

## Is a 16-Electron, $\sigma$ -Ethyl Intermediate Necessary for Hydrogen Scrambling in Ethylene-hydride Complexes?

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Evidence is presented for 'in-place' rotation of the methyl groups of agostic  $\eta^2$ -ethyl systems leading to hydrogen scrambling in ethylene-hydride complexes.

It has been shown that many complexes which were previously assigned ethylene-hydride structures in fact contain agostic  $M-H-C$  bonds in the ground state structure.<sup>1,2</sup> In 1977, Osborn and co-workers reported the crystal structure determination and dynamic n.m.r. studies of the molybdenum bis(ethylene)-hydride complex  $[Mo(dppen)_2(\eta^2-C_2H_4)_2H]-CF_3CO_2$  (**1**) (dppen = *cis*-Ph<sub>2</sub>PCH=CHPh<sub>2</sub>).<sup>3</sup>

The two ethylene ligands were observed to be mutually orthogonal and they each eclipse the P-Mo-P vectors in a pentagonal bipyramidal structure in the solid state. The mechanism shown in Figure 1 was proposed to account for the dynamic n.m.r. data.<sup>3</sup> These studies showed that the hydride ligand exchanged exclusively with the proximal ethylene, which underwent a further fluxional process which exchanged the ethylene carbons and the *trans* hydrogens, *i.e.* end-to-end exchange. The distal ethylene hydrogens were reported to show a single 4H resonance at 100 MHz and 183 K, which did not support or rule out an end-to-end exchange process.<sup>3</sup> In the proposed mechanism (Figure 1c), the distal ethylene does not undergo such exchange. Further, there is pairwise non-permutative exchange of the phosphorus nuclei even at 298 K where the ethylene-hydride exchange is fast on the <sup>31</sup>P n.m.r. timescale. This was proposed to arise from restricted rotation about the Mo-C<sub>α</sub> bond of an unobserved 16e  $\sigma$ -ethyl intermediate. We have reinvestigated the dynamic behaviour of (**1**) at higher magnetic fields, as described below.

Compound (**1**) was prepared by treatment of the neutral bis(ethylene) complex<sup>4</sup> with excess CF<sub>3</sub>CO<sub>2</sub>H at -20°C in toluene, and was isolated as an orange crystalline solid.† The 62.89 MHz gated-decoupled <sup>13</sup>C n.m.r. spectrum of (**1**) at 178 K showed four triplets for the ethylene carbons, thus conclusively establishing the compound as an ethylene-hydride.

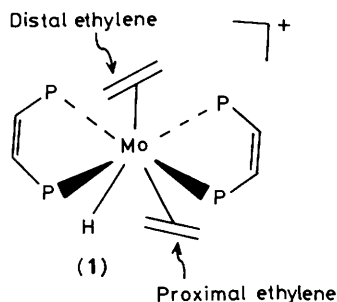
In the variable temperature 500 MHz <sup>1</sup>H n.m.r. spectra of (**1**) the ethylene-hydride exchange process is the first to be frozen-out on the n.m.r. timescale (slow exchange at  $T < ca.$  233 K,  $\Delta G^\ddagger 44 \pm 1$  kJ mol<sup>-1</sup>), and the hydride exchanges exclusively with one ethylene ligand, *i.e.* the proximal

ethylene. The spectra at  $T < 233$  K show that the proximal ethylene undergoes end-to-end exchange ( $\Delta G^\ddagger 38 \pm 1$  kJ mol<sup>-1</sup>). In addition, these spectra obtained at higher magnetic field clearly show that the distal ethylene is also undergoing such exchange ( $\Delta G^\ddagger 36 \pm 1$  kJ mol<sup>-1</sup>). The coupled, pseudorotation mechanism proposed by Osborn can be modified to include *net* end-to-end exchange of the distal ethylene by changing its sense of rotation with respect to the coupled rotation of the proximal ethylene and hydride ligands from *conrotatory* (as in Figure 1c) to *disrotatory* (as in Figure 1d). However, we propose that the stringent requirement of simultaneous and *coupled* rotation of the ethylene ligands by 90° is unnecessary. Their dynamic behaviour after proximal ethylene-hydride exchange has been frozen-out can be rationalised more simply by rapid rotation of the ethylene ligands about the metal-ethylene-centroid axes.

