_3(NH_3)(PPh_3)_2]$ and of oxo-complexes $[OsOX_3(PPh_3)_2]$ (X = Cl or Br). Some azido-complexes of iridium and rhodium were also characterised.

RHENIUM(V) forms multiple bonds to nitrogen rather easily. It is the only element known to form nitrido-complexes which contain tertiary phosphines, and a number of related arylimido-(arylnitrene) derivatives are also known.[1-3] The five-co-ordinated $[ReNCl_2(PPh_3)_2]$ was originally prepared by a somewhat complicated reaction from sodium per-rhenate, triphenylphosphine, and hydrazine dihydrochloride in boiling ethanol and the triphenylphosphine was displaced from it by other tertiary phosphines in boiling benzene to yield the six-co-ordinated complexes $[ReNCl_2(PR_3)_3]$ (PR_3 = PEt_2Ph, PEt_3, or PPr^n_3). The five-co-ordination of the triphenylphosphine complex and six-co-ordination of the diethylphenylphosphine complex have been established by *X*-ray structure determinations.[4,5] The bromides and iodides, $[ReNX_2(PPh_3)_2]$ and $[ReNX_2(PEt_2Ph)_3]$ (X = Br or I), were synthesised analogously.

This paper records an attempt to obtain further data concerning the M≡N bond (M = transition metal) in view of the possibility that it might provide some information as to how the metallo–enzyme nitrogenase catalyses the reduction of nitrogen gas. Our immediate aim was to prepare a variety of nitrido-complexes of rhenium, and extend the synthesis to analogous nitrido-complexes of other elements. We attempted this through the decomposition of azide, and the improvement of the hydrazine dihydrochloride method.

The Preparation of Nitride Complexes by Decomposition of Azide Complexes.—The thermal decomposition of azides to form the nitride ion and nitrogen has been known for many years.[6] However, the reaction products in any particular case depend upon the chemical environment of the azide ion. Thus, the decomposition of azidocarbonyl complexes produces not the nitride ion but the isocyanate ion,[7] whereas the products of the reaction of benzoylazide with $[IrCOCl(PPh_3)_2]$ are benzoylisocyanate and a nitrogen complex $[IrCl(N_2)(PPh_3)_2]$.[8] The ruthenium(III) complex $[Ru(NH_3)_5(N_3)]^{2+}$ undergoes spontaneous decomposition to form a nitrogen complex of ruthenium(II), $[Ru(NH_3)_5(N_2)]^{2+}$, with oxidation of the potential N^- ion to nitrogen gas.[9] To use this decomposition to form nitrido-complexes it is necessary to select a metal which can change its oxidation state relatively easily by two units, according to reaction (1) (L = charged or uncharged ligands).

$$[L_xM{-}N_3] \longrightarrow [L_xM{\equiv}N] + N_2 \qquad (1)$$

Rhenium, with easily accessible oxidation states of (III) and (V), seemed particularly appropriate. Accordingly, the complexes $[ReCl_3(PR_3)_3]$ (PR_3 = monotertiary phosphine) were treated with one equivalent of sodium azide in acetone or alcohol. In only one case, when PR_3 = PMe_2Ph, was there any indication of significant amounts of an azido-complex. With other tertiary phosphines the decomposition of azido- to nitrido-complexes occurred rapidly, as they were formed. The nitrido-complexes containing diethylphenylphosphine, dimethylphenylphosphine, and methyldiphenylphosphine were obtained by this route but the yields were small and the products were difficult to purify. Products containing nitrido-groups were also obtained from di-n-propyl- and di-n-butyl-phenylphosphines, but these could not be satisfactorily characterised.

The iridium and rhodium complexes $[Ir(N_3)(CO)(PPh_3)_2]$, $[Ir(N_3)Cl_2(PEt_2Ph)_3]$, and $[Rh(N_3)(PPh_3)_3]$ were prepared by metathetical reactions from the corresponding chlorides, but we were unable to decompose them either thermally or by u.v. irradiation to yield characterisable compounds. The azide method as a source of nitrido-complexes of Group VIII metals was therefore abandoned.

Preparation by the Hydrazine Dihydrochloride Method.—By careful control of conditions it was found that the reaction of a per-rhenate with hydrazine dihydrochloride in presence of the tertiary phosphine was a perfectly

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[1] J. Chatt, J. D. Garforth, and G. A. Rowe, *Chem. and Ind.*, 1963, 332.

[2] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 1962, 4019.

[3] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

[4] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 204.

[5] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[6] P. Gray, *Quart. Rev.*, 1963, **17**, 441.

[7] W. Beck and H. Smedal, *Angew. Chem.*, 1966, **78**, 267.

