Multihydrido-complexes of Osmium

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Summary Multihydrido-complexes of osmium of the types OsH_4L_3 and OsH_6L_2, L = tertiary phosphine or tertiary arsine, have been synthesised.

TREATMENT of *mer*-$[OsCl_3(PMe_2Ph)_3]$[1] with $NaBH_4$ in ethanol gives $[OsH_4(PMe_2Ph)_3]$ as colourless crystals, m.p. 80—81°. The complex shows a high field 1:3:3:1 quartet in the ^1H n.m.r. spectrum corresponding to a rapid intramolecular inversion process making all the hydrogens equivalent. A similar behaviour is observed with $[WH_6(PMe_2Ph)_3]$[2] and in various multihydrido-rhenium–tertiary phosphine complexes.[3,4] Treatment of *mer*-$[OsCl_3(PMe_2Ph)_3]$ with Cl_2 in visible light gives *trans*-$[OsCl_4(PMe_2Ph)_2]$ and this with $NaBH_4$ in ethanol gives $[OsH_6(PMe_2Ph)_2]$ as an unstable oil. The ^1H n.m.r. spectrum shows a hydride 1:2:1 triplet at τ 18·60, and integration confirms the presence of six hydrogens per osmium. We have similarly made the complexes OsH_4L_3 with L = PEt_2Ph, $AsEt_2Ph$, $AsMe_2Ph$, and PBu^n_3. $[OsCl_4(PMe_2Ph)_2]$ reacts with ligands L to give $[OsCl_3(PMe_2Ph)_2L]$ {L = PEt_2Ph, $AsMe_2Ph$, PPh_3, $P(OMe)_2Ph$, and $P(OEt)_3$} and these with $NaBH_4$–EtOH give the tetrahydrido-complexes $[OsH_4(PMe_2Ph)_2L]$.

These tetrahydrido-osmium complexes can be considered as part of a series; *i.e.* $[WH_6(PR_3)_3]$, $[ReH_5(PR_3)_3]$, $[OsH_4(PR_3)_3]$, and $[IrH_3(PR_3)_3]$ although the iridium complexes exist as *fac*- and *mer*-isomers with complex n.m.r. spectra which have so far not been interpreted. N.m.r. data for the PMe_2Ph complexes of W, Re, and Os are given in the Table and show regular changes.

N.m.r. data for $[WH_6(PMe_2Ph)_3]$, $[ReH_5(PMe_2Ph)_3]$, *and* $[OsH_4(PMe_2Ph)_3]$, *in benzene*

	Hydride resonance		Methyl resonance	
	τ	J(PH) Hz.	τ	^2J(PH) + ^4J(PH) Hz.
$[WH_6(PMe_2Ph)_3]$	11·94	36·9	8·25	7·8
$[ReH_5(PMe_2Ph)_3]$	16·12	14·2	8·33	7·2
$[OsH_4(PMe_2Ph)_3]$	18·81	9·8	8·37	6·5

The quartet hydride resonance of $[OsH_4(PMe_2Ph)_3]$ in benzene collapses to a singlet in the presence of a few mol. per cent of CF_3CO_2H and then gradually reappears. We attribute this to the formation of $[OsH_5(PMe_2Ph)_3]^+$ with very rapid intermolecular hydrogen exchange and then the gradual elimination of the acid as H_2. Conductimetric titration of $[OsH_4(PMe_2Ph)_3]$ by HCl in methanol at 0° shows a sharp break in the curve after the addition of 1 mol. of acid. In EtOD the hydridic hydrogens of $[OsH_4(PMe_2Ph)_3]$ exchange for deuterium, the exchange is catalysed by acid and completely inhibited by a base such as $NBu^n_4{}^+$ OH^-; *i.e.*, the exchange goes *via* protonation (deuteriation) of the filled non-bonding *d*-orbital on the osmium. Other transition metal hydrides containing tertiary phosphines, *e.g.*, of Ru^{II}, Ir^{III} and Re^{V}, show similar acid catalysed hydrogen-deuterium exchange.[5]

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