Paramagnetic Transition-metal Hydrides

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ALL known transition-metal hydrides are diamagnetic,[1] except perhaps Hein's $Li_3[Cr_2H_3Ph_6]$ and related less well defined species.[2] Recently Brintzinger[3] has suggested that a product of the reduction of dichlorobis(cyclopentadienyl)titanium is a paramagnetic hydride, to which he assigned the formula $[\{(C_5H_5)_2TiH\}_2]$, but no compound was isolated. We now report the first unambiguous isolation of crystalline paramagnetic transition-metal hydrides, which are stable in air. These show strong absorptions in the infrared spectra assignable to the metal–hydrogen stretching vibration within the wide range (2250–1725 cm.$^{-1}$) of those found in the closely similar diamagnetic, hydrido-complexes. As would be expected, the n.m.r. spectra show no signals assignable to the unique proton, up to +80 p.p.m. with respect to tetramethylsilane.

The paramagnetic hydride $[OsHCl_2(PBu^n{}_2Ph)_3]$ (I) was obtained by the reduction of $[OsCl_3(PBu^n{}_2Ph)_3]$ (II) with hydrazine hydrate in boiling ethanol (10 min.) as a red, crystalline solid, m.p. 139—142°, monomeric in benzene and a non-electrolyte in nitrobenzene. It has a magnetic moment of

1·9 B.M. at 20° and in methylcyclohexane solution at $-196°$ gives a broad e.s.r. absorption. The infrared spectrum in Nujol mull shows a strong sharp band at 2064 cm.$^{-1}$ assignable to the Os–H stretching frequency. Preliminary isotope exchange reactions have failed to yield a deuteride.

On boiling the solution of (I) in carbon tetrachloride for 4 hr. in air a solid isomeric hydride (III), m.p. 145—150°, was obtained as a red, monomeric non-electrolyte of magnetic moment 2·2 B.M. (20°). This compound has ν(Os–H) at 1915 cm.$^{-1}$. Both (I) and (III) react with hydrogen chloride in benzene to give hydrogen and the trichloride (II).

There are three possible isomers of $[OsHCl_2(PBu^n_2Ph)_3]$, two with the hydrogen *trans* to phosphorus and one with the hydrogen *trans* to chlorine. It seems likely, in view of its high ν(Os–H) that (I) is the isomer with hydrogen *trans* to chlorine.[4]

The isomerisation of (I) to (III) is not a simple reaction and involves the moisture in the carbon tetrachloride and oxygen in the air. When a solution of (I) in dry outgassed carbon tetrachloride *in vacuo* in a sealed ampoule was heated at 80—90° for 4 hr., it was converted to the original trichloride (II), with the formation of chloroform. In dry carbon tetrachloride under reflux under nitrogen, (I) is again converted to (II) with no intermediate formation of (III).

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[1] A. P. Ginsberg, *Transition Metal Chem.*, 1965, **1**, 115.

[2] F. Hein and R. Weiss, *Naturwiss.*, 1959, **4b**, 321.

[3] H. Brintzinger, *J. Amer. Chem. Soc.*, 1966, **88**, 4305, 4307.

[4] *cf.* Isomers of $[IrHCl_2(PEt_2Ph)_3]$, J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.