Pseudo-rotation in Seven-co-ordination: Implications in Catalysis. *X*-Ray Crystal Structure of $[HMo(C_2H_4)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$

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Summary The seven-co-ordinate complex, $[HMo(C_2H_4)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)]^+$, is pentagonal bipyramidal both in solution and in the solid state, and undergoes internal rearrangement by a pseudo-rotation process.

WE have suggested that intramolecular rearrangement in pentaco-ordinate transition metal intermediates may play an important role in certain catalytic processes.[1] We now report the observation of pseudo-rotation in seven-co-ordination {*e.g.*, in $[HMo(C_2H_4)_2(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$ (**1**)} and its significance to the hydride exchange previously described.[2] Compound (**1**) was prepared by known procedures[3] and crystals, although of poor quality, could be obtained from CH_2Cl_2 as the highly solvated $CF_3CO_2^-$ salt.

Crystal data: monoclinic, space group $P2_{1/n}$; $a = 20{\cdot}95(1)$, $b = 18{\cdot}42(1)$, $c = 17{\cdot}22(1)$ Å, $\beta = 97{\cdot}8(1)°$. One molecule of (**1**) and three CH_2Cl_2 molecules were located in the asymmetric unit. 5900 reflections were collected on a Phillips PW 1100 diffractometer (Mo-K_α radiation) of which 1528 with $I > 0{\cdot}33\sigma(I)$ were used in structure refinement and resolution. Anisotropic thermal parameters were assigned to the heavy atoms ($R = 0{\cdot}120$). The ORTEP perspective (Figure 1) shows that (i) the four P atoms and the Mo atom are nearly coplanar, (ii) the ethylene ligands eclipse the P–Mo–P vectors and are mutually orthogonal, and (iii) the C(1)–C(2) ethylene is unsymmetrically bound to the Mo atom indicating that the hydride ligand is placed on the C(1) $\cdots$ P(1) edge.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

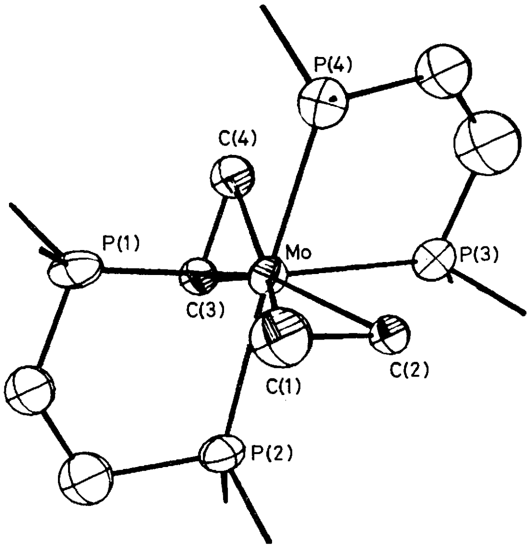

FIGURE 1

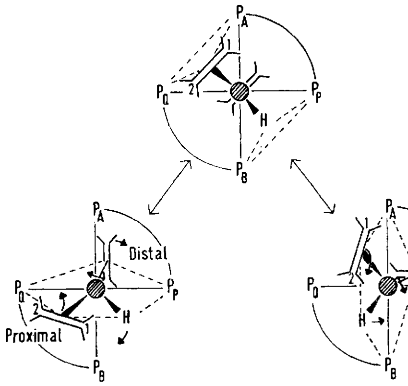

FIGURE 2

This pentagonal bipyramid structure is also preserved in solution. The ^{31}P{^{1}H} n.m.r. spectrum at −88 °C (CH_2Cl_2) shows an ABPQ pattern which yields a deceptively simple spectrum at −1 °C which results from simultaneous pairwise exchange of P nuclei (A ←→ Q, B ←→ P) ($\Delta G^{\ddagger}$ *ca.* 9·4 kcal mol^{-1}). The ^{1}H n.m.r. spectrum at −90 °C (CD_2Cl_2) shows resonances for the proximal olefin at τ 10·0 (2H) and 11·1 (2H), the distal olefin at τ 9·7 (4H), and the hydride at τ 19·5 (1H). At −75 °C, the signals at τ 10·0 and 11·1 coalesce into a single averaged peak ($\Delta G^{\ddagger}$ *ca.* 9·3 kcal mol^{-1}). This peak further coalesces with the hydride resonance at *ca.* −14 °C ($\Delta G^{\ddagger}$ *ca.* 11·2 kcal mol^{-1}). The ^{13}C{^{1}H} n.m.r. spectrum at −95 °C (CD_2Cl_2) shows olefin resonances at τ 41·2, 36·6, and 22·9 p.p.m. (*ca.* 1 : 1 : 2), the first two peaks coalescing into a singlet at −75 °C (again $\Delta G^{\ddagger}$ *ca.* 9·3 kcal mol^{-1}).

A single process with an activation barrier of *ca.* 9·3 kcal mol^{-1} which is consistent with the n.m.r. changes observed (before hydride–olefin proton exchange) is shown in Figure 2. We note that (a) the process pentagonal bipyramid ⇌ capped trigonal prism (or capped octahedron) ⇌ pentagonal bipyramid is analogous to the process trigonal bipyramid ⇌ square pyramid ⇌ trigonal bipyramid invoked in pentaco-ordination,[2,4] (b) the simultaneous pairwise exchange of P nuclei occurs with little motion of the P_4 framework, (c) the distal olefin serves as the pivot, but must also rotate through 90° during pseudo-rotation [*cf.* $PF_4(NR_2)$[5] and $Fe(CO)_4$(olefin)[6]], and (d) the remaining two ligands (proximal olefin and hydride) rotate as a pair, but in this case the rotation must occur in only one sense. This coupled rotation is conrotatory to the motion of the distal olefin. Overall, this seven-co-ordinate rearrangement can be formally regarded as equivalent to the addition of a rotating pair to a pentaco-ordinate process.

Further, the non-permutation of all four ^{31}P nucleii even after hydride–olefin exchange shows that (a) the insertion–deinsertion process involving hydride and proximal ethylene[3] occurs by addition of hydride specifically to one end of the ethylene molecule and (b) there is restricted rotation in the intermediate alkyl species.‡ Nevertheless, hydride exchange can occur at an equal rate with all protons of the proximal olefin because pseudo-rotation causes rapid equilibration of both ends of the ethylene molecule.

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‡ The possibility that such a species is a transition state and not an intermediate will be discussed in a full paper.

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