[8] J. P. Collman, M. Kubota, J.-Y. Sun, and F. Vastine, *J. Amer. Chem. Soc.*, 1967, **89**, 170.

[9] G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, the late D. Morelli, S. Cenini, and F. Bonati, *Chem. Comm.*, 1967, 739.

satisfactory method of preparing the nitrido-complexes of rhenium [reaction (2)].

$$NaReO_4 + PR_3 + N_2H_4,2HCl \xrightarrow{EtOH} [ReNCl_2(PR_3)_n] \quad (2)$$

Both five- and six-co-ordinate compounds were obtained as listed in the Table. The former are red, the latter yellow, and their structures are presumably analogous to those already described.[4,5] In the chloride series of complexes the balance between five- and six-co-ordination is reached in the ethyldiphenylphosphine complex. Here the five-co-ordinate species is formed either when the solid six-co-ordinate species is heated above 140°, or when solutions of it are warmed; the reverse change is effected by adding an excess of ethyldiphenylphosphine to the cold solution of the five-co-ordinate complex.

Nitrido complexes of rhenium and pertinent I.r. data

Compound	$\nu(Re{\equiv}N)$ (cm.$^{-1}$)	Principal bands in metal–halogen stretching region (400—100 cm.$^{-1}$) [a]
$[ReNCl_2(PMe_2Ph)_3]$	1061	390m, 367m, 345m, *288*s, 260m, *214*s
$[ReNBr_2(PMe_2Ph)_3]$	1062	389w, 349s, 315m, 255m, 216m, 193m, 133s
$[ReNCl_2(PEt_2Ph)_3]$ [b]	1052	366m, 328m, *285*s, 247m, 238m, *217*s
$[ReNBr_2(PEt_2Ph)_3]$ [b]	1052	385m, 364m, 328m, 303m, 249m, 235m, 190m, 135s
$[ReNCl_2(PPr^n{}_2Ph)_3]$	1054	396w, 389w, 374w, *292*s, 259w, *215*s
$[ReNCl_2(PBu^n{}_2Ph)_3]$	1056	387m, *294*s, 261m, *212*s
$[ReNCl_2(PMePh_2)_3]$	1056	349m, 340m, 296s, 263m, *216*s
$[ReNCl_2(PEtPh_2)_3]$	1045	
$[ReNCl_2(PPr^nPh_2)_3]$	1051	385w, 318w, *296*w, 276s, 236s
$[ReNCl_2(PEtPh_2)_2]$	1010	
$[ReNCl_2(PPr^nPh_2)_2]$	1036	347s, 324m, 284m
$[ReNCl_2(PPh_3)_2]$ [c]		*343*s, 322m, 308m, 261m
$[ReNBr_2(PPh_3)_2]$ [c]		284w, 269s, 261s, 250w, 225w, 211s

[a] Bands assigned to ν(ReCl) are in italics. [b] Reported previously, see ref. 3. [c] No assignment of $\nu(Re{\equiv}N)$ possible.

n-Propyldiphenylphosphine also gives both five- and six-co-ordinate complexes, but triphenylphosphine gives only the five-co-ordinate one. Steric factors seem predominant in determining the co-ordination number. If electronic factors had been predominant then the balance between the types, which occurs between the complex of methyldiphenylphosphine and the ethyl analogues, would have led us to expect that the less basic triphenyl- and methyldiphenyl-phosphines would give one type, and the more basic alkyldiphenylphosphines and highly alkylated phosphines the other. In fact it is the more bulky phosphines, irrespective of basicity, which give the five-co-ordinate complexes.

The degradation of hydrazine in a transition-metal complex to yield nitrido-complexes has so far been observed only in the complex chemistry of rhenium, although complex compounds containing higher degradation products such as NH^- and N_2H^- as ligands have been found in platinum chemistry[9] and N_2 in ruthenium chemistry.[10]

In rhenium chemistry the reaction of a per-rhenate and hydrazine hydrochloride in the presence of tertiary phosphine and ethanol has been variously reported to yield nitrido-,[1-3] oxotrichloro-,[2,11] and oxoethoxy-[2,11] complexes. We have therefore attempted to clarify the course of this reaction and find that any of these products may be isolated provided the solvent and the acidity are correctly adjusted. In the formation of nitrido-complexes the oxide alkoxide, $[ReO(OEt)Cl_2(PR_3)_2]$, is an essential intermediate, and in ethanol the presence of water and an excess of the phosphine together with the hydrazine dihydrochloride are necessary to give good yields of the nitrido-complex. This was established by using triphenylphosphine, which gives relatively insoluble complexes and thus allows easy isolation of intermediates and products as follows.

