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

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VERY few tetraco-ordinated complexes of cobalt(I) 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, ClO_4, BPh_4). On treating under nitrogen a benzene solution of $[Co(dp)_2]$[4] with a stoicheiometric amount of $CoBr_2(dp)_2$,[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 $NaClO_4$ or $NaBPh_4$. The i.r. spectrum of $[Co(dp)_2]\ ClO_4$ 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] ($X = Cl, Br, I$; $Y = Cl, Br, I, ClO_4, BPh_4$). They also add carbon monoxide and sulphur monoxide, to give five-co-ordinated 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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