

Nitrile Complexes of Rhenium(IV)

By G. ROUSCHIAS* and G. WILKINSON

(*Inorganic Chemistry Research Laboratories, Imperial College of Science and Technology, London, S.W.7*)

NITRILE complexes of transition metals have been divided into two groups according to their solvolytic nature, those of metals to the left of Group VIIB being very sensitive to moisture, those of metals to the right and of manganese(II) relatively stable.¹

We have now prepared the first simple nitrile complexes of rhenium,† $\text{ReCl}_4(\text{RCN})_2$ ($\text{R} = \text{Me}, \text{Pr}^n, \text{Ph}$) and shown that they occupy an intermediate position in their hydrolytic behaviour. Thus $\text{ReCl}_4(\text{MeCN})_2$ crystallises out unchanged when water is added to a cold acetone solution, whereas $\text{ReCl}_4(\text{PhCN})_2$ reacts with water at once to give a strongly coloured anionic complex which forms salmon-orange salts. All the complexes are rapidly hydrolysed by hot water to hydrated rhenium dioxide.

The complexes were obtained as greenish-yellow crystals by warming the intensely red-brown solution of ReCl_5 in the appropriate anhydrous nitrile, a reduction reaction analogous to that of

MoCl_5 and WCl_5 .⁴ The benzonitrile complex was also obtained from $\text{ReCl}_4(\text{MeCN})_2$ by ligand exchange. The complexes were characterized by elemental analyses, infrared spectroscopy, and magnetic measurements [$\mu_{\text{eff}} = 3.40$ B.M. for solid $\text{ReCl}_4(\text{MeCN})_2$], and were monomeric and nonconducting in organic solvents. The C-N stretching frequency was at 2292 cm^{-1} (vs) for $\text{ReCl}_4(\text{MeCN})_2$, and at 2260 (vs) and 2251 cm^{-1} (vs) for $\text{ReCl}_4(\text{PhCN})_2$.

The rhenium(IV) complexes ReCl_4L_2 ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$) were prepared from $\text{ReCl}_4(\text{MeCN})_2$ by ligand substitution, whereas primary aromatic amines gave orange, crystalline compounds which we believe to be complexes of *N*-aryl-amidines, $\text{ReCl}_4[\text{R}\cdot\text{C}(\text{:NH})\text{NHR}']$. Such a formulation, analogous to the well established amidine complexes of platinum(II)⁵ is consistent with the analytical, degradation, magnetic, and infrared results.

(Received, March 29th, 1967; Com. 303.)

† The other established nitrile complexes of rhenium are $\text{Re}_3\text{L}_9(\text{RCN})_3$ (ref. 2), and $\text{ReX}_3(\text{RCN})(\text{PPh}_3)_2$ ($\text{R} = \text{Cl}, \text{Br}$) (ref. 3).

¹ R. Walton, *Quart. Rev.*, 1965, **19**, 126.

² F. A. Cotton and R. A. Walton, *Inorg. Chem.*, 1966, **5**, 1802.

³ G. Rouschias and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, in the press.

⁴ E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 5431.

⁵ N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 801.