(1) $[ReO(OEt)Cl_2(PPh_3)_2]$ reacts with hydrazine dihydrochloride in the presence of water and of an excess of triphenylphosphine, in either tetrahydrofuran or ethanol, to form the nitrido-complex. If no phosphine is added, the mixture decomposes. If either system is kept anhydrous an isomer of $[ReOCl_3(PPh_3)_2]$, with $\nu(Re{=}O) = 986$ cm.$^{-1}$, is obtained.[11] Hence both phosphine, to remove oxygen from the rhenium as phosphine oxide which was detected spectroscopically, and water, possibly to help ionisation of the dihydrochloride, are essential.

(2) $[ReOCl_3(PPh_3)_2]$ (isomer with $\nu(Re{=}O) = 969$ cm.$^{-1}$) failed to yield any nitrido-complex in dry ethanol, or wet or dry tetrahydrofuran as solvent, and was merely converted into the isomer with $\nu(Re{=}O) = 986$ cm.$^{-1}$. However, in wet ethanol $[ReO(OEt)Cl_2(PPh_3)_2]$ was first formed, and then the nitrido-complex. Hence the reaction proceeds by way of an ethoxy-complex, which, as shown under (1), requires water for its conversion into nitrido-complex.

(3) When $[ReO(OEt)Cl_2(PPh_3)_2]$ was treated with the dihydrochloride and an excess of the phosphine in aqueous tetrahydrofuran, ethanol was produced during the reaction which yielded the nitrido-complex, and was identified by g.l.c. Taken with points (1) and (2) above this indicates that the hydrazinium ion probably replaces the ethoxy-group, rather than reacting with the doubly bonded oxygen to form the rhenium nitrogen bond.

(4) Nitrido-complexes are formed when hydrazine monohydrochloride, hydrazine dihydrochloride, or phenylhydrazine hydrochloride is used as the source of nitride ion. The monohydrochloride is not very useful, and appreciable decomposition occurs. Hydrazine hydrate yields no nitrido-complex. The dihydrochloride produces ammonium chloride in high yield during the reaction. Phenylhydrazine hydrochloride yields aniline hydrochloride and a little ammonium chloride as well as the nitrido-complex. It is evident that the pH of the mixture is important, and that only one nitrogen atom of the hydrazine becomes attached to the rhenium, the second appearing as an ammonium or

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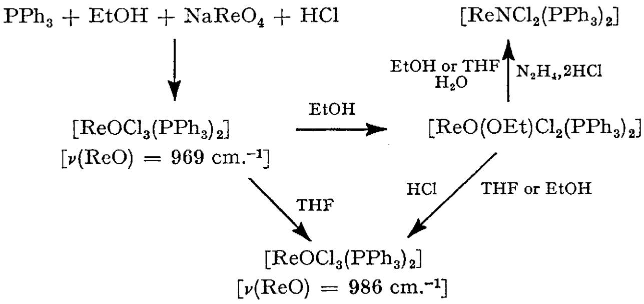
[10] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

[11] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.

amine salt. The overall reaction scheme is represented in the Scheme.

It seems that the alcoholysis of the oxotrichloro-complex to an oxoethoxydichloro-complex is the first step in the formation of the nitrido-complex, followed by protonation of the ethoxy-group and its displacement as ethanol by a $[NH_2-NH_3]^+$ ion. This, being electron-withdrawing, increases the electrophilic character of the oxo-group which, in turn, is removed by the nucleophilic phosphine. The hydrazine in the resultant rhenium(III) complex is then deprotonated and reduced by the rhenium(III), which becomes rhenium(V), to form a co-ordinated nitride ion and an ammonium ion, so giving the complex $[ReNCl_2(PR_3)_2]$, or, since there is an excess of the phosphine, $[ReNCl_2(PR_3)_3]$.



SCHEME

We attempted, by using hydrazine and its hydrochlorides, to prepare analogous nitrido-complexes of osmium. Although osmium forms a number of other nitrido-derivatives,[12] such as $[OsO_3N]^-$ and $[OsNCl_5]^{2-}$, we were unable to obtain analogues of the rhenium compounds. The reaction of potassium osmate, or of nitrido-osmate, with hydrazine dihydrochloride and triphenylphosphine in ethanol yielded $[OsCl_3(NH_3)(PPh_3)_2]$, a yellow, neutral, paramagnetic material the formulation for which has been established by *X*-ray structure analysis.[13] Alkarylphosphines yielded only complexes of type $[OsCl_3(PR_3)_3]$.[14]

We obtained an oxo-osmium complex, $[OsOCl_3(PPh_3)_2]$, by the reaction of triphenylphosphine with a solution of osmium tetroxide in ethanolic hydrogen chloride. This oxo-complex reacted with hydrazine salts in boiling ethanol to give $[OsCl_3(NH_3)(PPh_3)_2]$ in appreciably higher yield (50—60%) than in the above one-stage preparation (10—15%), and very much faster. For this reaction water was again found to be necessary together with a small excess of the phosphine to inhibit decomposition. An intermediate between the oxo-complex and the ammine was detected, but not isolated. This had a strong band in its i.r. spectrum at *ca.* 1200 cm.$^{-1}$, which increased in intensity as that of the 846 cm.$^{-1}$ band {$\nu(Os=O)$} decreased, and the ammine was generated later.

