196. *Nitrido- and Arylimido-complexes of Rhenium.*

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Rhenium(v) in combination with tertiary phosphines as ligands has a strong tendency to form multiple bonds to nitrogen. Three new series of complexes containing such bonds, of the types $[\mathrm{ReX_3(NAr)(PR_3)_2}]$, $[\mathrm{ReNX_2(PR_3)_2}]$, and $[\mathrm{ReNX_2(PR_3)_3}]$ (X = halogen, Ar = aryl, R = alkyl or aryl), are described. Imido-complexes are obtained by the reaction of the arylamine on the complexes $[\mathrm{ReOX_3(PR_3)_2}]$ or $[\mathrm{ReOX_2(OEt)(PR_3)_2}]$, and the nitrido complexes by hydrazine dihydrochloride reduction of potassium per-rhenate in the presence of the phosphine. The dipole moments, configurations, and structures of the new compounds are discussed.

Rhenium(v) halides in combination with tertiary phosphines have a strong tendency to form stable multiple bonds to atoms, such as oxygen and nitrogen, in the groupings Re=O and Re=NPh.[1] Dipole moments show the Re=O and Re=NPh bonds to have considerable triple-bond character and may be represented $\mathrm{Re}\overset{\leftarrow}{\equiv}\mathrm{O}$ and $\mathrm{Re}\overset{\leftarrow}{\equiv}\mathrm{NPh}$, the arrows representing the drift of *p*-electrons from the ligand into *d*-orbitals of the metal. The high bond order of the Re=O bond is also demonstrated by its length of 1·60 Å, as compared[2] with 1·87 Å in $[\mathrm{ReO_2(CN)_4}]^{2-}$.

A previous paper[1] described a considerable number of oxo-complexes but only one multiply-bonded nitrogen complex, namely *trans*-$[\mathrm{ReCl_3(NPh)(PEt_2Ph)_2}]$. This paper records the preparation and properties of similar nitrogen complexes and some new types containing nitrogen triply bonded to rhenium.[3]

$[\mathrm{ReCl_3(NPh)(PEt_2Ph)_2}]$ was made by the interaction of $[\mathrm{ReOCl_3(PEt_2Ph)_2}]$ with an excess of aniline in boiling benzene.[1] This procedure has been found to be general with various substituted anilines, and with α-naphthylamine, also with oxotrichlororhenium complexes containing tertiary phosphines other than diethylphenylphosphine. An alternative method employs $[\mathrm{ReOCl_2(OEt)(PEt_2Ph)_2}]$ as starting material in place of the oxotrichloro-complex. Details of the complexes prepared, together with physical properties, are summarised in Table 1. Of interest is that the bifunctional amines, *p*-phenylenediamine and biphenyl-4,4′-diamine, give mono- and not bi-nuclear complexes. The complexes, mostly green, are non-conductors in nitrobenzene and diamagnetic in the solid state at room temperature. The phenylimido-complex is monomeric in boiling benzene.

These uncharged complexes have nitrogen doubly bonded to rhenium, and it was of interest to see whether related complexes containing triply-bonded nitrogen, (Re≡N), exist. No such compounds appear to have been reported, but a charged complex $[\mathrm{ReO_3N}]^{2-}$, is known,[4] analogous to the trioxonitrido-osmates,[5] $[\mathrm{OsO_3N}]^{-}$, and the trioxonitridomolybdates,[6] $[\mathrm{MoO_3N}]^{3-}$.

It has now been found that the complexes previously described[1] as $[\mathrm{ReX_2(PPh_3)_2}]$, where X is Cl or I, contain nitrogen and should be reformulated as $[\mathrm{ReNX_2(PPh_3)_2}]$. The nitrogen was not originally suspected, particularly as elemental carbon and hydrogen analyses were perfectly satisfactory for the first formulation. Once it was suspected, the elemental carbon and hydrogen analyses were carried out with the usual precautions for nitrogen-containing compounds and gave good results for the new formulation. Presumably, in the original analyses, sufficient oxides of nitrogen were formed and weighed as carbon dioxide to compensate for the slightly lower carbon analyses that

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[1] Chatt and Rowe, *J.*, 1962, 4019.

[2] Ehrlich and Owston, *J.*, 1963, 4368.

[3] Chatt, Garforth, and Rowe, *Chem. and Ind.*, 1963, 332.

[4] Clifford and Olsen, *Inorg. Synth.*, 1960, **6**, 167.

[5] Fritsche and Struve, *J. prakt. Chem.*, 1847, **41**, 97.

[6] Watt and Davies, *J. Amer. Chem. Soc.*, 1948, **70**, 2041.

should have been obtained. Thus, N^{3-} is another example of the elusive small groups, such as H^-, O^{2-}, and CO, which can occur unexpectedly as ligands in complex compounds of high molecular weight, and remain undetected for some time.[7]

$[ReNCl_2(PPh_3)_2]$ was obtained originally by the interaction of a per-rhenate, triphenylphosphine, and hydrazine dihydrochloride in boiling ethanol–benzene containing some water, and dehydrated by azeotropic distillation.[1] If, instead, the reagents were mixed under anhydrous conditions and allowed to react at the boiling point, the product was a mixture of $[ReOCl_2(OEt)(PPh_3)_2]$ and the nitrido-complex, the latter generally in poor yield. Thus, the nitrido-complex is best obtained by the slow addition of an ethanolic solution of rhenium heptoxide to a refluxing mixture of the tertiary phosphine and hydrazine dihydrochloride in ethanol. This method works equally well with hydrazine monohydrochloride in place of the dihydrochloride, and similarly with the hydrazine hydrobromides it gives $[ReNBr_2(PPh_3)_2]$, but the iodide is not so obtained. It was previously obtained by metathetical reaction from the dichloride,[1] but has now been prepared directly by a modified azeotropic method using a 2 : 1 ratio of hydrazine to hydrogen iodide. Other methods gave predominantly $[ReOI_2(OEt)(PPh_3)_2]$.

