Hexahydridotris(dimethylphenylphosphine)tungsten(VI)

By J. R. MOSS and B. L. SHAW*

(*School of Chemistry, The University, Leeds,* 2)

TERTIARY phosphines are very important ligands in transition-metal chemistry, being particularly good at stabilizing transition-metal hydrides. We have now prepared hexahydridotris(dimethylphenylphosphine)tungsten(VI) as a white air-stable crystalline solid. Previously the only metal atom to which more than three hydrogens have been attached has been rhenium.[1-4] Oxidation of *cis*-$[W(CO)_4(PMe_2Ph)_2]$ with an excess of chlorine gives *trans*-$[WCl_4(PMe_2Ph)_2]$ as orange prisms. This complex is reduced by sodium borohydride in methanol to the hexahydrido-complex $[WH_6(PMe_2Ph)_3]$ as white fibrous needles, m.p. 110—112° (decomp.). The complex is very soluble in organic solvents, the solutions smelling slightly of free dimethylphenylphosphine. In benzene solution the ^{1}H n.m.r. spectrum shows a broad triplet at τ 8·25 due to the methyl protons and a 1 : 3 : 3 : 1 quartet at τ 11·94 (each with satellites due to ^{183}W, spin $\frac{1}{2}$, natural abundance 14·4%) due to the six hydrogens {J(P–H) 36·9 Hz and J(^{183}W–H) 27·8 Hz}. The i.r. spectrum (KCl disc) showed bands at 1834w, 1792s, 1755s, and 1731s cm.$^{-1}$ due to the tungsten–hydrogen stretching modes. With dilute hydrochloric acid [$WH_6(PMe_2Ph)_3$] reacts rapidly to give hydrogen and [$WCl_4(PMe_2Ph)_2$] mixed with a small quantity of another hydrido-species {ν(W–H) 1908s and 1800s cm.$^{-1}$}; this compound is under investigation. [$WH_6(PMe_2Ph)_3$] is clearly analogous to complexes of the type [$ReH_7(PR_3)_2$]. It seems likely that an anion WH_{6+x}^{-x} (x = 1, 2, or 3) will exist like the well established[4] ReH_9^{2-} and possibly similar multi-hydrido-complexes of osmium and tantalum.

We are very grateful to the Climax Molydenum Company for the generous gift of chemicals.

(*Received, April 24th*, 1968; *Com.* 495.)

---

[1] L. Malatesta, M. Freni, and V. Valenti, *Gazzetta*, 1964, **94**, 1278.

[2] J. Chatt and R. S. Coffey, *Chem. Comm.*, 1966, 545.

[3] P. G. Douglas and B. L. Shaw, unpublsihed results.

[4] C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 1964, **4**, 558.