In this and previous papers [1-3] a number of complexes containing Re–N multiple bonds have been described, and we have attempted to find the stretching frequencies of these bonds from the i.r. spectra. These frequencies together with the structures of a selection of the nitrido-complexes, which have been determined by Ibers and his co-workers,[4,5] show some interesting relationships.

The Re–Cl bond *trans* to nitrogen in $[ReNCl_2(PEt_2Ph)_3]$ is abnormally long (2·563 ± 0·004 Å) as compared with the normal *cis*-Re–Cl distance (2·454 ± 0·004 Å).[5] This suggests that the triply bonded nitrogen has a strong *trans*-influence and indeed in the five-co-ordinate complex $[ReNCl_2(PPh_3)_2]$ the position *trans* to the nitrogen atom is empty.[4] In the i.r. spectra of the six-co-ordinate complexes $[ReNCl_2(PR_3)_3]$ there are strong bands at approximately 285 and 215 cm.$^{-1}$. These, by comparison with the spectra of the bromo-derivatives, may be assigned to essentially Re–Cl stretching frequencies, and the abnormally large splitting (*ca.* 70 cm.$^{-1}$) suggests that the stretching force constants of the two Re–Cl bonds may be very different. It is tempting to assign the higher frequency to ν(Re–Cl) *trans* to phosphorus and the lower to ν(Re–Cl) *trans* to nitrogen. The frequency 215 cm.$^{-1}$ is exceptionally low for a metal–halogen stretching vibration, and could be the result of the high *trans*-influence of nitride. However, this conclusion must be accepted with reserve because considerable coupling of vibrations in these rather asymmetric complexes is certain to occur. Bright and Ibers have noted that in $[ReNCl_2(PEt_2Ph)_3]$ the Re≡N distance (1·788 ± 0·011 Å) [5] is longer than the formally Re=N distances in $[p\text{-}MeOC_6H_4NReCl_3(PEt_2Ph)_2]$ (1·690 ± 0·005 Å) and the corresponding p-$MeCOC_6H_4N$ derivative (1·709 ± 0·004 Å).[15] The Re=N–C angle is just less than 180° confirming that the Re–N bond has considerable triple-bond character. The apparently long triple-bond in the rhenium nitrido-complexes led us to question whether they were not in fact imido-complexes (Re=N–H). However, the mass spectrum of $[ReNCl_2(PEt_2Ph)_3]$ gave no indication of an additional proton. Also, the compounds and their properties (*e.g.* diamagnetism) would be very difficult to rationalise if the rhenium(V) nitrido-derivatives should really be formulated as rhenium(IV) imido-derivatives.

Some i.r. assignments also support the view that in compounds such as these the formally double bond may be stronger as well as shorter than the formally triple bond. It was impossible to assign ν(Re=N) in the arylimido-complexes with any certainty because the spectra are too complex. However, in $[Re(NMe)Cl_3(PPh_2Et)_2]$,[16] where the Re–N distance is 1·685 ± 0·011 Å, it may be assigned to a band at 1096 cm.$^{-1}$. This frequency is higher than ν(Re≡N) which is remarkably constant throughout the series of nitrido-complexes listed in the Table. The higher frequency may in part be caused by coupling of the Re–N and N–C vibrations [17]

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[12] W. P. Griffith, *Quart. Rev.*, 1965, **19**, 254.

[13] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1078.

[14] J. Chatt, G. J. Leigh, D. M. P. Mingos, and Rosemary J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

[15] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1099.

[16] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.

[17] *Cf.* K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 919.

but, in any case, it indicates that there is no marked decrease in Re–N bond force-constant in formal reduction of bond order from 3 to 2 in the above systems. It confirms the previous evidence from dipole moments that the bonds in both types of complexes are essentially triple.[2,3]

