Reactions of Dicyanodi-[1,2-bis(diphenylphosphino)ethane]cobalt(II) with Oxygen and Alkyl Halides

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Summary The reactions of $[Co(CN)_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ with EtX and $XCH_2{\cdot}CH_2X$ (X = Cl, Br, I) are reported and compared with those given by the pentacyanocobaltate(II) ion: the reaction with $ClCH_2{\cdot}CH_2Cl$ in the presence of oxygen leads to carbon dioxide.

IN an investigation of the five-co-ordinate complexes of cobalt(II) we have reported the preparation of the low-spin complexes $[Co(P)_3(CN)_2]$ (P = phosphorus atom of a tertiary or ditertiary phosphine).[1] Considerable effort has been devoted to the investigation of the reactions between the pentacyanocobaltate ion, $Co(CN)_5{}^{3-}$, and many organic and inorganic systems. We report some of our results relating to the reactions of the complex $[Co(dpe)_2(CN)_2]$ (I), [(dpe) = $Ph_2P(CH_2)_2PPh_2$] with oxygen, and organic halides and dihalides.

The compound was obtained by treating a CH_2Cl_2 solution of $[Co(dpe)_2Br]Br$ with an anionic resin in CN^- form.[1] The pink–red crystals obtained by evaporating the resulting solution are sparingly soluble in most organic solvents. The compound is non-conducting in freshly prepared CH_2Cl_2 solutions (10^{-3} M). The value of the magnetic moment (2·4 B.M.) and the visible spectra (one typical band at 20,800 cm^{-1} in the solid or in CH_2Cl_2) are closely similar to those of other five-co-ordinate complexes $[Co(P)_3(CN)_2]$.[1] We therefore formulate the compound as a five-co-ordinate complex of cobalt(II) in which one of the two diphosphines acts as a monodentate ligand.

In a standard apparatus a methanol solution of complex (I) was stirred under oxygen and the volume of absorbed gas was measured at the constant pressure of 1 atm. The manometric measurements showed that two moles of the complex absorbed one mole of oxygen. The reaction was complete after 10 min. at 25°. The resulting solution contained formaldehyde which was detected by gas chromatography. Treatment of the solution with $NaClO_4$ gave a yellow crystalline compound. Elemental analysis, conductivity in $PhNO_2$ (Λ_M 25·2 in 10^{-3}M-solution), and diamagnetism, showed that the compound was the perchlorate of the six-co-ordinate cobalt(III) complex $[Co(dpe)_2(CN)_2]^+$. These results strongly suggest that a "peroxide" $(CN)_2(dpe)_2Co{-}O{-}O{-}Co(dpe)_2(CN)_2$ is initially formed by reaction of (I) with oxygen. The peroxide reacts further with methanol yielding CH_2O and the cobalt(III) complex, in which both diphosphines are chelated.

In the absence of oxygen, complex (I) reacts slowly with EtI at 40° producing ethylene and ethane approximately in the ratio 10 : 1. The same hydrocarbons are formed in the reaction of (I) with EtBr at 40°. No reaction was observed when (I) was treated with boiling EtCl for 4 hr. Yellow crystals, which were identified as $[Co(dpe)_2(CN)_2]X$ (II) (X = Br, I), were collected from the solutions.

The dihalides $XCH_2{\cdot}CH_2X$ (X = Cl, Br) react slowly with (I) under exclusion of oxygen giving ethylene. The same reaction is complete in 10 min. for a benzene solution of $ICH_2{\cdot}CH_2I$ at room temperature.

The hydrocarbons formed in all of the above reactions are those already found in the analogous reactions given by $Co(CN)_5{}^{3-}$.[2]

When $ClCH_2{\cdot}CH_2Cl$ was treated with (I) at room temperature under oxygen (1 atm.) a rapid absorption of one mole of oxygen per two moles of complex was observed. This absorption step was followed by a slower absorption of oxygen, and by the simultaneous evolution of carbon dioxide. The latter was detected by gas chromatography and collected in the form of barium carbonate. The total amount of CO_2 produced in the reaction was found to correspond to 1 mole of CO_2 per mole of the cobalt complex.

The oxidation to CO_2 is the result of a series of consecutive steps. The first step seems to involve dehalogenation of the organic dihalide by reaction with the binuclear "peroxide". In fact the visible spectra of the solutions show that the formation of CO_2 is preceeded by the appearance of a broad multicomponent band in the 600—700 nm range, which is very similar to that characteristic of the tetrahedral complex $CoCl_4{}^{2-}$.

We believe that the reaction leading to CO_2 is unique in that it is the first example of complete autoxidation of carbon atoms of organic halides occurring in a single process at room temperature.

(*Received, April 1st*, 1970; *Com.* 455.)

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[2] P. B. Chack and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 582.