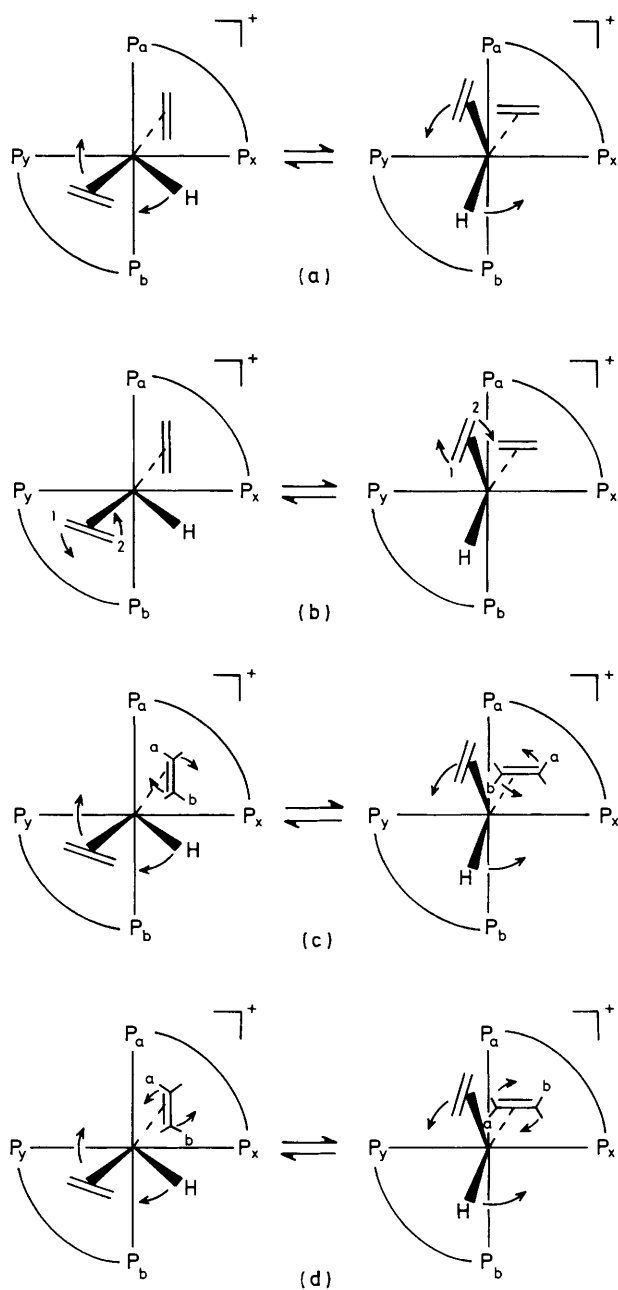
The <sup>31</sup>P-<sup>1</sup>H n.m.r. spectra of (**1**) at 183 and 298 K can be interpreted on the basis of the equilibrium shown in Figure 1a. Thus an AMXY spectrum with both  $J(P-P)_{trans} = 104$  Hz observed at 183 K is consistent with the static structures. As the temperature is increased there is pairwise coalescence of resonances ( $\Delta G^\ddagger 40.5 \pm 1$  kJ mol<sup>-1</sup>) which at 298 K gives an AA'BB' spectrum with both  $J(A-B)$  and  $J(A'-B')$  being 104 Hz. This is identical to  $J(P-P)_{trans}$  observed in the slow exchange limit spectrum, and clearly indicates an exchange process which scrambles the *cis* but not the *trans* phosphorus nuclei in (**1**). The spectra at intermediate temperatures have been adequately computer-simulated on the basis of the degenerate equilibrium shown in Figure 1a.

More importantly, since ethylene-hydride exchange is fast at 298 K, the observation of exclusive exchange of mutually *cis* phosphorus nuclei in (**1**) has significant implications on the mechanism of the ethylene-hydride exchange process. This process is expected to proceed *via* reversible ethylene insertion into the molybdenum-hydride bond and thus the initial formation of an unobserved agostic  $\eta^2$ -ethyl intermediate. It is normally proposed that the agostic hydrogen in this  $\eta^2$ -ethyl intermediate then dissociates to form an unobserved 16e  $\sigma$ -ethyl intermediate which we assume would be essentially *octahedral*, as are the large majority of 16e six-co-ordinate transition metal complexes. Rotation about the C<sub>α</sub>-C<sub>β</sub> bond followed by  $\beta$ -elimination would lead to the observed ethylene-hydride exchange. However, if this mechanism is operating in (**1**), random exchange of the phosphorus nuclei at the fast exchange limit will result unless there is restricted rotation about the Mo-C<sub>α</sub> bond. This is unlikely because the ethylene ligands, which are sterically more demanding than a  $\sigma$ -ethyl group, in the precursor to (**1**), namely [*trans*-Mo(dppen)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>], are observed to undergo free rotation.<sup>4</sup> These arguments suggest therefore that the rotation about the C<sub>α</sub>-C<sub>β</sub> bond in the 18e agostic ethyl intermediate occurs 'in-place' without dissociation of the agostic hydrogen. This new mechanism of hydrogen scrambling in ethylene-hydride complexes is shown in Figure 2.