The distortion of the metal–ligand bonds from orthogonality such that the ligand bonds *cis* to the nitrogen atom are bent away from it, and the lengthening of the Re–Cl bond *trans* to the nitrogen atom in $[ReNCl_2(PEtPh_2)_3]$ have been attributed to steric factors.[16] These were also involved to explain the anomaly whereby the formally Re≡N in $[ReNCl_2(PEt_2Ph)_3]$ is longer than the formal Re=N in the imido-complexes. Undoubtedly these steric factors are important in such overcrowded complexes but we consider that the change from terminal to linear co-ordination of the nitrogen atom also induces an increase in the *s*-orbital contribution of the nitrogen atom to the σ-component of the rhenium–nitrogen bond, which could also account for its slight shortening and apparent strengthening. Our evidence is as follows. A few complexes are known in which formally triply bonded nitrogen is bridging as in $[(PhEt_2P)_3Cl_2Re{\equiv}N{\rightarrow}BX_3]$ (X = Cl, Br, or I).[18] In these ν(Re≡N) is found at about 1140 cm.$^{-1}$, and so the higher ν(Re≡N) may be associated with the linearly two-co-ordinated nitrogen atom rather than with the formal bond order of the Re–N bond. This has an exact parallel in the chemistry of the organic nitriles, RCN. Unlike many ligands with multiply bonded ligand atoms, the multiple bond stretching frequency rises when the nitrile is co-ordinated to a metal, and all of this cannot be attributed to coupling.[17,19] The C≡N bond also shortens. Only exceptionally, when there is a very strong back donation from the metal into the anti-bonding π-orbitals of the nitrile, has a lowering of ν(N≡CR) been recorded.[20]

Purcell[19] has suggested that ν(C≡N) on complex formation by the nitrile is subjected to three effects, (1) polarization of the π-component of the bond (back donation and bond weakening), (2) coupling of the C≡N with the N→M bond which raises the observed frequency, and (3) a change in hybridisation of the nitrogen atom, owing to an increased *s*-orbital contribution by nitrogen to the σ-component of the C≡N bond. This is bond strengthening and he regards this effect as the most significant of the three. It is a result of an almost linear co-ordination of the nitrogen atom. Similarly, higher *s*-contribution by the nitrogen to the σ-bond system may account for the apparent bond strengthening of the rhenium–nitrogen bond in the atomic arrangements Re≡N→B and Re=N–R as compared with Re≡N in which the nitrogen uses mainly a *p*-orbital in the metal–nitrogen σ-bond, and the 'lone pair' electrons reside in a low energy *s*-atomic orbital.

We conclude that in both the nitrido- and organoimido-complexes of rhenium(v) the Re–N bond is essentially a triple bond. In the latter compounds it is shorter and of higher frequency owing to the combined effects of increased *s*-contribution and the coupling of the vibrations of the two bonds to nitrogen in the Re–N–R system.

This appears to be a general phenomenon and there is some evidence of similar behaviour in osmium chemistry. In the few nitrido-osmium compounds, ν(Os≡N) is never higher than 1090 cm.$^{-1}$ and in the negative ion $[OsO_3N]^-$ it occurs at 1023 cm.$^{-1}$.[21] However, in the similar $[OsO_3(\colon NCMe_3)]$[22] it has been assigned at 1184 cm.$^{-1}$. The difference of 161 cm.$^{-1}$ may in part be accounted for by the difference in charge on the complexes, but in any case it indicates that the formal double bond of the latter complex has a force constant at least as great as the formal Os≡N bond in the ion.

EXPERIMENTAL

Starting materials for the rhodium, iridium, rhenium, and osmium compounds were kindly loaned to us by Johnson, Matthey and Co. Ltd. Triphenylphosphine was obtained commercially and the other phosphines were synthesised by standard methods. The known nitrido-complexes were synthesised according to the literature.[1-3] I.r. spectra were taken in Nujol mulls on Unicam SP 1200 and Grubb Parsons DM 4 spectrometers, and also in Polythene discs using an R.I.I.C. FS620 interferometer. M.p.'s were taken in air on a Köfler block, unless otherwise stated. Molecular weights were measured osmometrically, usually in benzene. The mass spectrum was obtained using an AEI MS9 mass spectrometer. All manipulations were carried out in an atmosphere of pure, dry nitrogen.

Nitridodichlorotris(dimethylphenylphosphine)rhenium(v).—(*a*) Trichlorotris(dimethylphenylphosphine)rhenium(III)[14] (0·50 g) and sodium azide (0·052 g, 1·1 mol) were heated in refluxing ethanol (25 ml) for 1 h. The resultant yellow solution, evaporated to *ca.* half volume under reduced pressure and kept in a refrigerator overnight, deposited yellow crystals which, fractionally recrystallised from ethanol, yielded the *product* (0·20 g., 41%), m.p. 173—176° (decomp., *in vacuo*) (Found: C, 41·7; H, 5·1; Cl, 10·2; N, 2·2%; *M*, 702. $C_{24}H_{33}Cl_2NP_3Re$ requires C, 42·0; H, 4·8; Cl, 10·4; N, 2·04%; *M*, 685).

