Catalytic Synthesis of Some Dichlorotetra-ammineiridium(III) Complexes

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A convenient synthesis of *trans*-$[Ir(py)_4Cl_2]Cl.5H_2O$ (py = pyridine) was reported recently.[1] We report the synthesis of *trans*-$[Ir(en)_2Cl_2]ClO_4$.

Preparation of tetra-amine complexes of iridium(III) and rhodium(III) has met with difficulty due to the highly inert character of these systems. Delepine[2] noted that the addition of ethanol to reaction solutions of the less basic of the amine ligands (pyridine, αα′-bipyridyl,[1,3] *o*-phenanthroline[1,3]) and MCl_6^{3-} (where M = Rh^{III} or Ir^{III}), catalyses the formation of *trans*-dichlorotetra-amminemetal(III) complexes. The catalytic effect of many reducing agents has been noted in the synthesis of rhodium(III) complexes, but these preparations have not succeeded for the strongly basic amines such as ethylenediamine due to the formation of unreactive hydrated rhodium(III) oxide.[3]

We have found that hypophosphorous acid catalyses the formation of dichlorotetrapyridineiridium(III) and dichlorobis-(αα′-bipyridyl)iridium(III) ions when $IrCl_6^{3-}$ is refluxed with the appropriate amine. Strongly basic amines cause immediate precipitation of hydrated iridium oxide, unless buffered to a very low concentration of free amine. Heating $IrCl_6^{3-}$ at 80° with excess ethylenediamine dihydrochloride in acid solution with 10 mole per cent hypophosphorous acid causes the immediate precipitation of brown crystals. These crystals, insoluble in pure water, dissolve readily in large excess of aqueous ethylenediamine, without the formation of iridium oxide. Refluxing this solution with 10 mole per cent KH_2PO_2 for 20 min. and acidifying with $HClO_4$ results in a 40—50% yield of *trans*-$[Ir(en)_2Cl_2]ClO_4$,for which the proper elemental analysis was obtained. The *cis*-isomer has not been isolated from this reaction solution. This agrees with the mechanism proposed[4] for the catalysis, here presumably involving an Ir^{I}–Ir^{III} exchange process which can only generate the *trans*-iosmer. However, we have prepared *cis*-$[Ir(en)_2Cl_2]Cl$ by a different method and resolved it into its optical isomers. The *trans*-$[Ir(en)_2Cl_2]^+$ ion may be easily distinguished from the *cis*-isomer by its i.r. spectrum.[5] The intermediate brown crystals have not been completely characterized, but analysis indicates the formula $(enH_2)_2[IrCl_6]Cl$.

This same procedure has also been used to prepare *trans*-[Ir(trien)Cl_2]Cl (trien = triethylenetetramine). The method appears to be effective for strongly basic amine ligands in general.

Although reducing agents appear to have a catalytic effect on the formation of *trans*-tetra-ammine complexes of iridium(III), they do not appear to be effective catalysts in substitution reactions of *trans*-[Ir(en)$_2$$Cl_2$]$^+$. Hydrazine and sodium borohydride were found to increase the rate of removal of chloride from *trans*-[Rh(en)$_2$$Cl_2$]$^+$,[6] but neither hydrazine nor hypophosphorous acid have a catalytic effect on the analogous iridium(III) complex. Polarographic studies indicate that the reduction potential of *trans*-[Ir(en)$_2$$Cl_2$]$^+$ is too high for the complex to be affected by these reducing agents. Several *cis*- and *trans*-diacidobis(ethylenediamine)iridium(III) complexes have been prepared and their rates of substitution are being investigated.

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