TABLE 1.

Complex	Number	Colour	M. p. (decomp.)	Dipole moment μ (± 0·1 D)
Arylimido-complexes				
$[ReCl_3(NPh)(PEt_2Ph)_2]$	I	Green	201—205°	5·9
$[ReCl_3(p\text{-}N{\cdot}C_6H_4I)(PEt_2Ph)_2]$	II	,,	206—211	—
$[ReCl_3(p\text{-}N{\cdot}C_6H_4Br)(PEt_2Ph)_2]$	III	,,	216—220	5·2
$[ReCl_3(p\text{-}N{\cdot}C_6H_4Cl)(PEt_2Ph)_2]$	IV	,,	207—210	5·0
$[ReCl_3(p\text{-}N{\cdot}C_6H_4F)(PEt_2Ph)_2]$	V	,,	177—181	4·6
$[ReCl_3(p\text{-}N{\cdot}C_6H_4COMe)(PEt_2Ph)_2]$	VI	Dark green	146—148	4·5
$[ReCl_3(p\text{-}N{\cdot}C_6H_4CN)(PEt_2Ph)_2]$	VII	,,	203—210	—
$[ReCl_3(p\text{-}N{\cdot}C_6H_4Me)(PEt_2Ph)_2]$	VIII	Green	182—184	6·5
$[ReCl_3(p\text{-}N{\cdot}C_6H_4OMe)(PEt_2Ph)_2]$	IX	,,	168—170	7·2
$[ReCl_3(p\text{-}N{\cdot}C_6H_4NH_2)(PEt_2Ph)_2]$	X	Yellow	197—199	—
$[ReCl_3(p\text{-}N{\cdot}C_6H_4NMe_2)(PEt_2Ph)_2]$	XI	Brown	194—197	—
$[ReCl_3(pp'\text{-}N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2)(PEt_2Ph)_2]$	XII	Orange	195—210	—
$[ReCl_3(\alpha\text{-}NC_{10}H_7)(PEt_2Ph)_2]$	XIII	Brown-green	200—204	—
$[ReCl_3(NPh)(PEt_3)_2]$	XIV	,,	132—133	—
$[ReCl_3(NPh)(PEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)]$	XV	Pale green	245—280	—
$[ReI_3(NPh)(PEt_2Ph)_2]$	XVI	Golden yellow	191—193	—
Nitrido-complexes				
$[ReNCl_2(PPh_3)_2]$	XVII	Brick-red	219—221	1·6 (±0·3)
$[ReNBr_2(PPh_3)_2]$	XVIII	Orange red	213—216	1·5 (±0·3)
$[ReNI_2(PPh_3)_2]$	XIX	Dull reddish brown	178—180	0·75 (±0·5)
$[ReNCl_2(PEt_2Ph)_3]$	XX	Yellow	151—154	6·4
$[ReNBr_2(PEt_2Ph)_3]$	XXI	,,	151—155	5·8 *
$[ReNI_2(PEt_2Ph)_3]$	XXII	,,	115—118	6·5 *
$[ReNCl_2(PPr^n{}_3)_3]$	XXIII	,,	114—120	6·1 *
$[ReNCl_2(PEt_3)_3]$	XXIV	,,	90—96	6·2 *
Nitrogen-free complexes				
cis-$[ReOCl_3(PEt_2Ph)_2]$	XXV	Blue	157—160	10·8
trans-$[ReOCl_3(PEt_2Ph)_2]$	XXVI	Green	166—169	1·7
$[ReCl_3(PEt_2Ph)_3]$	XXVII	Yellow	163—166	6·3
$[ReBr_3(PEt_2Ph)_3]$	XXVIII	Brown	140—146	6·5

* Initial value (see Experimental section).

Interaction of potassium per-rhenate, diethylphenylphosphine, and hydrazine dihydrochloride in boiling ethanol did not give the diethylphenylphosphine analogue of $[ReNCl_2(PPh_3)_2]$ but gave instead the six-co-ordinated complex $[ReNCl_2(PEt_2Ph)_3]$. This procedure was not so satisfactory for the other halogen analogues, which are more conveniently prepared by treating the above complexes of the formula $[ReNX_2(PPh_3)_2]$

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[7] Chatt and Rowe, *Chem. and Ind.*, 1962, 92.

with an excess of diethylphenylphosphine in boiling benzene. Analogously, by using the appropriate tertiary phosphine, the complexes $[ReNCl_2(PEt_3)_3]$ and $[ReNCl_2(PPr^n{}_3)_3]$ were obtained.

The nitrido-complexes (Table 1) are stable substances, not hydrolysed by acid, and are non-conductors in nitrobenzene and diamagnetic in the solid state at room temperature. Representative examples were found to be monomeric in boiling benzene, as was solid $[ReNCl_2(PEt_2Ph)_3]$, shown by *X*-ray single crystal measurements.