(*b*) A suspension of potassium per-rhenate (0·63 g) and hydrazine dihydrochloride (0·32 g, 1·4 mol) in ethanol (25 ml) was mixed with dimethylphenylphosphine (2·50 g, 8·3 mol) and heated under reflux for 72 h. The resultant yellow solution was filtered hot and evaportated under low pressure to give yellow crystals which crystallised from ethanol to give the product (0·80 g, 54%).

Nitridodibromotris(dimethylphenylphosphine)rhenium(v).—Nitridodibromobis(triphenylphosphine)rhenium(v) (0·50 g) was suspended in hexane (30 ml) and heated under reflux with dimethylphenylphosphine (1·9 g, 12·8 mol) for 2 h. The mixture was cooled, and the product was recrystallised from ethanol to yield yellow *needles* (0·30 g, 61%), m.p. 185—188° (decomp.) (Found: C, 37·5; H, 4·4; N, 1·89%; *M* (osmometric, $CHCl_3$), 809. $C_{24}H_{33}Br_2NP_3Re$ requires

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[18] J. Chatt and B. T. Heaton, *Chem. Comm.*, 1968, 274.
[19] K. F. Purcell, *J. Amer. Chem. Soc.*, 1967, **89**, 247.
[20] P. C. Ford and R. E. Clarke, *Chem. Comm.*, 1968, 1109.
[21] J. Lewis and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.
[22] A. F. Clifford and C. S. Kobayashi, *Inorg. Synth.*, 1960, **6**, 204.

C, 37·2; H, 4·2; N, 1·81%; *M*, 775). The crystalline compound was diamagnetic.

Nitridodichlorotris(diethylphenylphosphine)rhenium(v).—Trichlorotris(diethylphenylphosphine)rhenium(III)[14] (1·50 g) and sodium azide (0·13 g, 1·1 mol) were heated under reflux in ethanol (75 ml) for 1 h. Overnight, the brown solution deposited brown crystals which, recrystallised from ethanol, yielded the *product* (0·30 g, 23%), m.p. 165—170° (decomp., *in vacuo*), identical with that of the previous specimens.[3]

Nitridodichlorotris(di-n-propylphenylphosphine)rhenium(v).—A suspension of potassium per-rhenate (0·70 g) and hydrazine dihydrochloride (1·00 g, 4·1 mol) in ethanol (50 ml) was heated under reflux with di-n-propylphenylphosphine (4·00 g, 8·5 mol) for 70 h. The resultant yellow solution was filtered hot and evaporated to small volume under reduced pressure. Methanol was added and the solution was kept at 0° for 16 h. Yellow crystals were obtained which, recrystallised from methanol, gave the *product* (0·90 g, 44%), m.p. 151—154°. (Found: C, 50·9; H, 6·7; N, 1·5%; *M*, 834. $C_{36}H_{57}Cl_2NP_3Re$ requires C, 50·6; H, 6·7; N, 1·6%; *M*, 853).

This compound was also obtained impure by the azide route in low yield (16%).

Nitridodichlorotris(di-n-butylphenylphosphine)rhenium(v).—A suspension of sodium per-rhenate (1·00 g) and hydrazine dihydrochloride (1·00 g, 2·7 mol) in ethanol (50 ml) was stirred under reflux with di-n-butylphenylphosphine (5·00 g, 6·1 mol) for 3 h. The yellow solution was filtered hot and the solvent was removed under reduced pressure to leave an oil which solidified when shaken for 15 min. with an aqueous solution (1 : 1) of concentrated hydrochloric acid. The solid was recrystallised from ethanol to yield pure *product* (2·10 g, 61%), m.p. 105—109° (Found: C, 53·8; H, 7·5; N, 1·5%; *M*, 920. $C_{42}H_{69}Cl_2NP_3Re$ requires C, 53·8; H, 7·4; N, 1·5%; *M*, 937). The azide method yielded only oils with this phosphine.

Nitridodichlorotris(methyldiphenylphosphine)rhenium(v).—(*a*) Trichlorotris(methyldiphenylphosphine)rhenium(III)[14] (3·60 g) and sodium azide (0·26 g, 1·0 mol) were warmed to 90° in 2-methoxyethanol (300 ml) for 2 h. The solvent was removed under reduced pressure to yield a dark brown oil which solidified under benzene–light petroleum (b.p. 60—80°). Repeated washing of the brown solid with cold acetone gave yellow crystals of the *product* (0·46 g, 13%), m.p. 219—223° (decomp., *in vacuo*) (Found: C, 53·9; H, 4·7; Cl, 7·6; N, 1·6%; *M*, 893. $C_{39}H_{39}Cl_2NP_3Re$ requires C, 53·7; H, 4·5; Cl, 8·2; N, 1·6%; *M*, 871).

