Group VI Tetrahydrides and Stereochemical Non-rigidity

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Summary A series of tungsten tetrahydrides $[WH_4(PR_3)_4]$ (PR_3 = tertiary phosphine) has been prepared; the ^1H n.m.r. spectra in deuteriobenzene at room temperature show metal hydride spectra consistent with a rigid structure.

Some molybdenum tetrahydrides have recently been described by Penella.[1] The ^1H n.m.r. spectrum of the hydride protons in $[MoH_4(PEtPh_2)_4]$ is a quintet centred at τ 12·20, $|^2J_{P-H}| = 34$ Hz. This apparent equivalence of all hydride ligands (and of the phosphines) was stated to be characteristic of polyhydrido-complexes which are other than tetra- or hexa-co-ordinate.[1] Here are described two rigid eight-co-ordinate hydrido-complexes.

We have prepared the first tungsten tetrahydrido-complexes, $[WH_4(PMe_2Ph)_4]$, $[WH_4(PMePh_2)_4]$, and $[WH_4(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ by the reduction of the corresponding $[WCl_4(PR_3)_2]$[2] in alcoholic solution with sodium borohydride in the presence of an excess of the phosphine. They are yellow, air-stable compounds, and ν(WH) is found as a complex pattern in the region 1850—1700 cm^{-1} of the i.r. spectrum.

The ^1H n.m.r. spectrum of $[MoH_4(PMePh_2)_4]$ in the hydride region is shown in the Figure. At 27°, the spectrum is characteristic of a non-rigid structure but, on cooling, a spectrum characteristic of a rigid structure is observed. In contrast, the ^1H n.m.r. spectrum of $[WH_4(PMePh_2)_4]$ in deuteriobenzene or toluene at 27° shows metal hydride signals in the range τ 10—13 characteristic of a rigid structure. On raising the temperature to above 50° the 'non-rigid' spectrum develops. At 70° the quintet is centred at τ 11·66, $|^2J_{P-H}| = 32$ Hz. The complex

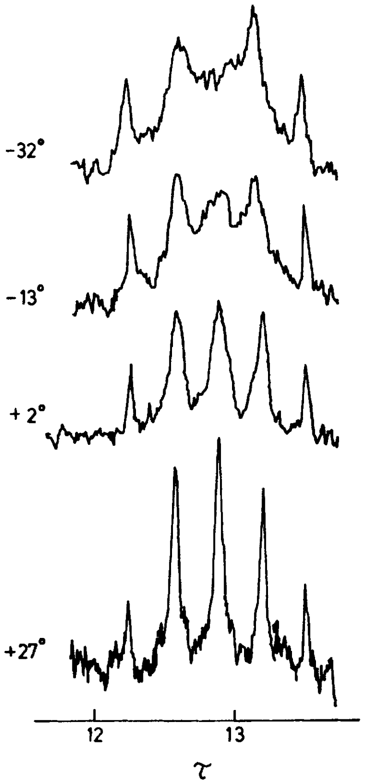

Figure. ^1H *N.m.r. spectrum of* $[MoH_4(PMePh_2)_4]$ *in dichloromethane solution as a function of temperature.*

$[WH_4(PMe_2Ph)_4]$ behaves similarly. These are the first polyhydridic complexes of type $[MH_x(PR_3)_y]$ $(x + y \neq 6)$ which are rigid at room temperature.

The form of the spectra of $[WH_4(PMePh_2)_4]$, $[WH_4(PMe_2Ph)_4]$, and $[MoH_4(PMePh_2)_4]$ change in the same way with temperature, but the transition from a rigid to a non-rigid structure occurs *ca.* 50° higher in the tungsten complexes.

These results emphasise the general observation that complexes of the third transition series are more rigid than their analogues of the second and first. Clearly considerably more information is required before the dependence of non-rigidity upon co-ordination number can be assessed.

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[1] F. Penella, *Chem. Comm.*, 1971, 158.

[2] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J. Chem. Soc.* (*A*), submitted for publication.