Hexahydrido-complexes of Tungsten Containing Dimethylphenylphosphine or Diethylphenylphosphine as Ligands

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Reduction of *trans*-[$WCl_4(PMe_2Ph)_2$], *trans*-[$WBr_4(PMe_2Ph)_2$] or [$WCl_4(PMe_2Ph)_3$] with sodium borohydride gives [$WH_6(PMe_2Ph)_3$], which is fluxional. Impure [$WH_6(PEt_2Ph)_3$] was similarly prepared. I.r. and ^1H n.m.r. data are given and discussed.

RECENTLY it has been shown that tertiary phosphines are useful ligands for stabilizing multihydrido-complexes of several transition metals. Before 1968 rhenium seemed to be unique among transition metals in forming multihydrides, *e.g.* [ReH_8L]$^-$, [ReH_7L_2] and [ReH_5L_3] (L = tertiary phosphine) [1-4] but we then reported the hexahydride of tungsten [$WH_6(PMe_2Ph)_3$] in a preliminary publication.[5] Since then hexa- and tetrahydrides of osmium [OsH_6L_2] and [OsH_4L_3],[6-8] pentahydrides of iridium [IrH_5L_3] [9-11] and tetrahydrides of iron [FeH_4L_3],[12] ruthenium [RuH_4L_3] [13] and molybdenum [MoH_4L_3] [14] have been described. Here we describe more fully the hexahydrides of tungsten [$WH_6(PMe_2Ph)_3$] and [$WH_6(PEt_2Ph)_3$] (obtained only as an oil).

Reduction of *trans*-[$WCl_4(PMe_2Ph)_2$] [15] with sodium borohydride in ethanol gave the hexahydride [$WH_6(PMe_2Ph)_3$] as long white needles. The same complex was prepared by reducing the corresponding tetrabromo-complex but there was no improvement in yield on reducing the seven-co-ordinate complex [$WCl_4(PMe_2Ph)_3$] [15] or *trans*-[$WCl_4(PMe_2Ph)_2$] in the presence of PMe_2Ph [1·5 mol per tungsten atom (all reductions with sodium borohydride)]. The sodium amalgam reduction of a [$WCl_4(PMe_2Ph)_3$]–PMe_2Ph mixture in an atmosphere of dihydrogen has been reported to give [$WH_6(PMe_2Ph)_3$].[16]

The constitution of [$WH_6(PMe_2Ph)_3$] follows from the microanalytical data: from the i.r. absorption spectrum, with values for ν(W–H) of 1834w, 1792w, 1755w and 1731s cm^{-1} (KCl disc): and mainly from the ^1H n.m.r. pattern (in benzene). This shows phenyl resonances, a triplet pattern for the phosphine methyls at τ 8·25 with the outer peaks separated by 7·8 Hz and a broader inner peak, and a 1 : 3 : 3 : 1 quartet hydride pattern with satellites due to splitting by ^{183}W ($I = \frac{1}{2}$, 14% abundance) at τ 11·94, *J*(P–H) 36·9 Hz, *J*(W–H) 27·8 Hz. The integrated relative areas of the methyl and hydride resonances are very close to the expected 3 : 1. Thus in [$WH_6(PMe_2Ph)_3$] the six hydride hydrogens are coupled equally to all three P-nuclei and the molecule is fluxional. Other multihydrides such as [$OsH_4(PMe_2Ph)_3$] and [$ReH_5(PMe_2Ph)_3$] are similarly fluxional.

It is thought that the characteristic high τ-values of transition metal hydrides are due to screening by *d*-electrons and therefore the low value for [$WH_6(PMe_2Ph)_3$] (d^0) is not surprising. The τ-values for the d^0 tantalum(V) hydride [$TaH_3(C_5H_5)_2$] are similarly low (11·63 and 13·20) but for tungsten(IV) hydride (d^2) the τ-value rises to 22·28.[17] τ-Values also rise along the series [$ReH_5(PMe_2Ph)_3$] (τ 16·12), [$OsH_4(PMe_2Ph)_3$ [τ 18·81) and *fac*-[$IrH_3(PMe_2Ph)_3$] (τ 22·7), *i.e.* as the number of *d*-electrons increases.

We have also attempted to prepare the corresponding diethylphenylphosphine complex [$WH_6(PEt_2Ph)_3$] by treating *trans*-[$WCl_4(PEt_2Ph)_2$] with an excess of sodium borohydride in ethanol. This gave a yellow oil which could not be induced to crystallize. The ^1H n.m.r. spectrum showed a 1 : 3 : 3 : 1 quartet at τ 12·75 with satellites indicating that the required hydride was probably present.

A methanolic solution of [$WH_6(PMe_2Ph)_3$] when treated with concentrated hydrochloric acid evolved hydrogen and gave [$WCl_4(PMe_2Ph)_2$], contaminated with what appears to be another hydride since quite strong peaks were present in i.r. spectrum at 1908 and 1800 cm^{-1}. We could not isolate this hydride species. Another hydride species appears to be formed when a benzene–ethanol solution of *trans*-[$WCl_4(PMe_2Ph)_2$] is shaken for several days in an atmosphere of dihydrogen. The resultant purple solid is a mixture and shows weak absorption bands at 2000, 1917, and 1825 cm^{-1} (KCl disc). We could not isolate any pure components of this mixture which is labile.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Preparations involving free tertiary phosphines were carried out in a nitrogen or argon atmosphere. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R10 60 MHz spectrometer at *ca.* 34°.

Hexahydridotris(dimethylphenylphosphine)tungsten(VI).—A suspension of *trans*-tetrachlorobis(dimethylphenylphos-

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phine)tungsten(IV) (0·61 g) in ethanol (30 ml) was treated with sodium borohydride (0·45 g) and the mixture boiled under reflux for 10 min. The orange prisms of the tetrachloro complex dissolved giving a yellow-brown solution. Water (25 ml) was added and the mixture extracted with benzene (3 × 40 ml). The extract was dried ($MgSO_4$) and the required product isolated by evaporation. It formed long white needles (0·149 g) from light petroleum (b.p. 40—60°) (Found: C, 46·65; 48·45; H, 6·15; 6·5. $C_{24}H_{39}P_3W$ requires C, 47·6; H, 6·45%).

Hexahydridotris(diethylphenylphosphine)tungsten.—A suspension of *trans*-tetrachlorobis(diethylphenylphosphine) tungsten(IV) (0·30 g) in ethanol (15 ml) was treated with sodium borohydride (0·30 g) and boiled under reflux for 20 min. The solvent was then removed under reduced pressure and the residue extracted with benzene. Evaporation gave a yellow oil which from its ^1H n.m.r. spectrum contained the required compound (see text).

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