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Tetraco-ordinated Complexes of Cobalt(I) and Iridium(I)

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VERV few tetraco-ordinated complexes of cobalt(1) have been described, namely $[Co(dipy)_2] ClO_4^1$ and $K_2[Co(CN)_3(CO)]^{2,3}$ We now report the isolation and the reactions of tetraco-ordinated complexes of cobalt(I) and iridium(I), of formula $[Co(dp)_2] X$ $[dp = C_2H_4(PPh_2)_2, X = ClO_4, BPh_4]$ and $[Ir(dp)_2]$ -X (X = Cl, Br, I, ClO₄, BPh₄). On treating under nitrogen a benzene solution of $[Co(dp)_2]^4$ with a stoicheiometric amount of $CoBr_2(dp)_{2,5}^5$ which is insoluble in benzene, a red-brown solution is obtained. The brown pentaco-ordinated [CoBr-(dp)₂], obtained after removal of the solvent under reduced pressure, readily undergoes solvolysis by polar solvents. It gives in ethanol a green-brown solution, from which the perchlorate and the tetraphenylborate are precipitated as deep purple crystalline solids on addition of excess of NaClO₄ or NaBPh₄. The i.r. spectrum of [Co(dp)₂] ClO₄ in Nujol mull and its electrical conductivity in solution clearly show that the perchlorate ion is not co-ordinated to the metal. The diamagnetism of these compounds suggests a planar configuration of the chelated cation.

By treatment of $[IrCl(CO)_2 \ o$ -toluidine] or $[IrCl(CO)(PPh_3)_2]$ in benzene solution with an excess of the diphosphine, $[Ir(CO)(dp)_2]$ Cl is obtained as a pale yellow crystalline solid. The corresponding bromide, iodide, perchlorate, and tetraphenylborate are readily obtained by exchange in alcoholic solution. These compounds lose carbon monoxide at 150° under vacuum to give red, diamagnetic, tetraco-ordinated complexes of iridium(I), of formula $[Ir(dp)_2] X$.

Both the tetraco-ordinated cobalt(I) and iridium(I) cation readily add hydrogen—and, in the crystalline state at room temperature and sub-atmospheric pressure, hydrogen halides and perchloric acid—to give the already known compounds of formula $[CoH_2(dp)_2] X$,⁶ $[CoHX(dp)_2] Y$,⁷ $[IrH_2(dp)_2] X$,⁸ and $[IrHX(dp)_2] Y$ ^{8,9} (X = Cl, Br, I; Y = Cl, Br, I, ClO₄, BPh₄). They also add carbon monoxide and sulphur monoxide, to give five-co-ordinated

CHEMICAL COMMUNICATIONS

complexes. The $[Co(CO)(dp)_2] X$, which was also obtained by an independent route,¹⁰ does not lose carbon monoxide before complete decomposition, nor does it give $[CoH_2(dp)_2] X$ by treatment with hydrogen, in contrast to the behaviour of the corresponding carbonyl complex of iridium(I). The greater stability of the pentaco-ordinated d^8 complexes of cobalt as compared with that of iridium d^8 -complexes is also shown by the fact that $[Co(dp)_2]^+$, but not $[Ir(dp)_2]^+$, readily abstracts carbon monoxide from benzoyl chloride. It is interesting to note that the corresponding rhodium-(I) derivative, $[Rh(dp)_2] X$,⁶ does not show any evidence of adding carbon monoxide or hydrogen under ambient conditions.

The tetraco-ordinated iridium(I) complex adds, readily and reversibly, molecular oxygen to give a stable pentaco-ordinated complex, whereas the corresponding cobalt(I) compound undergoes very easily complete oxidation to give a paramagnetic derivative of cobalt(II) and diphosphine dioxide.

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