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Complexes of Iridium(I) with the Optically Active Bisphosphine DIOP

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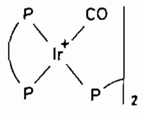
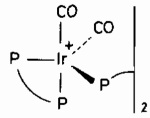
Asymmetric synthesis employing as catalysts complexes of transition metals with optically active ligands is a field of considerable current interest [1]. Explanations of the relative degree of asymmetric induction effected depend to a large extent on the postulated structures of the complex catalysts in question, many of which have not been, or cannot be, isolated [*e.g.* ref. 2]. Complexes of iridium(I) with tertiary phosphines are of importance with regard to hydrogenation of olefins [3] or ketones [4] and related reactions. Herein we report the isolation of a series of complexes of iridium(I) with the optically active bisphosphine, DIOP (DIOP = 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane) [5], which are precursors of catalytically active hydrido-complexes, and related carbonyl complexes.

Reaction in ethanolic solution of equivalent amounts of DIOP and $[Ir_2Cl_2(cod)_2]$ (cod = 1,5-cyclooctadiene) gave [IrCl(cod)DIOP]·EtOH as a well-defined crystalline complex [3]; the structure about iridium in this complex is close to trigonal bipyramidal, with DIOP occupying one axial and one equatorial position. We now report that this structure is retained in solution, as demonstrated by the ^{31}P n.m.r. (−50 °C, CD_2Cl_2) which is AB ($\delta_{P_A} = -8.7$ p.p.m., to high field from 85% H_3PO_4; $\delta_{P_B} = -19.15$ p.p.m.; $J_{AB} = 23.2$ Hz). The complex cation $[Ir(cod)(DIOP)]^+$ showed a single resonance ($\delta_P = +2.2$ p.p.m.). Addition of $[Ir_2Cl_2(cod)_2]$ to a solution containing two or more equivalents of DIOP in acetone, under an inert atmosphere, and subsequent addition of an excess of $NaBPh_4$ gave a red solution. Dilution of the solution with petroleum ether gave, as deep red crystals, the analytically pure 1:1 electrolyte, $[Ir(DIOP)_2]BPh_4$, *I* ($\Lambda = 104$ ohm^{-1} cm^{-1}; 10^{-3} *M* in acetone) [6].

When the latter reaction was performed at room temperature under an atmosphere of CO a very pale solution was formed. This solution was successively reduced in volume and diluted with petroleum ether, and the precipitate was washed with water to give, as a cream powder, $[Ir_2(CO)_2(DIOP)_3](BPh_4)_2$, *II*. A similar material was also prepared by the reaction of a solution of *I* in acetone with CO. The cream powder, *II*, readily dissolved in refluxing ethanol to give a red solution. On cooling the solution under an atmosphere of CO pale yellow crystals of $[Ir_2(CO)_4(DIOP)_3](BPh_4)_2$, *III*, precipitated. The infra-red spectrum of *II* showed ν(CO) at 1953 cm^{-1}, and the spectrum of *III* showed ν(CO) at 2008 (m) and 1937 (s) cm^{-1}. No complex isolated analysed as $[Ir(CO)(DIOP)_2]BPh_4$, and all attempts to date to isolate such a complex gave instead either *II* or *III*. The conductivity of a solution of *II* ($\Lambda = 74$ ohm^{-1} cm^{-1}; 6.0 X 10^{-4} *M* in acetone) is within the range expected for a 2:1 electrolyte.


II


III

(P⌒P = DIOP)

Reaction of $[Ir_2Cl_2(cod)_2]$ with a benzene solution of an equivalent amount of DIOP under an atmosphere of CO gave, as pale yellow crystals, the dinuclear complex $[IrCl(CO)(DIOP)]_2$, *IV* (Found: M, 1655; Calculated: M, 1508). With two or more equivalents of DIOP the product was the covalent yellow complex $[IrCl(CO)(DIOP)_2]$ *V*($\Lambda = 4$ ohm^{-1} cm^{-1}, 10^{-3} *M* in acetone). The infra-red spectrum of *IV* showed ν(CO) at 1960 cm^{-1} and ν(IrCl) at 307 cm^{-1}, and the spectrum of *V* showed ν(CO) at 1914 cm^{-1}. The spectrum of *IV* is consistent with a *trans* square-planar complex containing bridging bisphosphine ligands, analogous to complexes of $Ph_2P(CH_2)_nPPh_2$ (n = 1, 3, 4) [7]. When the latter reaction was performed in dichloromethane instead of benzene the material isolated appeared to be a mixture of *V* and $[Ir_2(CO)_2(DIOP)_3]Cl_2$, and showed i.r. bands at 1912 and 1953 cm^{-1} of variable relative intensities.

The above results illustrate the similarities and differences between the systems containing DIOP and rhodium [1, 8] or iridium. In the absence of CO-$[M_2Cl_2(cod)_2]$ (M = Rh or Ir) reacts with an equivalent amount of DIOP to yield [MCl(DIOP)(cod)]. Replacement of chloride by a non-coordinating ion (X) such as BPh_4^- gives [M(DIOP)(cod)]X. Excess DIOP gives in each case $[M(DIOP)_2]X$. When a similar reaction sequence is undergone in the presence of CO differences are apparent in the natures of the products. Reaction of $[Rh_2Cl_2(cod)_2]$ with excess DIOP and CO gave only $[Rh(CO)_2(\eta^1\text{-}DIOP)]Cl$ [8]. In contrast reaction of excess DIOP and CO with $[Ir_2Cl_2(cod)_2]$ in benzene gave $[Ir(CO)Cl(DIOP)_2]$, and in dichloromethane gave a mixture

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of products. Replacement of chloride by BPh_4^- gave $[Ir_2(CO)_n(DIOP)_3](BPh_4)_2$ (n = 2 in acetone, n = 4 in ethanol).

Each of the complexes described was obtained analytically pure: *I*, Found: C, 68.52; H, 5.89%; Calculated: C, 68.47; H, 5.61%. *II*, Found: C, 67.40; H, 5.74; P, 6.81%; Calculated: C, 66.71; H, 5.32; P, 7.22%. *III*, Found: C, 66.39; H, 5.32; P, 6.64%; Calculated: C, 66.21; H, 5.21; P, 7.06%. *IV*, Found: C, 50.75; H, 4.47%; Calculated: C, 50.96; H, 4.28%. *V*, Found: C, 60.24; H, 5.41; P, 9.38%; Calculated: C, 60.40; H, 5.15; P, 9.89%.

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