The infrared spectra of the nitrido- and imido-complexes have been investigated by Dr. D. M. Adams who found that absorption bands due to the phosphine ligands complicated the regions where ν(Re=NPh) and ν(Re≡N) might be expected. In the arylimido-complexes ν(Re=NPh) could well fall within the 700—800 cm.$^{-1}$ region. This would be close enough in energy to an N–Ph stretching mode to couple with it, causing displacement of both frequencies from their true values. In the case of $[ReCl_3(NPh)(PEt_3)_2]$ there are 3 bands in the 700—800 cm.$^{-1}$ region, 780vs, 728s, and 690s. Two of these bands, 728 and 690 cm.$^{-1}$, are most probably due to C–H bending modes of the phenyl ring[8] which are found in the regions 730—770 and 690—710 cm.$^{-1}$. It would thus appear that the 780 cm.$^{-1}$ band is due to a vibration of Re=N–Ph, but the second mode expected from this group was not found. In the absorption region under discussion the complex $[ReCl_3(NPh)(PEt_2Ph)_2]$ had three bands 770vs, 731m, and 681s cm.$^{-1}$, and the complex $[ReI_3(NPh)(PEt_2Ph)_2]$ at 765vs, 725m, and 677s cm.$^{-1}$. Parallel argument to the above would allocate the 770vs and 765vs cm.$^{-1}$ bands, respectively, to a vibration of the Re=N–Ph group. For nitrido-complexes, two examples have a strong sharp band near 1050 cm.$^{-1}$, $[ReNCl_2(PPr^n{}_3)_3]$ at 1053s cm.$^{-1}$ and $[ReNCl_2(PEt_2Ph)_3]$ at 1052s cm.$^{-1}$, each being close to a band of the phosphine ligand. The two bands near 1050 cm.$^{-1}$ are comparable with that at 1025 cm.$^{-1}$ assigned to ν(Re≡N) in potassium trioxonitridorhenate,[4] $K_2[ReO_3N]$, and to ν(Os≡N) in $[OsO_3N]^-$ (1023 cm.$^{-1}$) and $[OsCl_5N]^{2-}$ (1073 cm.$^{-1}$).[9]

No bands attributable to ν(Re–H) or ν(N–H) were found in any spectra except ν(N–H) in those of the complexes derived from the aryldiamines (X and XII).

The proton magnetic resonance spectra of the complexes $[ReNCl_2(PEt_2Ph)_3]$ and $[ReNI_2(PPh_3)_2]$ were examined in deuterochloroform by Dr. D. T. Thompson. No evidence of N–H was found, thus eliminating the possibility that the nitrido-complexes might be imido-complexes. The diamagnetism also supports the nitrido-structure.

Dipole Moments and Structures.—All the compounds have dipole moments (Table 1) which are too low [<10 D cf. (XXV)] for a *cis*-configuration of tertiary phosphine groups in any orthogonal arrangement of ligands. The arylimido-complexes (I), (III)—(VI), (VIII), and (IX) must therefore have the *trans*-configuration A, exactly analogous to the green isomer of the oxo-complex (XXVI).[1,2] By analogy it is very probable that all the complexes (I)—(XVI), except (XV), have this configuration.

Since the dipole moments fall with increasing moment of the C_{ar}–X bond (X = Br, Cl, or F) it is evident that the arylimido-groups in compounds (I)—(XIV) and (XVI) lie at the positive end of the dipole, as required by our suggestion[1] that the arylimido-group acquires considerable positive charge relative to the chlorine atom in the *trans*-position to it. This charge results from mesomeric drift of the lone-pair electrons on the nitrogen atom into a vacant *d*-orbital of the rhenium atom, and compensating drift of electrons from the aromatic system to the nitrogen. This explanation is consistent with the rather high dipole moment (7·2 D) of compound (IX) containing the *p*-NC_6H_4·OMe group, which, because of the strong mesomeric effect of the methoxyl group, can cause exceptional electron drift across the aromatic system towards the positive nitrogen atom and the negative end of the dipole. The bond in these compounds is thus best represented $Re \overset{\triangle}{\equiv} N$.

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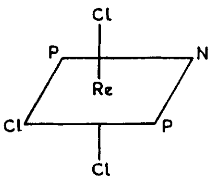
[8] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1st edn., 1953, p. 65.
[9] Lewis and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **6**, 12.

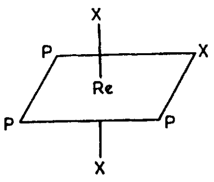
All attempts to obtain aliphatic analogues, *e.g.*, $[\mathrm{ReCl_3(NEt)(PEt_2Ph)_2}]$ and the imine $[\mathrm{ReCl_3(NH)(PEt_2Ph)_2}]$, have failed, probably because the aliphatic radicals and hydrogen are not mesomerically electron-releasing groups.

The polarity of the Re≡N bond in the nitrido-complexes can be estimated by comparison of the hexa-co-ordinated complexes (XX)—(XXIV) with (XXVII) and (XXVIII), all of which are expected to have an essentially octahedral arrangement of ligands as has the oxo-complex (XXVI).[2]

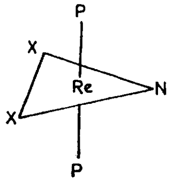
The compounds (XXVII) and (XXVIII) must have the configuration B to account for the dipole moments of about 6·5 D. An all-*cis*-arrangement of the tertiary phosphine ligands would result in a much higher moment (about 13 D). The nitrido-complexes must also have configuration B, but with one of the halogen atoms replaced by nitrogen. This replacement scarcely affects the dipole moment, cf. (XX) and (XXVII). Other compounds of the $[\mathrm{ReNX_2(PR_3)_3}]$ type, (XXI)—(XXIV) (Table 1), undergo some reversible measurably slow change in solution, but the initial values are close to those of the nitrido-chloride (XX), and the trihalides (XXVII) and (XXVIII), indicating that all have initially the same configuration B.



