Osmium Tetrahydrides and their High-field ^1H Nuclear Magnetic Resonance Spectra

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Summary The complexes $[OsH_4L_3]$ ($L = PMe_2Ph$, PEt_2Ph, PPh_3, and $AsPh_3$) are described, and the high-field n.m.r. spectra of these and some related complexes are discussed.

TRANSITION-METAL phosphine hydride complexes may be divided into two classes on the basis of their high-field ^1H n.m.r. spectra. In one class these spectra show a variety of chemical shifts and coupling constants J_{PH} dependent upon the stereochemistry of the complex. In the other, the hydride ligands apparently possess identical chemical shifts and couple equally with all phosphorus atoms in the molecule. Evidence presented below indicates that this latter phenomenon, previously observed in rhenium polyhydride complexes and attributed to rapid inter- or intramolecular rearrangement,[1] is more extensive than has hitherto been recognised.

We have synthesised the complexes $[OsH_4L_3]$ $\{L = PMe_2Ph$ (I), PEt_2Ph (II), PPh_3 (III), or $AsPh_3$ (IV)$\}$ by reduction of either $[OsCl_3L_3]$[2] (I and II) or ammonium bromo-osmate and an excess of ligand with sodium borohydride. The compounds have been characterised by analysis, molecular-weight determination (I and II), magnetic measurements, and spectroscopic data. Thus (II) is diamagnetic and shows ν(Os–H) at 1760vs, 1982s, 2030m, and 2050w cm.$^{-1}$ (Nujol mull). Its ^1H n.m.r. spectrum exhibits an apparent quartet pattern (intensity ratios approximately 1:3:3:1) centred at *ca.* τ 18·9, J 9 Hz (deuteriobenzene).

The osmium tetrahydrides complete the sequence $[WH_6(PR_3)_3]$,[3] $[ReH_5(PR_3)_3]$,[1] and *mer*-$[IrH_3(PR_3)_3]$,[4] all members of which show a similar apparent quartet pattern in their high-field ^1H n.m.r. spectra, suggesting coupling of the hydride ligands with three equivalent phosphorus nuclei. Our observation of a high-field singlet in the ^1H n.m.r. spectrum of $[OsH_4(AsPh_3)_3]$ confirms the assignment of this coupling. For iridium(III) hydrides this behaviour is apparently confined to the *mer*-trihydride isomer; thus *fac*-$[IrH_3(PEt_2Ph)_3]$ and *mer*-$[IrH_2Cl(PEt_2Ph)_3]$ (hydrides *cis*) show complex high-field n.m.r. spectra typical of "rigid" hydride complexes.

The high-field ^1H n.m.r. spectra of the hydride complexes $[MH(PR_3)_4]$ $\{M = Co, Rh, or Ir; PR_3 = PF_3$[5] or P(O aryl)$_3$[6]$\}$ show a 1:4:6:4:1 quintet pattern which suggests that all four ^{31}P nuclei couple equally with the hydride ligand. *X*-Ray powder photographs and i.r. data indicate that these complexes possess tetrahedral metal–phosphorus skeletons similar to those in their nickel(0), palladium(0), and platinum(0) analogues. A geometry of this type would be expected on steric grounds, and easily arises by distortion of a trigonal bipyramidal (axial hydride) structure $\{cf.$ $[RhH(CO)(PPh_3)_3]\}$. However, the high-field ^1H n.m.r. spectra are not readily interpreted in terms of this rigid structure.

We consider that the apparent magnetic equivalence of the phosphorus and hydride nuclei in the complexes discussed above either may arise from a rapid intramolecular rearrangement or may be an n.m.r. artefact[7] (*cf.* virtual coupling). Further studies including ^{31}P and variable-temperature n.m.r. experiments on these and related compounds are in progress.

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