A Convenient Synthesis of Iridium(III) Complexes

By R. D. GILLARD* and B. T. HEATON
(*Chemical Laboratory, University of Kent at Canterbury*)

DESPITE the value of comparative work involving cobalt, rhodium, and iridium, there has been little work on iridium complexes with nitrogen-containing ligands. The revival of interest in the chemistry of rhodium(III) complexes is due partly to the discovery of convenient synthetic methods involving catalysis of nucleophilic displacement at rhodium(III) by hydridic compounds, such as ethanol or molecular hydrogen.[1] We now report a striking catalysis of replacement at iridium centres, which provides a useful route for the preparation of highly inert iridium(III) complexes.

Exhaustive reaction (50 hr. at 100° or 4 hr. in a sealed tube at 130°) of aqueous solutions of iridium trichloride, or the hexachloroiridate(III) ion, with pyridine was found to give some dichlorotetrapyridineiridium(III) chloride, (I), but the main product was a mixture of the 1,2,3- and 1,2,6-trichlorotripyridineiridium(III) isomers.[2] We find that addition of ethanol to the above reaction mixture catalyses the formation of (I), which can be obtained in 40% yield after heating under reflux for 2 days.

However, the most striking effect is observed when a solution containing the hexachloroiridate(III) and hexachloroiridate(IV) ions in aqueous ethanol is refluxed with pyridine. The desired product *trans*-$[\mathrm{Ir^{III}py_4Cl_2}]\mathrm{Cl,5H_2O}$, (I), is obtained in good yield in twenty minutes. It has been characterised by analysis and conductivity, and the electronic spectrum was found to be identical to that described by Jørgensen.[3] The *trans*-structure has been established by far infrared spectral measurements and by the synthesis of some derivatives.

These derivatives are the "acid adducts", *trans*-$[\mathrm{Ir\,py_4Cl_2}][\mathrm{H(NO_3)_2}]$ and *trans*-$[\mathrm{Ir\,py_4Cl_2}](\mathrm{H_5O_2})\mathrm{Cl_2}$, which are both isomorphous with the corresponding known complexes of rhodium(III). Both these "adducts" are remarkably stable.

We find that the corresponding complexes of *o*-phenanthroline and αα′-bipyridyl are readily obtained and extensions of the present synthesis to other ligands are being investigated. The use of the complex (I) as an intermediate in the synthesis of other iridium(III) complexes (for example of ethylenediamine) is being studied.

(*Received, December 6th*, 1967; *Com.* 1305.)

---

[1] (a) R. D. Gillard, J. A. Osborn, P. B. Stockwell, and G. Wilkinson, *Proc. Chem. Soc.*, 1964, 284; (b) R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1965, 1951.

[2] M. C. Delepine, *Ann. Chim.* (*France*), 1923, **19**, 174.

[3] C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 151.