Intramolecular Rearrangement in $Cr[P(OMe)_3]_5H_2$

By FREDERIC A VAN-CATLEDGE, STEVEN D ITTEL, CHADWICK A TOLMAN, and J PETER JESSON

(*Central Research and Development Department, E I du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware* 19898)

Summary $Cr[P(OMe)_3]_5H_2$ is fluxional on the n m r time scale allowing the first detailed mechanistic analysis of intramolecular exchange in a seven co-ordinate complex having all monodentate ligands

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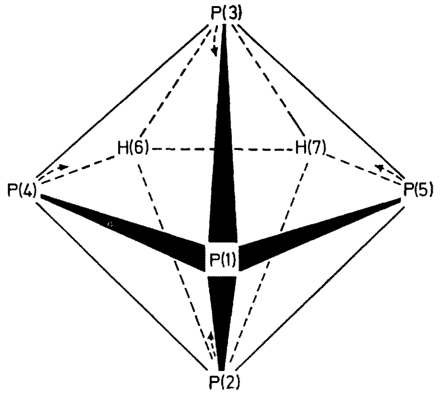
THERE have been many studies of fluxional behaviour in seven co-ordination,[1] but, in general, the mechanisms of ligand exchange are poorly understood The cases for which mechanistic information has been extracted are confined to complexes containing chelating ligands[1,2] and are usually complicated by the presence of more than one isomer or the possibility of 'arm-off' mechanisms More importantly, the mechanistic possibilities are restricted by the multidentate character of ligands and do not relate as clearly to the fundamental questions of seven co-ordinate stereochemistry

$Cr[P(OMe)_3]_6$ **(1)**

$Cr[P(OMe)_3]_5H_2$ **(2)**

The co-condensation of chromium atoms with $P(OMe)_3$ onto a liquid nitrogen cooled surface in an apparatus described previously[3] or a Planer VSP-302 vapour synthesis plant gives (**1**)[4] in good yield. Reaction of (**1**) in pentane solution with one atmosphere of hydrogen gives (**2**),[4] almost quantitatively.

All nucleii co-ordinated to the chromium centre in (**2**) are magnetically active, giving rise, in the slow exchange limit, to an $AB_2CC'XX'$ spin system. The spin system is established by analysis of the 90 MHz ^1H and 36·43 MHz $^{31}P\{^1H\}$ n.m.r. spectra. The −130 °C $^{31}P\{^1H\}$ n.m.r. spectrum is shown in the Figure together with a simulation based on an AB_2C_2 spin system and the n.m.r. parameters listed in the Figure. The temperature-dependent behaviour of the n.m.r. spectra of (**2**) is independent of concentration and added phosphite. The high temperature limit ^{31}P and ^1H spectra give rise to a triplet and sextet, respectively. The effective unimolecular character and the preservation of spin correlation[5] define an intramolecular process.



(3)

A review of the commonly found geometries in seven co-ordination,[6] an extension of a recent analysis of diatomic ligand co-ordination modes,[7] and n.m.r. coupling arguments suggest that configuration (**3**) is the most reasonable formulation for (**2**). The complex will certainly be distorted from idealized pentagonal bipyramidal geometry in a manner which moves the phosphorus ligands 2, 3, 4, and 5 toward the hydride ligands [see arrows in configuration (**3**)]

For a 'labelled' CrP_5H_2 framework, permutations which generate all other possible labelled P_5H_2 arrangements comprise a group order of 5! × 2! = 240, *i.e.*, the product of all permutations of the phosphorus nuclei among themselves and all permutations of the hydrogens among themselves. These 240 configurations include many arrangements related by the symmetry operations of the point group of the molecules (C_{2v}). For this case, there are 240/4 = 60 unique Hamiltonians for the spin system.

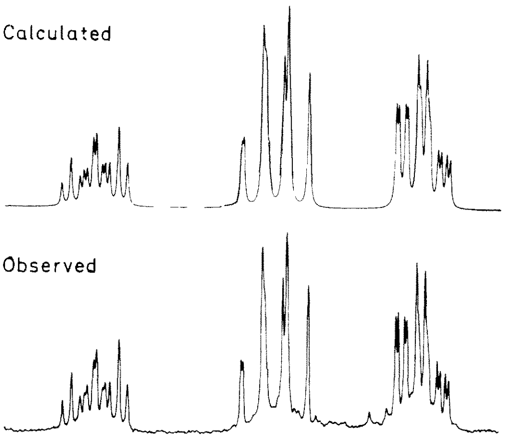


FIGURE. 36·4 MHz $^{31}P\{^1H\}$ n.m.r. spectrum for $Cr[P(OMe)_3]_5H_2$ at −130 °C in $CHClF_2$ solution together with a simulation obtained assuming an AB_2C_2 spin system and the n.m.r. parameters: $J_{AB}(J_{12},J_{13}) = \pm 86$ Hz, $J_{AC}(J_{14},J_{15}) = \pm 32$ Hz, $J_{BC}(J_{24},J_{25},J_{34},J_{35}) = \pm 78$ Hz; $\delta_A(\delta_1) = 222{\cdot}5$ p.p.m., $\delta_B(\delta_2,\delta_3) = 204{\cdot}6$ p.p.m., and $\delta_C(\delta_4,\delta_5) = 190{\cdot}1$ p.p.m.

In the case of this AB_2C_2 spin system, the permutational subgroup is of order 5! = 120. There are 30 unique Hamiltonians and eight basic permutational sets which affect Hamiltonian exchange. The methods employed for generation of the basic permutational sets and lineshape calculations have been described elsewhere.[8]

Comparison of the observed $^{31}P\{^1H\}$ spectra (as a function of temperature) with those simulated for the eight possible basic permutational sets show that only one of the sets agrees with experiment. The equivalent sets for this particular set of permutations are given in the Table.

TABLE

E	C_2	σ_v	σ_v'
(12) (345)	(1243)	(12) (34)	(12453)
(12) (354)	(1253)	(12) (35)	(12543)
(13) (245)	(1342)	(13) (24)	(13452)
(13) (254)	(1352)	(13) (25)	(13542)

Symmetry operations: C_2 = (23) (45), σ_v = (45), σ_v' = (23).

It is beyond the scope of this communication to discuss the various physical processes which correspond to the observed permutational behaviour. Analysis of the ^1H data coupled with high field ^{31}P data may further limit the mechanistic possibilities. It should be noted, however, that the C_2 representation of the basic set corresponds closely to the Berry pseudorotation mechanism associated with pentaco-ordinate species, and involves the simultaneous exchange of the two 'axial' phosphorus ligands with two of the 'equatorial' phosphorus ligands.

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