The Interaction of Dinitrogen† Complexes of Rhenium and Osmium with Metal Salts

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Summary The reaction of $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ with silver salts, cupric chloride, ferric chloride, or halogens produces salts of the anion $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]^+$, and there is no suggestion of any bridged species.

THERE are two well-defined complexes containing a dinitrogen bridging two metal ions, $[(NH_3)_5Ru(N_2)Ru(NH_3)_5]_4^{4+}$ [1] and $[(NH_3)_5Ru(N_2)Os(NH_3)_5]^{4+}$,[2] and dinitrogen bridged compounds were inferred as possible components of the unstable mixture of the products from the reaction of $[Os(NH_3)_5(N_2)]^{2+}$ with Ag^+ and Cu^{2+}.[3] These were not isolated, but were characterised by an i.r. band assigned to $\nu(N{\equiv}N)$ at about 200 cm^{-1} higher frequency than in the original cation. We have attempted to form similar bridged compounds from rhenium(I) dinitrogen complexes,[4] but have obtained oxidised products.

Yellow $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]$[4] (A) reacts with Ag^I salts in ethanol to give a purple solution from which the salts of the anion $[ReCl(N_2)(Ph_2PCH_2{\cdot}CH_2{\cdot}PPh_2)_2]^+$ (B) may be isolated. An excess of cupric chloride or ferric chloride also oxidises (A) to (B), which is isolated as the dichlorocuprate(I) and tetrachloroferrate(III), respectively. The presence of discrete $[FeCl_4]^-$ ions in the latter was shown by its Mössbauer spectrum. Quantitative addition of halogen to a suspension of (A) in chloroform at −30° yields the chloride, tribromide, or tri-iodide of (B). Analogues of (A) containing the diphosphines *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2PCH_2PPh_2$, and $Ph_2P(CH_2)_3PPh_2$ behave similarly.

The salts of (B) all have $\nu(N{\equiv}N)$ at 2060 cm^{-1} in chloroform solution, some 80 cm^{-1} higher than in the parent (A). In Nujol mulls $\nu(N{\equiv}N)$ is generally in the range 2035—2045 cm^{-1} and is almost independent of anion, in marked contrast to the dependence of $\nu(N{\equiv}N)$ in $[Ru(NH_3)_5(N_2)]^{2+}$ [5] and $[Os(NH_3)_5(N_2)]^{2+}$ [6] on the counter-anion. In the solid state the salts of (B) exist in purple and green isomeric forms which have similar e.s.r., diffuse reflectance, and i.r. spectra. The only substantial differences in the i.r. spectra are found between 400 and 600 cm^{-1}. Both isomers give identical purple solutions, but the purple form appears to be metastable with respect to the green in the solid state. The carbonyl analogues of (A) with various diphosphines are oxidised similarly, but only the green forms of the products have been obtained either in solution or in the solid state.

The oxidation of the rhenium(I) complex suggested that the reaction of $[Os(NH_3)_5(N_2)]Cl_2$ [$\nu(N{\equiv}N) = 2010\ cm^{-1}$] with silver(I) and copper(II) salts might be similar. We have repeated the experiments of Das *et al.*[3] and have observed the band at about 2230 cm^{-1} in the products. However, on changing the reaction solvent from water to ethanol, and employing the tetraphenylborate salt instead of the perchlorate, three i.r. bands were observed in the crude product, at 2050, 2140, and 2225 cm^{-1}. Oxidation by one unit in the rhenium complexes causes an increase in $\nu(N{\equiv}N)$ of about 80 cm^{-1}, and therefore by analogy the band at 2140 cm^{-1} could be due to $[Os(NH_3)_5(N_2)]^{3+}$. The band at 2225 cm^{-1} may correspond to a further oxidation to $[Os(NH_3)_5(N_2)]^{4+}$, rather than the formation of a bridged

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† According to IUPAC nomenclature, N_2 is called dinitrogen. Complexes containing two nitrogen molecules are bis(dinitrogen) complexes.

species. Treatment of an ethanolic solution of $[Os(NH_3)_5(N_2)][BPh_4]_2$ with iodine gives an unstable mixture, which shows a strong band at 2130 cm^{-1} assignable to $\nu(N{\equiv}N)$ in $[Os(NH_3)_5(N_2)]^{3+}$. It cannot be assumed therefore that the rise in $\nu(N{\equiv}N)$ upon reaction of $[Os(NH_3)_5(N_2)]^{2+}$ with oxidising salts is caused by dinitrogen bridging, until the possibility of simple oxidation has been excluded.

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