A



B



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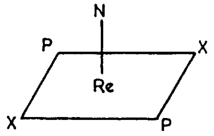

D

This evidence points to the Re≡N bond having a dipole moment close to that of the Re–Cl bond, perhaps about 1·5—2·0 D, the excess of negative charge on the nitride ion being neutralised by strong π-type dative bonding to the metal ion so that the bond is more correctly represented as Re≡N, than $\mathrm{Re} \longleftarrow \mathrm{N^{3-}}$.

The configurations of the penta-co-ordinated complexes (XVII), (XVIII), and (XIX) are not certain. The most likely shapes are trigonal bipyramidal or square pyramidal, and the very small dipole moments indicate that the tertiary phosphine ligands must be in diametrically opposed positions as in configurations C and D, respectively. The nitrogen atom has been assigned to the unique apex in D on symmetry grounds only.

This work, with ref. 1, shows that rhenium(V) with tertiary phosphine ligands has an extraordinary capacity for forming stable multiple bonds to oxygen and nitrogen, all bonds Re=O, Re=NAr, and Re≡N having bond orders greater than two, and being unexpectedly stable to hydrolysis.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are corrected. All reactions were carried out under nitrogen. The following compounds are in the same order as in Table 1 which provides a key to the Roman numerals and summarises some physical properties. All the imido- and nitrido-complexes described below are non-conductors in nitrobenzene and in the solid state are diamagnetic at 20°.

Phenylimido-complexes.—Method (*a*). A solution of rhenium heptoxide (5·5 g.), diethylphenylphosphine (11·0 g.), and concentrated hydrochloric acid (7·0 c.c.) in ethanol (100 c.c.) was refluxed for 24 hr. and then cooled. The resultant crystalline precipitate of green, blue, and violet complexes [1,9a] was washed with ethanol and dried (12·4 g.).

Trichloro(phenylimido)bis(diethylphenylphosphine)rhenium(V) (I). A benzene solution (50

[9a] Chatt, Garforth, Johnson, and Rowe, *J.*, 1964, 601.

c.c.) of mixed complexes (2 g.) and aniline (5 c.c.) was refluxed for 18 hr., then evaporated almost to dryness at water-pump pressure. Addition of aqueous acetic acid (1 : 1; 50 c.c.) gave a green solid, which recrystallised from benzene–light petroleum (b. p. 30—40°) as *needles* (1·73 g.) (Found: C, 43·6; H, 4·95; N, 2·05; *M*, ebullioscopically in 1·84% benzene solution, 741; *X*-ray, 712·6 ± 7. Calc. for $C_{26}H_{35}Cl_3NP_2Re$: C, 43·6; H, 4·95; N, 1·95%; *M*, 716). Crystal data: monoclinic, $a = 15{\cdot}11 \pm 0{\cdot}05$, $b = 10{\cdot}68 \pm 0{\cdot}03$, $c = 23{\cdot}69 \pm 0{\cdot}08$ Å, $\beta = 130{\cdot}65°$, $U = 2900 \pm 13$ Å^3, $D_m = 1{\cdot}632 \pm 0{\cdot}005$ g. cm.$^{-3}$ (by flotation); $Z = 4$, Space group $P2_1/c$ (C^5_{2h} No. 14). The infrared spectrum had 3 bands, 770vs, 731m, and 681s cm.$^{-1}$, which were relevant to ν(Re=NPh).

The following complexes were prepared by the above method but using the appropriate amines: *trichloro-*(p-*iodophenylimido)bis(diethylphenylphosphine)rhenium*(v) (II), was obtained in 25% yield as prisms (Found: C, 37·4; H, 4·05; N, 1·65. $C_{26}H_{34}Cl_3INP_2Re$ requires C, 37·1; H, 4·05; N, 1·65%); *trichloro-*(p-*bromophenylimido)bis(diethylphenylphosphine)rhenium*(v), (III), was obtained in 68% yield as prisms (Found: C, 39·5; H, 4·4; N, 1·85. $C_{26}H_{34}BrCl_3NP_2Re$ requires C, 39·3; H, 4·3; N, 1·75%); *trichloro-*(p-*chlorophenylimido)bis(diethylphenylphosphine)rhenium*(v), (IV), was obtained in 61% yield as needles (Found: C, 42·0; H, 4·6; N, 1·95. $C_{26}H_{34}Cl_4NP_2Re$ requires C, 41·6; H, 4·55; N, 1·85%); *trichloro-*(p-*fluorophenylimido)bis(diethylphenylphosphine)rhenium*(v), (V), was obtained in 41% yield as prisms (Found: C, 42·8; H, 4·7; N, 2·05. $C_{26}H_{34}Cl_3FNP_2Re$ requires C, 42·55; H, 4·65; N, 1·9%); *trichloro-*(p-*acetylphenylimido)bis(diethylphenylphosphine)rhenium*(v), (VI), was obtained in 57% yield, after 64 hr. refluxing, as prisms (Found: C, 44·2; H, 5·0; N, 2·0. $C_{28}H_{37}Cl_3NOP_2Re$ requires C, 44·35; H, 4·9; N, 1·85%); *trichloro-*(p-*cyanophenylimido)bis(diethylphenylphosphine)rhenium*(v), (VII), was obtained in 18% yield, after 66 hr. refluxing, as needles (Found: C, 43·6; H, 4·8; N, 3·95. $C_{27}H_{34}Cl_3N_2P_2Re$ requires C, 43·75; H, 4·6; N, 3·8%); *trichloro-*(p-*methylphenylimido)bis(diethylphenylphosphine)rhenium*(v), (VIII), was obtained in 50% yield as prisms (Found: C, 44·6; H, 5·1; N, 2·05. $C_{27}H_{37}Cl_3NP_2Re$ requires C, 44·4; H, 5·1; N, 1·9%); *trichloro-*(p-*methoxyphenylimido)bis(diethylphenylphosphine)rhenium*(v), (IX), was obtained in 52% yield as prisms (Found: C, 43·15; H, 4·95; N, 2·05; OMe, 4·05. $C_{27}H_{37}Cl_3NOP_2Re$ requires C, 43·45; H, 5·0; N, 1·9; OMe, 4·15%); *trichloro-*(p-*aminophenylimido)bis(diethylphenylphosphine)rhenium*(v), (X), was obtained in 60% yield as needles (Found: C, 42·85; H, 5·15; N, 3·9. $C_{26}H_{36}Cl_3N_2P_2Re$ requires C, 42·7; H, 4·95; N, 3·85%). The infrared spectrum (Nujol mull) had absorption bands at 3497m and 3351s cm.$^{-1}$, indicative of ν(N–H). There was no evidence of reaction involving both amino-groups of the *p*-phenylenediamine to give a binuclear complex.

