

Synthesis of the First Ruthenium(III) High Spin Complex: Novel {RuNO} 5 d Electron and {RuNO} 7 d Electron Complexes

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Nitrosyl chloride reacts with hydrated ruthenium trichloride in the presence of triphenylphosphine (Ru : PPh₃ = 1 : 8) to give the pink Ru^{III} high spin complex NH₄[Ru(NO)Cl₅], NH₄Cl, and the green {RuNO} 7 d electron complex [Ru(NO)Cl₂(PPh₃)₂] which reacts with PPh₃ to give the yellow {RuNO} 7 d electron complex Ru(NO)Cl₂(PPh₃)₂.

All the complexes of ruthenium(III) so far reported are low spin, six co-ordinate. No nitrosyl or nitro complexes of Ru^{III} are known, and only two {RuNO} 7 d electron complexes [Ru(NO)Cl(bipy)₂]I and [Ru(NO)(MeCN)(bipy)₂]PF₆ (bipy = 2,2'-bipyridyl) have been isolated as solids.^{1,2} We now report (i), an Ru^{III} high spin complex NH₄[Ru(NO)Cl₅]

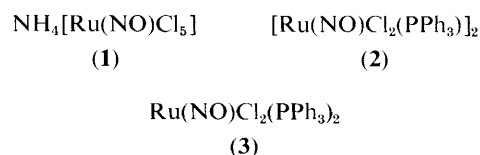
having an {RuNO} 5 d electron moiety, (ii), formation of NH₄Cl from NOCl, and (iii), neutral {RuNO} 7 d electron complexes [Ru(NO)Cl₂(PPh₃)₂] and Ru(NO)Cl₂(PPh₃)₂.

Treatment of NOCl with RuCl₃·H₂O in the presence of PPh₃ (Ru:PPh₃ = 1:8) in EtOH-CH₂Cl₂ affords NH₄-[Ru(NO)Cl₅] (1), [Ru(NO)Cl₂(PPh₃)₂] (2), and NH₄Cl. De-

creasing the amount of PPh_3 results in the formation of $\text{Ru}(\text{NO})\text{Cl}_3(\text{PPh}_3)_2$. The complex (2), on refluxing with PPh_3 in CH_2Cl_2 , gives $\text{Ru}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$ (3).

The complex (1) is pink, air stable, and forms a 1:1 electrolyte in water.† The i.r. spectrum exhibits ν_{NO} 1900, $\nu_{\text{Ru-Cl}}$ 330 and 285 cm^{-1} , and bands due to NH_4^+ . The magnetic moment ($\mu = 5.86 \mu_{\text{B}}$), which does not vary with changing temperatures, corresponds to five unpaired electrons suggesting a high spin d^5 ($t_{2g}^3 e_g^2$) configuration for the Ru^{III} ion. The e.s.r. spectrum of (1) is typical of a d^5 spin-free system having six lines [g_{av} 2.003, $A_{\text{ISO}}(^{101}\text{Ru})$ 46 G]. In the electronic spectrum [λ_{max} (ϵ), 520 (6.5), 390 (10), 360 (23), 265 (1436), and 212 nm (4244)] the intensity of the lowest energy bands is more than that expected for spin forbidden transitions. This is due to the fact that the lowest energy bands correspond to $d \rightarrow d$ transitions with the occupied metal orbital having some Cl character.³

Complex (2), the other product from the reaction, gives green crystals which are air stable and does not form an electrolyte in nitrobenzene.† The molecular weight, obtained by field desorption mass spectrometry is 927. The i.r. spectrum shows ν_{NO} 1878, $\nu_{\text{Ru-Cl}}$ 342 and 240 cm^{-1} and the magnetic moment for (2) ($\mu = 1.56 \mu_{\text{B}}$) is lower than the spin-only value. The complex (2) was shown to be paramagnetic by e.s.r. spectroscopy (g_{av} 2.13, g_z 2.028, $g_x = g_y$ 2.18). For an {MNO} 7 d electron system the additional electron could be in either the ($d_{z^2} - \sigma_{\text{NO}}$) or the ($\pi_{x,y}^* - d_{xz}d_{yz}$) orbital which would result in a 2A_1 or 2E state, respectively.⁴ For the



linear 2A_1 ground state the possible structure of complex (2) would be square pyramidal with a chloro-bridge.

The complex $\text{Ru}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2$ (3) is a yellow crystalline solid and a non-electrolyte: ν_{NO} 1868 and $\nu_{\text{Ru-Cl}}$ 340 cm^{-1} , $\mu = 1.6 \mu_{\text{B}}$.† The e.s.r. spectrum is very broad with g_{av} 2.12, and g_z 2.00 is obtained by resolution of the broad spectrum. This indicates a ground state of 2A_1 with the structure of the complex (3) being square pyramidal. Diamagnetic complexes of a similar type, *i.e.* $\text{Ru}(\text{NO})\text{I}_2\text{L}_2$ [$\text{L}_2 = (\text{pyridine})_2$, bipy, and tertiary phosphine], have been reported earlier.⁵

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† Satisfactory analytical data were obtained for all new compounds.