# Nitrido-complexes as Ligands: μ-Nitrido-complexes

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RECENTLY described were the stable non-ionic nitrido-complexes of the types $[ReNX_2(PPh_3)_2]$ and $[ReNX_2(PR_3)_3]$ ($X = Cl$, Br, or I; $R =$ alkyl or phenyl groups) in which the nitrogen is covalently bonded to the rhenium atom by a triple bond.[1] Two crystal structures are known.[2] It is of interest to see whether the nitrogen in the nitrido-complexes can behave as a ligand atom, and here we report that *mer*-$[ReNCl_2(PEt_2Ph)_3]$ (I), with N *trans* to Cl, shows a close resemblance to acetonitrile and benzonitrile in its electron-donor properties. We have isolated the pale blue to purple compounds $[(PEt_2Ph)_3Cl_2Re{\equiv}N{\rightarrow}BX_3]$ ($X = F$, Cl, or Br) and the unstable red-brown

$[(PEt_2Ph)_3Cl_2Re{\equiv}N{\rightarrow}PtCl_2(PEt_3)]$ (II)

by the reaction of the nitrido-rhenium complex in dry benzene under nitrogen, with the appropriate boron halide or with the bridged complex $[Pt_2Cl_4(PEt_3)_2]$ respectively.

The boron compounds are nicely crystalline and contain one molecule of crystal benzene. They are sensitive to moisture and dissociate into their components on warming their benzene solutions. They react with pyridine (1 mol.) to form $[BCl_3.py]$, and free the rhenium compound.

The platinum compound has a *trans*-configuration [$\nu(Pt{-}Cl) = 336$ cm.$^{-1}$] and the molecular weight of 1092, determined osmometrically, (required: 1154) indicates that it is an adduct of the nitride and half of the bridged complex. It can be formulated as (II) above or as a rhenium(III)-platinum (IV) derivative,

$[(PEt_2Ph)_3Cl_2Re{-}N{=}PtCl_2(PEt_3)]$ (III),

with 4-co-ordinate platinum(IV). However, its properties indicate that it is essentially a platinum(II) derivative.

Organic nitriles react with platinum bridged complexes to form similar adducts in solution:

$$[Pt_2Cl_4(PR_3)_2] + 2RCN \rightleftharpoons 2[PtCl_2(PR_3)(RCN)].$$

However, because the bridged complexes are the least soluble components they separate on evaporating the solution, and the nitrile complex can rarely be isolated.[3] Similarly the complex $[ReNCl_2(PPh_3)_2]$ gave a red colour with $[Pt_2Cl_4(PEt_3)_2]$ in benzene, but the poorly soluble nitrido-complex separated first on evaporating the solvent, indicating the existence of a similar equilibrium. Evidently the $Re{\equiv}N$ tends to keep its triple bond character and little or no stabilisation comes from the possible canonical form (III).

This supposition is supported by the i.r. spectra. On forming organic nitrile complexes of boron halides the $C{\equiv}N$ stretching frequency rises by 70—110 cm.$^{-1}$,[4] and in platinum complexes, $[PtCl_2(RCN)(PR_3)]$, the rise is about 40 cm.$^{-1}$.[3] In the complex (I), a strong band at 1052 cm.$^{-1}$ was tentatively assigned to $\nu(Re{\equiv}N)$.[1] In its boron halide complexes this band appears to be shifted by some 90 cm.$^{-1}$, and in the platinum complex by 18 cm.$^{-1}$, towards higher frequencies. These frequency changes indicate a strong similarity between the co-ordination of RCN and $[Cl_2(PEt_2Ph)_3ReN]$ as ligands.

Acceptor molecules of type $[IrCl(CO)(PR_3)_2]$ also give red solutions with (I) in benzene but the red products dissociate again into their components on evaporation of the solution.

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