

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

The n.m.r. spectra of compounds (I) contain a triplet on the high-field side of Me_4Si 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 $J_{\text{P-H}} = 19.6$ 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.*, $[\text{ReH}_5(\text{PEt}_2\text{Ph})_3]$ in C_6H_6 has $\tau = 16.8$, $J_{\text{P-H}} = 18.1$ c./sec.

The n.m.r. spectrum of the red dimeric complex $[\text{ReH}_x(\text{PEt}_2\text{Ph})_2]_2$ [type (II)] in C_6D_6 has a quintet, $\tau = 16.6$, $J_{\text{P-H}} = 9$ 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; $\text{PR}_3 = \text{PPh}_3$) 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 5*d*-, 6*s*-, and 6*p*-orbitals are bonding indicates that screening or other effects of electrons in non-bonding *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 $[\text{ReH}_5(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{AsPh}_3$ and various amines), obtained by reaction of L with $[\text{ReH}_7(\text{PPh}_3)_2]$, 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 intra- or inter-molecular exchange. 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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² See: A. P. Ginsberg, *Transition Metal Chem.*, 1965, 1, 111.

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⁴ J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 601.

⁵ L. Malatesta, M. Freni, and V. Valenti, *Gazzetta*, 1964, 94, 1278.

⁶ S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 1964, 3, 558.

⁷ M. Freni and V. Valenti, *Gazzetta*, 1961, 91, 1357.

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