

Spectroscopic and Theoretical Studies on $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\text{Et}(\text{PMe}_2\text{Ph})]^+$: Evidence for Dynamic Inversion of Chirality at Cobalt

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The ethyl protons of the complex $[\text{Co}(\eta\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_5)(\text{PMe}_2\text{Ph})]^+$ which contains a 3-centre, 2-electron M–H–C interaction, interchange by a combination of three identifiable processes which have been modelled by Extended Hückel Molecular Orbital (EHMO) calculations: M–H cleavage/methyl rotation, inversion of chirality at cobalt, and β -elimination/olefin rotation.

The intense current interest in complexes containing C–H bonds co-ordinated to metal atoms has focussed largely on the activation of the C–H bond towards cleavage.¹ We report here on a different aspect of the reactivity of such complexes, namely their susceptibility to uncoupling of the C–H–metal interaction, releasing an unsaturated metal fragment.

At -80°C the ^1H n.m.r. spectrum[†] of $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\text{Et}(\text{PMe}_2\text{Ph})]\text{BF}_4$ (**1**) in CD_2Cl_2 shows separate resonances for each of the five ethyl protons. A pair of doublets are observed for the diastereotopic methyl groups of the phosphine ligand, consistent with the chiral ground state structure expected for (**1**) by analogy with the structure² of $[\text{Co}(\eta\text{-C}_5\text{Me}_5)\text{Et}\{\text{P}(p\text{-tolyl})_3\}]^+$ (**2**) in the solid state. As the temperature is raised the three β -C–H signals coalesce (-40°C), whereas the two methylene signals remain separate, as do the resonances of the phosphine methyl groups. At -10°C the $\text{P}(\text{CH}_3)_2\text{Ph}$ signals coalesce to give one doublet ($^2J_{\text{PH}}$ 9.1 Hz), and the CH_2CH_3 signals also coalesce. There are, by implication, two dynamic processes at work. The lower energy ($\Delta G^\ddagger 40 \pm 4 \text{ kJ mol}^{-1}$)[‡] process allows exchange of CH_2CH_3 protons between terminal and bridging (Co–H–C) sites. A higher energy process ($\Delta G^\ddagger 56 \pm 4 \text{ kJ mol}^{-1}$) inverts the chirality at cobalt rapidly on the n.m.r. time scale. This process is depicted in Scheme 1.

Evidence for a third, high energy ($\Delta G^\ddagger > 60 \text{ kJ mol}^{-1}$), process came from spin saturation transfer experiments carried out at 30°C which established an exchange of protons between the α - and β -carbon atoms of the ethyl group. This exchange presumably requires the transfer of H to the cobalt atom (affording an intermediate hydrido ethylene complex) coupled with rotation of the ethylene ligand, as postulated by Schmidt and Brookhart.³

To shed light on the mechanisms of these rearrangements we have carried out Extended Hückel Molecular Orbital

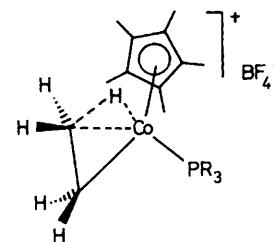
(EHMO)⁴ calculations on a model for (**1**) and (**2**), $[\text{Co}(\eta\text{-C}_5\text{H}_5)\text{Et}(\text{PH}_3)]^+$, in geometries derived from the crystal structure of (**2**) (with all C–H set to 1.09 \AA , $\text{Co}-\text{C}_\alpha-\text{H} = \text{C}_\alpha-\text{C}_\beta-\text{H} = 109.5^\circ$). Calculations were carried out at four geometries: with $\text{Co}-\text{C}_\alpha-\text{C}_\beta$ angle = 74.5° and with eclipsed and staggered conformations about $\text{C}_\alpha-\text{C}_\beta$, and with $\text{Co}-\text{C}_\alpha-\text{C}_\beta = 109.5^\circ$ and eclipsed and staggered conformations. This allows examination of the dissociation of the Co–HC $_\beta$ interaction ($\text{Co}-\text{C}_\alpha-\text{C}_\beta$ going from 74.5 to 109.5°) and exchange of methyl hydrogens *via* methyl rotation. The relative energies of these geometries were: 0, 64, 14, and 4 kJ mol^{-1} respectively. Thus methyl hydrogen exchange is calculated to proceed most easily by rotation about the $\text{C}_\alpha-\text{C}_\beta$ bond after cleaving the $\text{C}_\beta-\text{H} \cdots \text{Co}$ interaction, the calculated barrier to $\text{C}-\text{H} \cdots \text{Co}$ cleavage being *ca.* 14 kJ mol^{-1} . The barrier to 'in-place' rotation of the methyl group, without opening of the $\text{Co}-\text{C}_\alpha-\text{C}_\beta$ angle, is calculated to be *ca.* 64 kJ mol^{-1} . Calculations on a model olefin hydride species $[\text{Co}(\text{PH}_3)(\text{H})(\text{C}_2\text{H}_4)(\eta\text{-C}_5\text{H}_5)]$ indicate that the preferred olefin conformation has the C–C bond approximately parallel to the Co–H bond. This is preferable on both electronic and 'steric' grounds,^{4c} and the barrier to olefin rotation is calculated to be $\approx 51 \text{ kJ mol}^{-1}$. These EHMO calculations cannot give quantitative estimates for the magnitudes of barriers to the processes described. They do however, allow qualitative evaluation of the mechanisms for the exchange processes observed. Thus methyl group rotation is found to occur by opening out the $\text{Co}-\text{C}_\alpha-\text{C}_\beta$ angle,[§] and to be more facile than β -elimination/olefin rotation, in accord with experiment.

