The Formation of Transition-metal Hydrides from Water

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WE have recently characterized[1,2] platinum(II) and palladium(II) carbonyl cations which are isoelectronic with the remarkable compound, *trans*-$[IrCl(CO)(Ph_3P)_2]$ of Vaska,[3] and its rhodium(I) analogues.[4] The platinum(II) cations, *trans*-$[PtCl(CO)(R_3P)_2]^+$, are generally less reactive[5] than the corresponding iridium and rhodium complexes: they do not, for example, combine under mild conditions with hydrogen or yield molecular nitrogen complexes on treatment with benzoyl azide (*cf.* refs. 4 and 6). However, we now describe a ready conversion of the platinum(II) carbonyl cations to the corresponding hydrides, the reaction being remarkable in that the hydridic hydrogen apparently originates from water.

Treatment of *trans*-$[PtCl(CO)(Et_3P)_2][BF_4]$ (I) or *trans*-$[PtCl(CO)(Ph_3P)_2][BF_4]$ (II) with water, under reflux, produces *trans*-$[PtHCl(R_3P)_2]$, and carbon dioxide. The reaction of (II) is slow and is accompanied by considerable decomposition but (I) reacts fairly rapidly (~30 min.) and gives good yields. The origin of the hydridic hydrogen is confirmed by reaction of (I) with D_2O when the Pt–D absorptions[7] at 1595 and 580 cm.$^{-1}$ are observed in the i.r. spectrum of the product. When a methanol–water mixture is used the carbonyl (I) is fairly soluble and the yield of hydride is essentially quantitative.

The conversion of (II) to the corresponding hydride can be more easily achieved in a stepwise fashion. Treatment of (II) with methanol or ethanol at 25° yields the white, crystalline compounds (III), $[PtCl(Ph_3P)_2(CO_2R)]$, (R=Me or Et), which are characterized by analytical, i.r., and n.m.r. data including i.r. absorptions due to the $>C=O$ groups at 1630 (R=Et) and 1660 (R=Me) cm.$^{-1}$. The complexes (III) are stable under normal conditions but, with water at 120°, in a sealed tube, in the presence of a salt catalyst such as ammonium or potassium chloride, they are converted into *trans*-$[PtHCl(Ph_3P)_2]$ and carbon dioxide, in good yield. Proton n.m.r. evidence suggests that the other product is ROH but this has not been rigorously established. A similar reaction (R=Me) with D_2O again yields a Pt–D derivative [ν(Pt–D) = 1585 cm.$^{-1}$] and infrared studies show that *trans*-$[PtHCl(Ph_3P)_2]$ does not exchange with D_2O under similar conditions. In contrast, treatment of (III) with a strong aqueous acid, for example, aqueous HBF_4, leads to elimination of ROH and reformation of (II).

Treatment of (I) with reagent grade methanol does not yield a compound of type (III) since the small percentage of water present reacts preferentially to yield hydride as described above. Reaction with anhydrous methanol gives an unstable material which has not yet been characterized.

Metal hydrides may be vital intermediates in several biochemical processes, for example in nitrogen fixation, and the formation of hydrides from biologically available materials is therefore of great importance. In this context the present reactions involving extraction of a hydridic hydrogen from water are of considerable significance as models for this type of process.

(*Received, March 25th,* 1968; *Com.* 368.)

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