Trichloro-(p-*dimethylaminophenylimido)bis(diethylphenylphosphine)rhenium*(v), (XI), was obtained in 62% yield as *needles* (Found: C, 43·95; H, 5·4; N, 3·65. $C_{28}H_{40}Cl_3N_2P_2Re$ requires C, 44·3; H, 5·3; N, 3·7%); *trichloro-(4′-amino-4-biphenylylimido)bis(diethylphenylphosphine)rhenium*(v), (XII), was obtained in 54% yield as plates (Found: C, 47·75; H, 5·0; N, 3·55. $C_{32}H_{40}Cl_3N_2P_2Re$ requires C, 47·6; H, 5·0; N, 3·45%). This compound tended to retain benzene of crystallisation and heating it for 3 hr. at 56° under reduced pressure was necessary to remove the benzene. The infrared spectrum had absorption bands at 3478 and 3367 cm.$^{-1}$ indicative of ν(N–H). There was no evidence of a reaction, involving both amino-groups of the benzidine, to give a binuclear complex; *trichloro-(α-naphthylimido)bis(diethylphenylphosphine)rhenium*(v), (XIII). was obtained in 66% yield, after 64 hr. refluxing, as prisms (Found: C, 46·75; H, 4·95; N, 1·9. $C_{30}H_{37}Cl_3NP_2Re$ requires C, 46·9; H, 5·1; N, 1·85%).

Trichloro(phenylimido)bis(triethylphosphine)rhenium(v), (XIV). This complex was prepared from a mixture of *cis*- and *trans*-oxotrichlorobis(triethylphosphine)rhenium(v) [1] as starting material. It was obtained in 40% yield as prisms (Found: C, 34·85; H, 5·7; N, 2·45. $C_{18}H_{35}Cl_3NP_2Re$ requires C, 34·85; H, 5·7; N, 2·25%). The infrared spectrum was complicated but had 3 bands, at 780vs, 728s, and 690s cm.$^{-1}$ which were connected with ν(Re=NPh).

Trichloro(phenylimido)tetraethylethanediphosphinerhenium(v), (XV). A suspension of oxotrichlorotetraethylethanediphosphinerhenium(v) [1] (0·25 g.) in benzene (25 c.c.) was refluxed with aniline (1·5 c.c.) for 40 hr. The new complex was precipitated from the cooled solution as needles (0·235 g.) (Found: C, 32·55; H, 5·0; N, 2·5. $C_{16}H_{29}Cl_3NP_2Re$ requires C, 32·55; H, 4·95; N, 2·35%).

Method (*b*). *Trichloro(phenylimido)bis(diethylphenylphosphine)rhenium*(v), (I). A benzene solution (25 c.c.) of oxoethoxydichlorobis(diethylphenylphosphine)rhenium(v) [1] (0·13 g.) and aniline (1 c.c.) was refluxed for 7 hr., and the resultant green solution evaporated almost to dryness at water-pump pressure. Addition of aqueous acetic acid (1 : 1; 20 c.c.) gave a solid which recrystallised from benzene–light petroleum (b. p. 30—40°) as needles (0·055 g.) (Found: C, 43·7; H, 4·85; N, 2·2%).

Tri-iodo(phenylimido)bis(diethylphenylphosphine)rhenium(v), (XVI). A benzene solution (25 c.c.) of oxoethoxydi-iodobis(diethylphenylphosphine)rhenium(v) (0·30 g.) and aniline (1 c.c.) was refluxed for 20 hr.and then evaporated almost to dryness at water-pump pressure. Addition of aqueous acetic acid (1 : 1; 20 c.c.) gave a brown solid which recrystallised from benzene–light petroleum (b. p. 30—40°) as *plates* (0·09 g.) (Found: C, 31·85; H, 3·55; N, 1·5. $C_{26}H_{35}I_3NP_2Re$ requires C, 31·5; H, 3·55; N, 1·4%). The infrared spectrum had 3 bands, 765vs, 725m, and 677s cm.$^{-1}$ which were relevant to ν(Re=NPh).

