The Formation of an Aquotetracyanomethylrhodate(III) Complex from a Tetracyanorhodate(I) Intermediate

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The cyanide ligand is capable of stabilising cobalt alkyls[1] and hydride[2] in anionic complex form. The only known analogous rhodium complex $[Rh(CN)_5(C_2F_4H)]^{3-}$ may be prepared by treating $[RhH(CN)_4H_2O]^{2-}$ with tetrafluoroethylene. With ethylene it did not form the corresponding ethyl complex.[3] Herein is reported a mechanism for the formation of certain aquotetracyanoalkylrhodate(III) complexes, the methyl analogue is used as an example. Sodium cyanide reacts with $[Rh(CO)_2Cl]_2$ in aqueous methanol, evolving carbon monoxide to form the anion $[RhH(CN)_4H_2O]^{2-}$; this implies the intermediate formation of a rhodium complex with powerful reducing properties, capable like the pentacyanocobaltate(II) species of reacting with water.[2] Thus, if methyl iodide (or bromide) and $[Rh(CO)_2Cl]_2$ react with sodium cyanide in dry methanol, under nitrogen, a complex dipotassium aquotetracyanomethylrhodate(III) is isolable, and evidence for the formation of an acylrhodium complex is also obtained.

The nature of the products of this reaction is very dependent upon the reaction conditions, thus:

(i) When sodium cyanide (10 moles) is added rapidly to $[Rh(CO)_2Cl]_2$ (1 mole) and methyl iodide (5 moles), the evaporated product shows a ^1H n.m.r. spectrum (in D_2O): a doublet at τ 9·73 (area = 0·8), $J(^{103}Rh–^{1}H) = 1·9 \pm 0·1$ c./sec.; a singlet at τ 7·3 (area = 0·2); a singlet at τ 6·60 (area = 1·0). The latter peak is consistent with the retention of 1 mole of methanol by the complexes. Alkaline hydrolysis does not affect the doublet, but the singlet at τ 7·3 disappears, and a peak of the same area appears in the identical position to acetate, τ 7·90. The solid shows two cyanide stretching vibrations at 2108 and 2116 cm.$^{-1}$; a slight peak at 1560 cm.$^{-1}$ can be attributed to a carbonyl stretching vibration, though this is obscured by the water bending mode at 1630 cm.$^{-1}$.

(ii) When $Rh(CO)_2Cl_2$ (0·05M, 1 mole) is added slowly to sodium cyanide (0·5M, 10 moles) and methyl iodide (5 moles) in methanol only formation of the methylrhodium complex occurs. Precipitation with potassium acetate in aqueous methanol gives a white salt $K_2[CH_3Rh(CN)_4H_2O]$, cyanide stretch 2108 cm.$^{-1}$, *M*, 330 ± 20 (calc. 318) from the ^1H n.m.r. spectrum.

(iii) When reagents and conditions are as in (i), but the sodium cyanide is added slowly, 80—90% of the acylrhodium complex may be formed. Attempts to isolate the acyl complex have so far failed. If only four equivalents of cyanide are used, two resonances (τ 7·23, 7·30) of unequal areas are observed in the ^1H n.m.r. spectrum. Addition of more cyanide causes the low-field line to disappear, whilst the high-field line increases by an equivalent amount, and carbon monoxide is evolved from the solution. The τ 7·23 line probably represents an acylrhodium carbonyl complex.

(iv) If methyl iodide is added after an excess (10 moles) of sodium cyanide to $[Rh(CO)_2Cl]_2$, neither the methyl- nor the acyl-rhodium complex is formed; though if only four moles of cyanide per mole of rhodium are used, the acyl complex only is formed in reduced yield.

Thus at least three reactive species are possible, $Rh(CN)_4^{3-}$, $Rh(CN)_3(CO)^{2-}$, and $Rh(CN)_2(CO)_2^{-}$, the reaction being an addition of methyl iodide in a two-electron oxidation analogous to the reaction between $(Ph_3P)_2Ir(CO)Cl$ and methyl iodide.[4]

No evidence can be obtained for the retention of iodide in the complexes, this is in keeping with the high *trans*-effect of the methyl group, the single cyanide stretching mode supports a *trans*-configuration for $[CH_3Rh(CN)_4H_2O]^{2-}$. In $[CH_3Rh(CN)_4(CH_3OH)]^{2-}$ the methanol is labile.

The failure to form any of the methylrhodium complex in (iv) might be attributed to the formation of unreactive polymeric species, or to coordination of further cyanides.

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