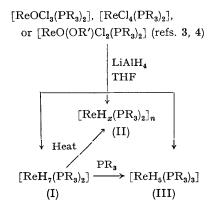
Rhenium Hydrides Stabilised by Tertiary Phosphines

By J. CHATT and R. S. COFFEY

(Imperial Chemical Industries Limited, Heavy Organic Chemicals Division, Billingham, Co. Durham)

SINCE the first observation that transition-metal hydrido-complexes can be stabilised by tertiary phosphines¹ a great number of such complexes have been characterised² but those of rhenium have proved particularly intractable because of their apparent variety. Only triphenylphosphine derivatives have hitherto been described (by Malatesta and co-workers), and there is some doubt about their formulation. The present position is summarised in ref. 2 (p. 139).

Using various tertiary phosphines we have now prepared and characterised beyond doubt three types of hydrido-derivative (I), (II), and (III); they are obtained mixed together where all three from any particular phosphine are known and their relative proportions depend on the experimental



R = alkyl or aryl, R' = alkyl; x = ca. 4, n=2when PR₃ = PEt₂Ph

conditions of preparation. The conversion of (I) into (II) occurs on heating a solution of (I). The compounds isolated were as follows: (I; $PR_3 =$ PEt_2Ph , $PEtPh_2$, or PPh_3), [I; $(PR_3)_2 = Ph_2PCH_2$ - CH_2PPh_2], [II; $PR_3 = PEt_2Ph$ (n = 2) or PPh_3 (n unknown because of insolubility)] and (III; $PR_3 = PEtPh_2$ or PPh_3). Malatesta *et al.*⁵ have described compounds $[ReH_5(PPh_3)_3]$ and $[ReH_5-(PPh_3)_2]$. We agree with their first formulation, but their second compound appears to be our compound (I; R = Ph).

The compounds (I) may be regarded as derivatives of $[\operatorname{ReH}_9]^{2-}$ where 2 H- have been replaced by 2 PR₃. Like K₂ReH₉⁶ they are colourless with no bands in the electronic spectrum assignable to *d*electron transitions. On the other hand compounds (III) have bands at 300-400 m μ .

The compounds were characterised by analysis, molecular-weight determination, [except (II; R = Ph)], and i.r. and n.m.r. spectra. The number of hydridic protons was further characterised by quantitative reaction with HCl. The measured quantities are given in parentheses.

$$\begin{split} [\operatorname{ReH}_5(\operatorname{PEt}_2\operatorname{Ph})_3] &+ 3\operatorname{HCl} \rightarrow \\ & (1 \text{ mol.}) & (3\cdot 2 \text{ mol.}) \\ & [\operatorname{ReCl}_3(\operatorname{PEt}_2\operatorname{Ph})_3] &+ 4\operatorname{H}_2 \\ & (3\cdot 92 \text{ mol.}) \\ [\operatorname{ReH}_7(\operatorname{PEt}_2\operatorname{Ph})_2] &+ 4\operatorname{HCl} \rightarrow \\ & (1 \text{ mole.}) & (\operatorname{excess}) \\ & [\operatorname{ReCl}_4(\operatorname{PEt}_2\operatorname{Ph})_2] &+ 5\cdot 5\operatorname{H}_2 \\ & (5\cdot 58 \text{ mol.}) \end{split}$$

The i.r. spectra indicate there are no Re=O or Re-OR' groups³ in any of the compounds but there

are Re-H groups (v_{Re-H} in the region 1800-2000 cm.⁻¹ and $\delta_{\text{Re-H}}$ 780—850 cm.⁻¹, both shifted by a factor of ca. $2^{-\frac{1}{2}}$ in the corresponding deuterides).

The n.m.r. spectra of compounds (I) contain a triplet on the high-field side of Me₄Si due to the hydridic protons coupled with two equivalent phosphorus nuclei, e.g., $[\text{ReH}_7(\text{PEt}_2\text{Ph})_2]$ in C_6D_6 has $\tau = 15.8$ and $J_{P-H} = 19.6$ c./sec. The intensity of the signal indicates that there are 6.6-7 hydridic protons in compounds (I), but $[\text{ReH}_{7}(\text{PPh}_{3})_{2}]$ is insufficiently soluble for accurate measurement. Complexes of type (III) give quartets due to coupling of the hydridic protons with three equivalent phosphorus nuclei and here intensity measurements indicate that there are 5 hydridic protons per rhenium, e.g., [ReH₅(PEt₂-Ph)₃] in C₆H₆ has $\tau = 16.8$, $J_{P-H} = 18.1$ c./sec.

The n.m.r. spectrum of the red dimeric complex $[\operatorname{ReH}_{x}(\operatorname{PEt}_{2}\operatorname{Ph})_{2}]_{2}$ [type (II)] in C₆D₆ has a quintet, au = 16.6, $J_{P-H} = 9$ c./sec. This indicates a coupling of the hydridic protons with four equivalent phosphorus nuclei, so providing strong evidence for a Re-Re bond in the molecule. We are still uncertain about the value of x but it appears to be about 4. The analogous red complex (II; $PR_3 = PPh_3$) which was first described by Freni and Valenti⁷ who suggested the formula $[\text{ReH}_{3}(\text{PPh}_{3})_{2}]$, is probably also a dimer containing a Re–Re bond.

The cause of the large τ -values of hydridic protons attached to a transition metal has been the subject of much speculation. The large τ -values observed for compounds of type (I), in which all 5d-, 6s-, and 6p-orbitals are bonding indicates that screening or other effects of electrons in nonbonding d-orbitals is not the determining factor. Instead it may be a factor of very little consequence because compounds of type (II) with an electron pair in a non-bonding orbital have only slightly greater τ -values.

The hydridic hydrogen atoms in all of the above compounds give only one n.m.r. signal which is split by the phosphorus nuclei. This is also true of a series of compounds $[\text{ReH}_5(\text{PPh}_3)_2L]$ (L = AsPh₃ and various amines), obtained by reaction of L with $[\operatorname{ReH}_7(\operatorname{PPh}_3)_2]$, which show only a triplet signal from the five hydrogen atoms. Since geometry precludes the hydrogen atoms occupying equivalent positions in all of these compounds, the single signal must be caused by their rapid intraor inter-molecular exhange. This behaviour is in marked contrast to that of the similar iridium hydrido-complexes where the n.m.r. absorption by individual Ir-hydrogen atoms could be used to determine the stereochemistry.8

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- ¹ J. Chatt, L. A. Duncanson, and B. L. Shaw, Proc. Chem. Soc., 1957, 343.
- ² See: A. P. Ginsberg, Transition Metal Chem., 1965, 1, 111.

- ⁸ J. Chatt, R. S. Coffey, and B. L. Shaw, J. Chem. Soc., 1965, 7391.