(*b*) A suspension of potassium per-rhenate (0·70 g) and hydrazine dihydrochloride (1·00 g, 4·1 mol) in methanol (30 ml) was heated under reflux with methyldiphenylphosphine (5·10 g, 10·5 mol) for 16 h. The resultant yellow solution was filtered hot, evaporated to low volume under reduced pressure, and then filtered again; the white solid was rejected. Addition of methanol and light petroleum (b.p. 80—100°) to the filtrate caused the solution to deposit yellow crystals of *product* (0·80 g, 38%) after several hours at room temperature. The product was recrystallised from methanol.

Nitridodichloribis(ethyldiphenylphosphine)rhenium(v).— A suspension of sodium per-rhenate (0·60 g) and hydrazine dihydrochloride (1·0 g, 4·6 mol) in ethanol (50 ml) was heated with ethyldiphenylphosphine (3·90 g, 4·2 mol) under reflux for 3 h. Initially, purple $[ReO(OEt)Cl_2(PEt_2Ph)_2]$ was precipitated after which the solution became yellow and finally the whole mixture turned brown. The mixture was kept at room temperature for 72 h after which it was heated under reflux for a further 6 h; a brick-red solid separated which was recrystallised from benzene–ethanol to give hexagonal plates of the *product* (0·56 g, 36%), m.p. 209—212° (decomp.) (Found: C, 48·3; H, 4·3; N, 2·2%; *M*, 711. $C_{28}H_{30}Cl_2NP_2Re$ requires C, 48·1; H, 4·3; N, 2·0%; *M*, 699).

Nitridodichlorotris(ethyldiphenylphosphine)rhenium(v).—Ethyldiphenylphosphine (0·84 g, 13·7 mol) was added to a hot solution of nitridodichlorobis(ethyldiphenylphosphine)-rhenium(v) (0·20 g, 1·0 mol) in benzene (20 ml); the solution was cooled and kept at 0° for 5 h. It was then evaporated under reduced pressure without heating to yield an oil. Ethanol was added, the solution was filtered and the filtrate was cooled to 0° to cause slow precipitation of a yellow solid which, carefully recrystallised from benzene–ethanol, gave the *product* (0·20 g, 72%). On attempting to melt it, the compound decomposed to the red bis(phosphine) derivative at 143—144° (Found: C, 55·1; H, 5·1; N, 1·6%; *M*, 509. $C_{42}H_{45}Cl_2NP_3Re$ requires C, 55·2; H, 4·9; N, 1·5%; *M*, 913). This compound in benzene or any other solvent changed from yellow to brick-red upon being warmed probably owing to the loss of a phosphine ligand. The yellow colour redeveloped when the solution was cooled.

Nitridodichlorotris(n-propyldiphenylphosphine)rhenium(v).—Nitridodichlorobis(triphenylphosphine)rhenium(v)[3] (0·70 g) was heated with n-propyldiphenylphosphine (2·1 g, 13·9 mol) under reflux in benzene (20 ml) for 1 h, after which the solvent removed under reduced pressure to leave an oil, which solidified when shaken with pentane for 1 h. The yellow solid was dissolved in benzene and *ca*. 2·0 g, n-propyldiphenylphosphine was added to the solution; solvent was removed to produce an oil which solidified upon being shaken with pentane for 1 h; yield 0·57 g (63%) (Found: C, 56·3; H, 5·4; N, 1·2%; *M*, 476. $C_{45}H_{51}Cl_2NP_3Re$ requires C, 56·5; H, 5·3; N, 1·5%; *M*, 955. The compound decomposes to give a red solid at 138° and dissociates in solution as does its ethyl analogue discussed above.

Nitridodichlorobis(n-propyldiphenylphosphine)rhenium(v).—The above tris(phosphine) derivative was suspended in hot hexane and benzene was added until it just dissolved. Red crystals were slowly deposited and were filtered off and dried; m.p. 188° (decomp.) (Found: C, 50·2; H, 5·0; N, 1·9%; *M*, 672. $C_{30}H_{34}Cl_2NP_2Re$ requires C, 49·5; H, 4·7; N, 1·9%; *M*, 727).

Nitridodichlorobis(benzyldiphenylphosphine)rhenium(v).—The preparation of this compound by the per-rhenate route was never completely successful. The initial product was recrystallised from chloroform–ethanol to give an orange solid which, from its i.r. spectrum, appeared to be a mixture of the red nitrido-bis(phosphine) complex and oxoethoxy-dichlorobis(benzyldiphenylphosphine)rhenium(v).

Osmium ammine and oxo-complexes were prepared as follows, but no nitrido-complex was obtained.