Nitrido-complexes.—Nitridodichlorobistriphenylphosphinerhenium(v), (XVII). (*a*) One preparation of this *complex* has been described in a previous publication [1] under the name of dichlorobis(triphenylphosphine)rhenium(II). Carbon and hydrogen analyses on samples dried at ∼56° under reduced pressure (oil pump) for 1 hr., the usual precautions being taken for a compound containing nitrogen, gave satisfactory results (Found: C, 54·4; H, 4·0; N, 1·75; *M*, *X*-ray, 786 ± 12. $C_{36}H_{30}Cl_2NP_2Re$ requires: C, 54·35; H, 3·8; N, 1·75%; *M*, 795·7). Crystal data: monoclinic, $a = 15{\cdot}65 \pm 0{\cdot}01$, $b = 9{\cdot}52 \pm 0{\cdot}02$, $c \sin \beta = 21{\cdot}48 \pm 0{\cdot}02$ Å, $U = 3200 \pm 14$ Å^3, $D_m = 1{\cdot}632$ g. cm.$^{-3}$ (by flotation), $Z = 4$, Space group *Ia* (C_s^4 No. 9) or *I*2/*a* (C^6_{2h} No. 15). When precautions for a compound containing nitrogen were not taken the carbon results were falsely high and similar to those required for dichlorobis(triphenylphosphine)rhenium(II) as previously reported.[1] Crystallographic data showed that it could not be a dimer in the solid state as the minimum Re–Re distance ≃ 8 Å.

(*b*) A suspension of finely divided hydrazine dihydrochloride (1 g.) in ethanol (50 c.c.) containing triphenylphosphine (5 g.) was refluxed for ½ hr., then during 15 min. an ethanolic solution (30 c.c.) of rhenium heptoxide (1 g.) was added, and refluxing continued for a further ½ hr. The resultant suspension was filtered hot and the residue washed successively with hot ethanol, hot water, hot ethanol, and then ether. The product (1·94 g.) was recrystallised from benzene–ethanol to yield plates of the complex (XVII) (Found: C, 54·25; H, 3·9; N, 1·85).

(*c*) Dropwise addition of hydrazine hydrate (0·36 c.c.) was made to a gently shaken suspension of hydrazine dihydrochloride (0·77 g.) in ethanol (50 c.c.) then triphenylphosphine (5 g.) was added and the whole refluxed for ½ hr. The resultant solution of hydrazine monohydrochloride and triphenylphosphine was then treated with a solution of rhenium heptoxide (1 g.) in ethanol (30 c.c.) and subsequently worked up as described under (*b*) to give the complex (XVII) (1·05 g.). The properties and infrared spectrum of the product were identical with those obtained from (*a*) and (*b*).

Nitridodibromobis(triphenylphosphine)rhenium(v), (XVIII). (*a*) This complex was obtained by a similar method to that described for the dichloro-analogue (XVII*a*, and ref. 1) potassium per-rhenate (2·12 g.), hydrazine dihydrobromide (2 g.), and triphenylphosphine (10 g.) being used. The product (2·64 g.) recrystallised from benzene–ethanol as *plates* (Found: C, 48·8; H, 3·6; N, 1·8. $C_{36}H_{30}Br_2NP_2Re$ requires C, 48·9; H, 3·4; N, 1·6%).

(*b*) By a similar procedure to that of experiment (XVII*b*) but with hydrazine dihydrobromide (1 g.), a comparable yield (2·1 g.) of the complex (XVIII) was obtained of identical elemental analysis and infrared spectrum.

(*c*) Repetition of experiment (XVII*c*) with hydrazine dihydrobromide (1·47 g.) and hydrazine hydrate (0·36 c.c.) gave the complex (XVIII) (1·5 g.) (Found: C, 49·0; H, 3·6; N, 1·7%).

Nitridodi-iodobis(triphenylphosphine)rhenium(v), (XIX). Attempts to prepare this compound by the procedures of experiments (XVII*a* and *b*) gave predominantly oxoethoxydi-iodobis(triphenylphosphine)rhenium(v).[1] Application of the method detailed under (XVII*c*) gave a mixture of the oxoethoxy-complex and the desired nitrido-complex in proportions sufficient to make separation tedious. The preferred method used a 2 : 1 ratio of hydrazine to hydrogen iodide as under:

Hydriodic acid (s.g. 1·94; 66%; 1 c.c.) was added to a solution of hydrazine hydrate (1 c.c.) in ethanol (50 c.c.), and this was mixed with an ethanolic solution (150 c.c.) of triphenylphosphine (10 g.). Benzene (100 c.c.) was then added and the whole slowly distilled with simultaneous dropwise addition of ethanol (100 c.c.), until the residual volume in the distillation flask was ∼100 c.c. Ethanol (50 c.c.) was then added, the solution brought to the boiling point and an ethanolic solution (50 c.c.) of rhenium heptoxide (2 g.) added dropwise over 15 min. The mixture was refluxed for a further ½ hr., then filtered hot, and the residue washed successively with hot ethanol, hot water, hot ethanol, and then ether. The product (1·65 g.) recrystallised from benzene–ethanol as *plates* (Found: C, 44·4; H, 3·2; N, 1·45; *M*, *X*-ray, 987 ± 12. $C_{36}H_{30}I_2NP_2Re$ requires C, 44·2; H, 3·1; N, 1·45%; *M*, 978·6). Crystal data: monoclinic, $a \sin \beta = 22{\cdot}41 \pm 0{\cdot}07$, $b = 9{\cdot}71 \pm 0{\cdot}03$, $c = 15{\cdot}94 \pm 0{\cdot}06$ Å, U = 3407 Å³, $D_m = 1{\cdot}891$ g. cm.$^{-3}$ (by flotation), $Z = 4$, Space group $I2/a$ (C^6_{2h} No. 15) or Ia (C^4_s No. 9). It was identical in m. p. and infrared spectrum with the complex erroneously described as di-iodobis(triphenylphosphine)rhenium(II) in ref. 1 and prepared by metathetical reaction from nitridodichlorobis(triphenylphosphine)rhenium(V) (XVII and ref. 1). Crystallographic data showed that it could not be a dimer in the solid as the minimum Re–Re distance ≃ 8 Å.

