Nitrogen Complexes of Rhenium(0)

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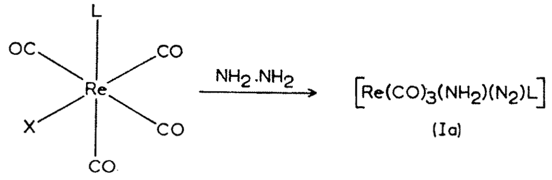
Summary The reaction of *cis*-[Re(CO)$_4$Br (PMe$_2$Ph)] and *trans*-[Re(CO)$_3$ Cl (PMe$_2$Ph)$_2$] with hydrazine leads to the formation of compounds having co-ordinated molecular nitrogen and a σ-NH$_2$ ligand.

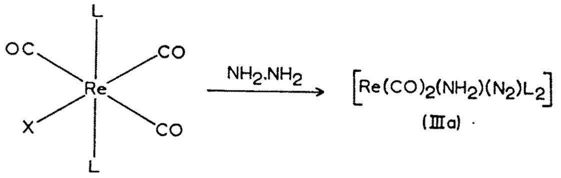
CHATT, DILWORTH, and LEIGH[1] have recently reported the first series of nitrogen complexes of a non-Group VIII metal, *viz.* [Re(Cl)N$_2$L$_4$], although a number of complexes containing molecular nitrogen co-ordinated to Group VIII transition metals have been reported over the last three years.[2] We now report another series of rhenium–nitrogen complexes containing nitrogen, which are stable and crystalline in the absence of air.

The reactions of rhenium carbonyl with tertiary phosphines and arsines produce a series of substituted rhenium carbonyl derivatives. These, in turn, are readily converted into halogen derivatives either by splitting the metal–metal bond of the binuclear complexes or by oxidation of the paramagnetic mono-nuclear complexes, Re(CO)$_x$-L$_y$ ($x + y = 5$) by halogens or halogenated solvents.[3]

Attempts to reduce (I), (II), and (III) to the corresponding hydride, using reducing agents such as NaBH$_4$, LiAlH$_4$, and Zn–dimethylformamide at room temperature yielded no isolable products, but with hydrazine molecular-nitrogen-containing complexes were formed. The *cis*-isomer of (III) failed to react with hydrazine even under drastic conditions.[4] Compounds (Ia) and (IIIa) have been isolated and they are unstable in the presence of air, changing from pale yellow-brown crystalline complexes into dark purple-red viscous materials. The reaction product of (II) with hydrazine is similarly air-sensitive. Compounds (Ia) and (IIIa) are soluble in benzene, whereas the product from (II) is only soluble in water and ethanol, is not precipitated by large anions, and it has not been characterized.



(I) L = PMe$_2$Ph, X = Br
(II) L = AsMe$_2$Ph, X = Br



(III) L = PMe$_2$Ph, X = Cl

The i.r. spectra of (Ia) and (IIIa) reveal very sharp and intense bands at 2220 and 2225 cm.$^{-1}$ which are assigned to ν(N$\equiv$N). These are the highest N$\equiv$N stretching frequencies recorded for molecular nitrogen complexes but are well below that for unco-ordinated nitrogen (2331 cm.$^{-1}$).[5] The ν(N$\equiv$N) band disappeared when (Ia) and (IIIa) reacted with dry HCl gas, the resulting products being water-soluble salts. Organometallic cations are precipitated from these aqueous solutions with large anions such as BPh_4^-. Evidence for the formation of a molecular nitrogen compound from (II) is given by a strong sharp absorption at 2240 cm.$^{-1}$ (KBr disc) which is assigned to $\nu(N\equiv N)$. The absorptions at 3500—3200, 1600—1150, and 750—690 cm.$^{-1}$ are attributed to N–H vibrations, but are not consistent with those for a hydrazine complex,[6] an N_2H_2 complex,[7] or an ammine complex,[8] but appear to be consistent with a σ-NH_2 system.[9] This conclusion is further supported by the n.m.r. spectra. Deuteriation of complex (IIIa) results in the appearance of a medium-intensity band at 2680 cm.$^{-1}$ due to ν(N–D) and in the marked reduction of the intensity of the bands assigned to N–H. The i.r. spectra of (Ia) and (IIIa) also show strong absorption bands due to $\nu(C\equiv O)$. Medium-intensity bands at 368 and 372 cm.$^{-1}$ in the i.r. spectra of (I) and (III), respectively, which are assigned to ν(M–halogen),[10] are absent in the spectra of compounds (Ia) and (IIIa). $\nu(M{-}NH_2)$ appears at 410 cm.$^{-1}$ (Ia) and 430 cm.$^{-1}$ (IIIa),[9] and $\nu(M{-}N_2)$ appears at 520 cm.$^{-1}$ (Ia) and 530 cm.$^{-1}$ (IIIa) as medium-intensity bands.[8]

The ^1H n.m.r. spectra of (Ia) and (IIIa) show multiplets at τ 2·45 and 2·51, respectively, due to the phenyl hydrogens of the phosphine ligand. Multiplets arise at τ 8·05 (Ia) and 8·0 (IIIa) due to the methyl hydrogens. The complexity of both these multiplets indicates that in both cases there is a plane of symmetry through the P atom of the ligand.[11] In the case of (Ia), a four-line multiplet is observed instead of the expected doublet,[11] and in (IIIa) a five-line multiplet is observed which might arise from the overlapping of two triplets, which are caused by the methyl groups of the ligand occupying different environments. Two rather broad one-proton singlets are observed in each case. In both cases they disappear on deuteriation, while the rest of the spectrum is unaffected, and they are thus assigned to protons attached to N. This result is consistent with the formulation of a σ-NH_2 group, bonded to the rhenium, in which each hydrogen bonded to the N has a unique environment. In view of the hydrogens being bonded to a quadrupolar N atom, this assignment could be criticised. However, Ariyaratne and Green[12] have reported a comparable feature in the n.m.r. spectrum of $[\pi\text{-}C_5H_5Fe(CO)_2{-}CH_2{=}C{=}NH]^+$, where two NH resonances were observed at τ 6·25 and 7·30, corresponding to the *endo*- and *exo*-positions of the N–H hydrogen.

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