Trichloroamminebis(triphenylphosphine)osmium(III).— A solution of triphenylphosphine (5·00 g, 6·3 mol) in ethanol (100 ml) and water (10 ml) was added to a suspension of potassium osmate (1·02 g, 1·0 mol) and hydrazine dihydrochloride (0·64 g, 2·1 mol) in ethanol (10 ml). The mixture was heated under reflux and stirred for 48 h and then filtered to give an orange-yellow solid (0·30 g, 11·8%) which, recrystallised from chloroform–ethanol, gave the *product*, m.p. 223—226° (Found: C, 51·9; H, 3·3; Cl, 13·3; N, 1·8%; *M*, 791. $C_{36}H_{33}Cl_3NOsP_2$ requires C, 51·2; H, 3·9; Cl, 12·6; N, 1·7%; *M*, 844). This compound is a non-conductor in nitrobenzene, and paramagnetic in the solid state. A much higher yield was obtained when the potassium osmate was replaced in the above preparation by the oxotrichloro-complex prepared as follows.

Oxotrichlorobis(*triphenylphosphine*)*osmium*(V).—To a solution of osmium tetroxide (1·00 g) in ethanol (30 ml) and concentrated hydrochloric acid (5 ml) was added a solution of triphenylphosphine (5·00 g, 5·0 mol) in ethanol (20 ml). The mixture was heated under reflux for 20 min. to precipitate the orange-brown *product* (2·50 g, 77%) which was separated and washed successively with water, diethyl ether, and ethanol. It was too insoluble for recrystallisation from common solvents and had m.p. 178—182° (decomp.) (Found: C, 51·8; H, 3·8; Cl, 12·0; O, 2·6. $C_{36}H_{30}Cl_3OOsP_2$ requires C, 51·3; H, 3·6; Cl, 12·6; O, 1·9%). The compound was a non-conductor in nitrobenzene, but was too insoluble for molecular-weight determination.

Oxotribromobis(*triphenylphosphine*)*osmium*(V).—This was prepared analogously as a brown *solid*, m.p. 167—173°, in 60% yield (Found: C, 45·8; H, 3·2. $C_{36}H_{30}Br_3OOsP_2$ requires C, 44·3; H, 3·1%). It is a non-conductor in nitrobenzene and was too insoluble for molecular-weight determination.

Azidocarbonylbis(*triphenylphosphine*)*iridum*(I).— Chlorocarbonylbis(triphenylphosphine)iridium(I) [23] (0·5 g) dissolved in acetone (30 ml), was heated under reflux with sodium azide (0·6 g, 14·4 mol) for 16 h; the yellow *product* was filtered off and washed with water. More product was obtained from the filtrate by evaporation to small volume, and the whole was recrystallised from benzene; yield 0·42 g (84%), m.p. 204—206° (Found: C, 56·4; H, 4·0; N, 5·3%; *M*, 800. $C_{37}H_{30}IrN_3OP_2$ requires C, 56·5; H, 3·8; N, 5·3%; *M*, 786). The i.r. spectrum showed bands, $\nu(N_3)$ at 2081 cm.$^{-1}$ and ν(CO) at 1954 cm.$^{-1}$.

Azidodichlorotris(*diethylphenylphosphine*)*iridium*(III).— Trichlorotris(diethylphenylphosphine)iridium(III) [24] (0·33 g) and sodium azide (0·027, 1·0 mol) in ethanol (20 ml) were heated under reflux for 1 h; the solution was cooled, to deposit the *product* as yellow crystals which, recrystallised from ethanol, had m.p. 193—195° (0·27 g, 82%) (Found: C, 45·3; H, 5·8; Cl, 8·6; N, 5·0%; *M*, 800. $C_{30}H_{45}Cl_2IrN_3P_3$ requires C, 44·8; H, 5·7; Cl, 8·8; N, 5·2%; *M*, 804). The compound is a non-conductor in nitrobenzene and its i.r. spectrum showed $\nu(N_3)$ at 2047 cm.$^{-1}$.

Azidotris(*triphenylphosphine*)*rhodium*(I).— Chlorotris(triphenylphosphine)rhodium(I) [25] (0·70 g) suspended in acetone (50 ml) was heated under reflux for 90 min. in the presence of sodium azide (1·0 g, 14·3 mol) and triphenylphosphine (1·0 g, 3·5 mol). The resultant orange solution was concentrated to yield orange crystals of the *product* (0·65 g, 65%), m.p. 189—191° (decomp., *in vacuo*) (Found: C, 69·1; H, 5·2; N, 4·3%; *M*, 470. $C_{54}H_{45}N_3P_3Rh$ requires C, 69·6; H, 4·9; N, 4·5%; *M*, 931). Like the chloride, this compound evidently dissociates in benzene solution. It is a non-conductor in nitrobenzene and its i.r. spectrum shows $\nu(N_3)$ at 2037 cm.$^{-1}$.

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