Nitridodichlorotris(diethylphenylphosphine)rhenium(V) (XX). (*a*) Potassium per-rhenate (1·1 g.), hydrazine dihydrochloride (0·55 g.), and diethylphenylphosphine (5·22 g.) in ethanol (25 c.c.) were stirred and refluxed for 70 hr. then filtered and allowed to cool. The resultant yellow precipitate (0·9 g.) was recrystallised from chloroform–ethanol to give *rhombs* (Found: C, 46·5; H, 5·9; N, 1·8; Cl, 9·8; *M*, ebullioscopic in 3·632% benzene solution, 738, *X*-ray, 774·5 ± 7. $C_{30}H_{45}Cl_2NP_3Re$ requires C, 46·8; H, 5·9; N, 1·6; Cl, 9·2%; *M*, 769·8). Crystal data: monoclinic, $a = 15{\cdot}75 \pm 0{\cdot}04$, $b = 11{\cdot}50 \pm 0{\cdot}04$, $c = 18{\cdot}22 \pm 0{\cdot}04$ Å, $\beta = 93{\cdot}7 \pm 0{\cdot}1°$, U = 3293 Å³, $D_m = 1{\cdot}562$ g. cm.$^{-3}$ (by flotation), $Z = 4$, Space group, $P2/c$ (C^5_{2h} No. 14). The infrared spectrum showed no absorption characteristic of –NH– or R=O but had a strong band at 1052 cm.$^{-1}$, possibly ν(Re≡N).

(*b*) A suspension of nitridodichlorobis(triphenylphosphine)rhenium(V) (1·5 g.) in a benzene solution (200 c.c.) of diethylphenylphosphine (5·2 g.) was refluxed for 20 hr. and then evaporated under reduced pressure (11 mm.). The oily residue was treated with diethyl ether (20 c.c.) and kept in the refrigerator overnight. The resultant precipitate (0·99 g.) was recrystallised from acetone so yielding complex (XX) (Found: C, 46·85; H, 6·1; N, 1·75%). The infrared spectrum was identical with that of the compound described under (*a*).

Nitridodibromotris(diethylphenylphosphine)rhenium(V), (XXI). Nitridodibromobis(triphenylphosphine)rhenium(V) (1·5 g.), treated with diethylphenylphosphine (3·7 g.) as for the chloro-analogue (XX*b*), gave *prisms* (1·3 g.) (Found: C, 42·05; H, 5·3; N, 1·6%; *M*, ebullioscopic in 2·422% benzene solution, 844. $C_{30}H_{45}Br_2NP_3Re$ requires C, 41·95; H, 5·3; N, 1·65%; *M*, 858·7).

Nitridodi-iodotris(diethylphenylphosphine)rhenium(V). (XXII). Treatment of nitridodi-iodobis(triphenylphosphine)rhenium(V) (1·5 g.) with diethylphenylphosphine (4·0 g.) as described for the chloro-analogue (XX*b*) gave *prisms* (1·0 g.) (Found: C, 37·7; H, 4·8; N, 1·55. $C_{30}H_{45}I_2NP_3Re$ requires C, 37·8; H, 4·75; N, 1·5%).

*Nitridodichlorotris(tri-*n*-propylphosphine)rhenium*(V), (XXIII). A suspension of nitridodichlorobis(triphenylphosphine)rhenium(V) (1·0 g.) in a benzene solution (200 c.c.) of tri-n-propylphosphine (1·99 g.) was refluxed for 21 hr. then evaporated under reduced pressure to ~25 c.c. The cold solution was passed through an alumina column (8 in. × 1 in.; Woelm acid alumina, grade 1), then washed with benzene (~400 c.c.) to remove the excess of tri-n-propylphosphine and the triphenylphosphine that had been displaced from the original complex. The product retained on the column was then eluted with ethanol–benzene (1 : 20 v/v; 125 c.c.), and the solution evaporated under reduced pressure (11 mm.). The yellow residue was recrystallised from light petroleum (b. p. 40—60°) to give *prisms* (0·5 g.) (Found: C, 43·0; H, 8·35; N, 1·85. $C_{27}H_{63}Cl_2NP_3Re$ requires C, 43·15; H, 8·45; N, 1·85%). The infrared spectrum had a strong band at 1053 cm.$^{-1}$ which was most probably ν(Re≡N).

Nitridodichlorotris(triethylphosphine)rhenium(V), (XXIV). Treatment of nitridodichlorobis(triphenylphosphine)rhenium(V) (1·0 g.) with a benzene solution (200 c.c.) of triethylphosphine (1·25 g.) and with a similar purification of the product as described for (XXIII) gave *prisms* (0·24 g.) (Found: C, 34·35; H, 7·2; N, 2·3. $C_{18}H_{45}Cl_2NP_3Re$ requires C, 34·55; H, 7·25; H, 2·25%).

cis- and *trans*-Oxotrichlorobis(diethylphenylphosphine)rhenium(V), (XXV and XXVI) and trichlorotris(diethylphenylphosphine)rhenium(III), (XXVII), were prepared as previously described.[1]

Tribromotris(diethylphenylphosphine)rhenium(III), (XXVIII). A benzene solution (150 c.c.) of oxotribromobis(triphenylphosphine)rhenium(V) [1] (2·0 g.) and diethylphenylphosphine (2·0 g.) was refluxed for 42 hr., then evaporated under reduced pressure (11 mm.), and the residue

TABLE 2.

