Photochemical Aquation of Iridium(III) Phenanthroline and Related Complexes

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RECENT communications have illustrated both the potential utility of photochemical reactions[1] and the need for convenient synthetic pathways[2] in the preparation of Werner complexes of the inert second and third transition series elements. We report here successful photochemical aquations of *cis*-$[IrX_2phen_2]^+$ (phen = 1,10-phenanthroline, X = Cl^- or Br^-) and $[IrX_4phen]^-$.

Although *cis*-$[IrX_2phen_2]^+$ complexes do not hydrolyse in boiling 0·1M-toluene-*p*-sulphonic acid over a period of a week, and reaction takes several days at 95° in a 1000-fold excess of hydroxide ion, hydrolysis is rapid in the presence of strong sunlight or a xenon source. At room temperature the photochemical aquation of *cis*-$[IrX_2phen_2]^+$ to yield $[IrXH_2Ophen_2]^{+2}$ is 95% complete in 360 min.; the reaction products have been characterised by analysis and conductivity measurements. Further, the dark reaction of $[IrCl_4phen]^-$ to produce $[IrCl_3H_2Ophen]$ takes 24 hr. in boiling 0·1M-toluene-*p*-sulphonic acid, but occurs within minutes in the presence of u.v. light. The orange product from the photochemical reaction is less soluble than the yellow product from the dark reaction but has the same analytical composition. The two non-electrolytes are probably *fac–mer*-isomers.

We have also found that $[CoCl_2phen_2]Cl$ and $[RhCl_2phen_2]Cl$ are likewise photochemically aquated, the reaction of the cobalt(III) complex being extremely rapid. In contrast, a solution of the analogous $[CrCl_2phen_2]Cl$ compound does not demonstrate photochemical behaviour.

(*Received, July* 31*st*, 1968; *Com.* 1041.)

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† On sabbatical leave at Department of Chemistry, Stanford University, Stanford, California, from Australian National University.

[1] R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2437.

[2] R. D. Gillard and B. T. Heaton, *Chem. Comm.*, 1968, 75.