The key step in the new mechanism of intramolecular ethylene-hydride exchange processes involves an associative pathway and the transition state A which has an  $\eta^3$ -ethyl

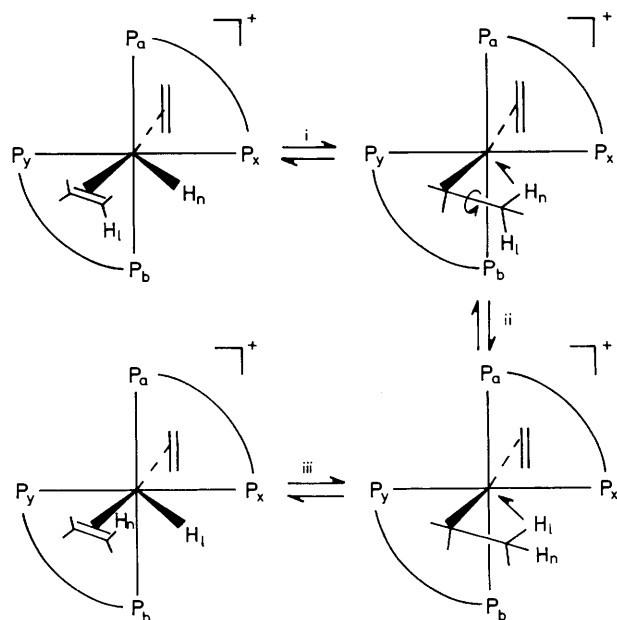


† In ref. 3, (**1**) was prepared by treatment of the precursor bis(ethylene) complex with 1 equivalent of CF<sub>3</sub>CO<sub>2</sub>H in benzene at 5°C. We found that this method gave low yields (*ca.* 10%) of (**1**) and purification was difficult.

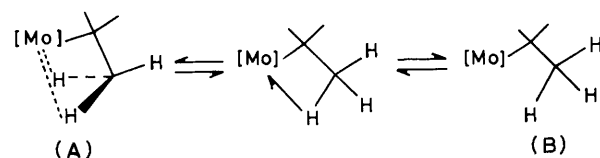


**Figure 1.** The pseudorotation mechanism proposed by Osborn for the dynamic processes in (1). For clarity the rotation processes are shown separately, the mechanism is a combination of processes in (a), (b), and (c). The process shown in (d) is the modified version of the proposed mechanism. The arrows denote the direction of the 90° rotations. (a) Coupled rotation of the proximal ethylene and the hydride ligands giving rise to scrambling of the *cis* phosphorus nuclei *only*. (b) Rotation of the proximal ethylene about the metal-ethylene-centroid axis. This rotation is *disrotatory* with respect to the process shown in (a) and results in end-to-end exchange of the ethylene ligand. (c) *Conrotatory* motion of the distal ethylene with respect to the coupled rotation shown in (a), and does not result in end-to-end exchange. (d) *Disrotatory* motion of the distal ethylene which may account for the observed end-to-end exchange. See texts for details.

group. In the normally proposed mechanism, which proceeds *via* the 16e  $\sigma$ -ethyl intermediate **B**, a dissociative pathway is followed.



**Figure 2.** The in-place rotation mechanism *via* an associative step proposed for intramolecular hydrogen scrambling in the ethylene-hydride complex (1).



The associative, in-place rotation mechanism may also be invoked in complexes such as  $[\text{Co}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_2\text{Ph})(\eta^2\text{-Et})]$  reported by Orpen and co-workers.<sup>5</sup> Three dynamic processes were observed. A low energy process ( $\Delta G^\ddagger$  ca. 40 kJ mol<sup>-1</sup>) exchanges the  $\beta$ -hydrogens of the agostic ethyl group. A second process ( $\Delta G^\ddagger$  ca. 56 kJ mol<sup>-1</sup>) scrambles the chirality at the cobalt centre. A third, highest energy process ( $\Delta G^\ddagger > 60$  kJ mol<sup>-1</sup>) allows scrambling of all the hydrogens of the agostic ethyl group. It was proposed that scrambling of the  $\beta$ -hydrogens proceeds *via* reversible dissociation of the  $\beta$ -agostic hydrogen to form the 16-electron pyramidal intermediate  $[\text{Co}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_2\text{Ph})(\sigma\text{-Et})]^+$  in which there was rotation about the C $_{\alpha}$ -C $_{\beta}$  bond. It was further proposed, on the basis of theoretical calculations, that the activation energy of chirality scrambling at the cobalt centre arises from an inversion barrier in the pyramidal 16e intermediate. Finally, reversible  $\beta$ -elimination and ethylene rotation gives rise to complete scrambling of the ethyl hydrogens.

In the light of the evidence for an associative pathway for  $\beta$ -hydrogen scrambling in ethyl species, an alternative interpretation, which is also consistent with the data, can be put forward. Thus the exchange of the  $\beta$ -hydrogens of the agostic  $\eta^2$ -ethyl group may occur by an in-place rotation of the methyl fragment. The rate limiting step for chirality inversion is the dissociation of the agostic hydrogen to form a 16e intermediate, which then undergoes racemisation. The 16e intermediate may be planar or pyramidal, and there may be a barrier to inversion if the latter structure is adopted. These two mechanisms are distinguished by whether it requires more energy to break the agostic Co  $\leftarrow$  H-C bond or to invert the configuration of the 16e intermediate.

In conclusion, the mechanism of in-place rotation of the methyl group of an agostic ethyl intermediate for hydrogen scrambling processes in ethylene-hydride complexes has been proposed. We believe that this new mechanism may be quite general for such processes.

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