Dipole moments.

Compound	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$
I	2·094	5·951		
	3·959	5·862		
	2·324	5·823		
	36·02		11·15	
	30·33		10·09	
	5·734			0·523
	6·239			0·505
III	3·84	4·143		
	4·53	4·231		
	10·73		9·51	
	16·32		9·78	
	6·56			0·534
	6·68			0·539
IV	2·86	4·153		
	2·59	4·132		
	14·18		10·20	
	18·89		9·70	
	4·25			0·541
	4·84			0·537
V	6·967	3·616		
	3·908	3·657		
	24·57		9·85	
	20·37		9·84	
	8·27			0·532
VI	3·401	3·456		
	5·656	3·429	(11·10)	(0·540)
VIII	2·085	6·829		
	3·593	6·865		
	24·15		8·98	
	15·25		9·46	
	15·08		9·24	
	2·68			0·485
	2·99			0·468
IX	3·388	7·953		
	9·178	7·988		
	13·726		11·09	
	17·780		11·23	
	6·560			0·534
	9·084			0·550
XVIII	2·561	0·822		
	2·275	0·807		
	2·871			0·592
	2·875		(11·64)	0·591
XX	4·71	6·276		
	3·63	6·229		
	17·35		9·87	
	50·58		10·02	
	4·71			0·488
	3·85			0·520
XXI	5·513	4·681	(10·78)	(0·580)
		6·249	(10·78)	(0·580)
XXII	3·806	5·438	(11·83)	(0·630)
		1·221	(11·83)	(0·630)
XXIII	3·735	5·796	(8·68)	(0·500)
		4·930	(8·68)	(0·500)
XXIV	2·963	7·099	(7·44)	(0·500)
		6·522	(7·44)	(0·500)
XXVII	4·972	6·006		
	5·195	6·008		
	30·64		11·35	
	45·58		11·19	
	6·052			0·496
	7·617			0·499
XXVIII	3·564	5·509		
	1·934	5·500		
	5·414			0·573
	6·054		(10·83)	0·595

Compound	${}_{\mathrm{T}}P$	${}_{\mathrm{E}}P$	${}_{\mathrm{O}}P$	μ ($\pm$0·10)
I	923·23	178·27	718·22	5·93
III	771·65	186·51	557·16	5·22
IV	721·59	176·55	518·66	5·04
V	637·52	173·78	437·67	4·63
VI	628·60 *	(184·7)	416·20 *	4·51 *
VIII	1087·54	182·30	877·90	6·55
IX	1257·15	180·07	1050·07	7·17
XVIII	277·48	(203·1)	43·9 *	1·5 * ($\pm$0·3)
XX	1054·95	189·98	836·47	6·40
XXI	902·1 *	(195·7)	677·1 *	5·8 * → 6·8 *
XXII	1113·6 *	(208·9)	873·3 *	6·5 * → 2·4 *
XXIII	965·9 *	(180·0)	758·9 *	6·1 * → 5·2 *
XXIV	957·3 *	(145·3)	790·1 *	6·2 * → 5·9 *
XXVII	1048·30	201·40	816·70	6·3
XXVIII	1113·65	(210·0)	872·15*	6·5 *

* Calc. by using estimated values of densities and refractivities, shown in parentheses.[11]

washed with ether. The product (1·6 g.) recrystallised from acetone–benzene as *needles* (Found: C, 39·25; H, 4·85; *M*, ebullioscopic in 0·928% benzene solution, 883. $C_{30}H_{45}Br_3P_3Re$ requires C, 38·95; H, 4·9%, *M*, 924·6). Its infrared spectrum had no Re=O band, and the complex was a non-conductor in nitrobenzene solution and was diamagnetic in the solid state at 20°.

Dipole moments of selected complexes were measured as in ref. 10 where the symbols used in Table 2 are defined. The apparent moments of four compounds changed with time becoming constant after about 1½ hr. The initial and final values are give, *e.g.*, 5·8 → 6·8 for $[ReNBr_2(PEt_2Ph)_3]$.

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[10] Chatt and Shaw, *J.*, 1959, 705, 4020.

Proton magnetic resonance data quoted as τ values [11] were obtained by using a Varian Associates A60 spectrometer. A dilute, but saturated, solution of $[ReNI_2(PPh_3)_2]$ in deuterochloroform gave a multiplet at 2·1 τ which can be assigned to the phenyl protons. There were no other bands between 1 and 18 τ. A solution of $[ReNCl_2(PEt_2Ph)_3]$ (200 mg.) in deuterochloroform (0·5 c.c.) gave a spectrum consisting of two complex multiplets at 2·7 and 8·2 τ, which can be assigned to the phenyl and ethyl protons, respectively. The ratio of the areas of the two multiplets is 0·51 (required: 0·50). If an additional proton signal had been hidden under the first multiplet the ratio would be 0·53, and if under the second, 0·48. Since there was no other resonance peak between −7 and 18 τ there can be no NH proton in the molecule.

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[*Received, March 7th,* 1963.]

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[11] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.