The result of opening out $\text{Co}-\text{C}_\alpha-\text{C}_\beta$ to *ca.* 109.5° is to produce a $16e$, d^6 $(\text{C}_5\text{H}_5)\text{ML}_2$ type of intermediate, of the sort postulated⁶ in dissociative substitution and racemization reactions of, for example, $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})(\text{PR}_3)]$. For (**1**) the dissociation step $[(\text{A}) \rightarrow (\text{B})]$, Scheme 1) has a lower

[†] ^1H n.m.r. data for (**1**) (CD_2Cl_2 , 200 MHz, Jeol FX 200). At -85°C : δ -12.40 (1H, m, $\text{CH}_2\text{CH}_2\text{H}^*$); -0.55 (1H, m, $\text{CH}_2\text{CH}_2\text{H}^*$); -0.13 (1H, m, $\text{CH}_2\text{CH}_2\text{H}^*$); 1.13 (3H, d, J_{PH} 9.1 Hz, PMe_2Ph); 1.40 (1H, $\text{CH}_2\text{CH}_2\text{H}^*$, obscured); 1.45 (3H, d, J_{PH} 9.1 Hz, PMe_2Ph); 1.55 (15H, s, C_5Me_5); 2.83 (1H, m, $\text{CH}_2\text{CH}_2\text{H}^*$); 7.51 – 7.83 (5H, m, PMe_2Ph). At -40°C : no peaks for $\text{CH}_2\text{CH}_2\text{H}^*$; δ 1.25 (3H, d, J_{PH} 9.1 Hz, PMe_2Ph); 1.40 (1H, $\text{CH}_2\text{CH}_2\text{H}^*$, obscured); 1.41 (3H, d, J_{PH} 9.1 Hz, PMe_2Ph); 2.83 (1H, m, $\text{CH}_2\text{CH}_2\text{H}^*$). At $+25^\circ\text{C}$: δ -4.32 (3H, m, $\text{CH}_2\text{CH}_2\text{H}^*$); 1.34 (6H, d, J_{PH} 9.1 Hz, PMe_2Ph); 2.1 (2H, br, $\text{CH}_2\text{CH}_2\text{H}^*$). *N.b.* Shifts of C_5Me_5 and Ph signals do not vary with temperature.

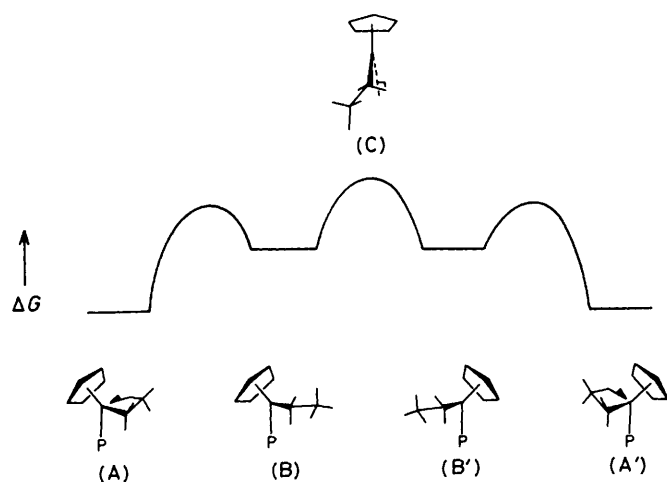
[‡] Coalescence temperatures (T_c) were estimated from variable temperature ^1H n.m.r. spectra and free-energy barriers were derived using the expression shown below; the quoted errors reflect the estimated precision of the measurements.

$$\Delta G^\ddagger = -RT_c \ln \frac{\pi \Delta\nu}{\sqrt{2kT_c}}$$



(**1**) $\text{PR}_3 = \text{PMe}_2\text{Ph}$
 (**2**) $\text{PR}_3 = \text{P}(p\text{-tolyl})_3$

[§] We note that *ab initio* calculations on a related agostic palladium species $[\text{Pd}(\text{H})(\text{PH}_3)\text{Et}]$ imply the same pathway for methyl H exchange, *i.e.* by opening of $\text{H}-\text{C}_\alpha-\text{C}_\beta$ followed by rotation about the $\text{C}_\alpha-\text{C}_\beta$ bond.⁵



Scheme 1. Free energy diagram for $C_{\beta}\text{-H}\cdots\text{Co}$ cleavage and inversion of chirality at cobalt *via* the planar 16e species (C).

activation energy than the inversion process [(B)→(B')] allowing experimental determination of both barriers. The relative stability of the pyramidal geometry (B) with respect to the planar form (C) of such 16-electron species has been indicated by both EHMO⁷ and *ab initio* calculations.⁸ Thus both experimental and theoretical evidence is consistent with the 'planar' geometry for the 16e d⁶ (C₅H₅)ML₂ species being a transition state. The η^2 -ethyl complexes (1), (2), etc.

therefore contain a lightly stabilized, thermally accessible 16e Co^{III} centre. In this context it seems likely that the polymerization of ethylene by (2), noted previously,² occurs by co-ordination of ethylene following uncoupling of the β -C-H interaction, that is by the capture of the chiral intermediate (B).

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