Mechanism of Internal Rotation in Dicarbonyl(hexaethylbenzene)thiocarbonylchromium(0) and Cyclopentadienyl(hexaethylbenzene)iron(II) Hexafluorophosphate

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The variable-temperature ^{13}C high-field n.m.r. spectrum of (heb)$Cr(CO)_2(CS)$ (**1**) (heb = hexaethylbenzene) has been shown to be entirely explicable in terms of restricted ethyl group rotation about the arene, and a recent analysis in terms of restricted rotation about the arene–chromium bond cannot therefore be considered conclusive; furthermore, ethyl group rotation in [(heb)$Fe(C_5H_5)]PF_6$ (**2**), previously claimed as too rapid at accessibly low temperatures for observation by even high-field n.m.r. spectroscopy, is in fact slowed sufficiently at 140 K to result in the coexistence of multiple heb stereoisomers in equilibrium.

McGlinchey and co-workers have recently reported structural and variable-temperature ^{13}C n.m.r. spectral studies for (heb)$Cr(CO)_2(CS)$ (**1**)[1] and [(heb)$Fe(\eta^5-C_5H_5)]PF_6$ (**2**).[1,2] In the crystal of (**1**) hexaethylbenzene (heb) exists as stereoisomer *a* (Figure 1 shows the four stereoisomers postulated[3] to be favoured for heb bound to a tripodal moiety). Although it was conceded that the spectrum of (**1**) could be interpreted in terms of restricted ethyl group rotation about the arene, this would require a different heb stereoisomer (*c* or *e*) in solution from that found in the crystal, and an interpretation based on restricted rotation about the arene–chromium bond was preferred ('stopping a chromium carousel').[1] Such a claim is totally unprecedented for a (η^6-arene) complex without special steric factors, as in (p-$Bu^t_2C_6H_4)Ru(CO)(SiCl_3)_2$,[4] or special electronic factors, as in $[(MeC_6H_4CHR)Cr(CO)_3]^+$.[5]

We have established[6] that for (heb)$Cr(CO)_2(PMe_3)$ (**3**) the major heb stereoisomer found in solution is different from that of the crystal. The 145.79 MHz $^{31}P-\{^1H\}$ n.m.r. spectrum of (**3**) showed that all four favoured heb stereoisomers coexist in equilibrium in CD_2Cl_2 solution at low temperature, and an interconversion scheme involving only uncorrelated ethyl group rotation was used to simulate the experimental spectrum. Thus, even for a heb complex with a sterically demanding substituent as in (**3**), there is no need to invoke slowed tripodal rotation to explain the variable-temperature n.m.r. spectrum.

We therefore re-examined the variable-temperature high-field (90.1 MHz) $^{13}C-\{^1H\}$ n.m.r. spectrum of (**1**) in CD_2Cl_2 solution and have found that at 163 K its arene subspectrum exhibits the four previously reported[1] resonances at 112.8, 113.4, 119.9, and 121.7 p.p.m. (Figure 2). A similar interconversion scheme to that used for (**3**) and involving only uncorrelated ethyl group rotation† was successfully used to simulate the arene subspectrum of (**1**). Excellent fit was obtained with the four resonances assigned to the six label isomers of stereoisomer *c*. Allowing heb stereoisomer interconversion to occur only by single ethyl group rotation requires the assumption of low intensity unobserved resonances for the six label isomers of stereoisomer *e* and for the unique label isomer of stereoisomer *h*. Provided that the assumed populations of *e* and *h* do not exceed about 5% of that of *c* the chemical shifts and intensities actually assigned to the unobserved resonances are unimportant to the appearance of the simulated exchange-broadened spectrum. In the interconversion scheme the two vertices corresponding to the label isomers of stereoisomer *a* were removed from the siamese cubes previously described.[6] As resonances were not observed for stereoisomers *e* and *h*, only the $\Delta G^{\ddagger}_{200}$ value of 37.7 ± 2.0 kJ mol^{-1} obtained for uncorrelated ethyl group

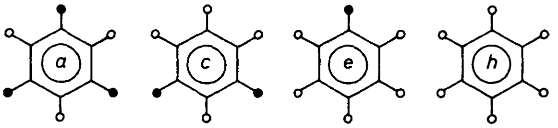

Figure 1. The four favoured heb stereoisomers for (η^6-heb)ML_3 complexes. The metal atom is the point of reference and should be viewed as residing over the ring and above the plane of the paper. The filled (open) circles represent proximal (distal) methyl groups projecting toward (away from) the observer. We retain the previously introduced[7] conformational descriptors (*a*—*h*) for the eight possible heb stereoisomers.

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† Empirical force-field calculations have shown that ethyl group rotation in free heb is completely uncorrelated.[7]

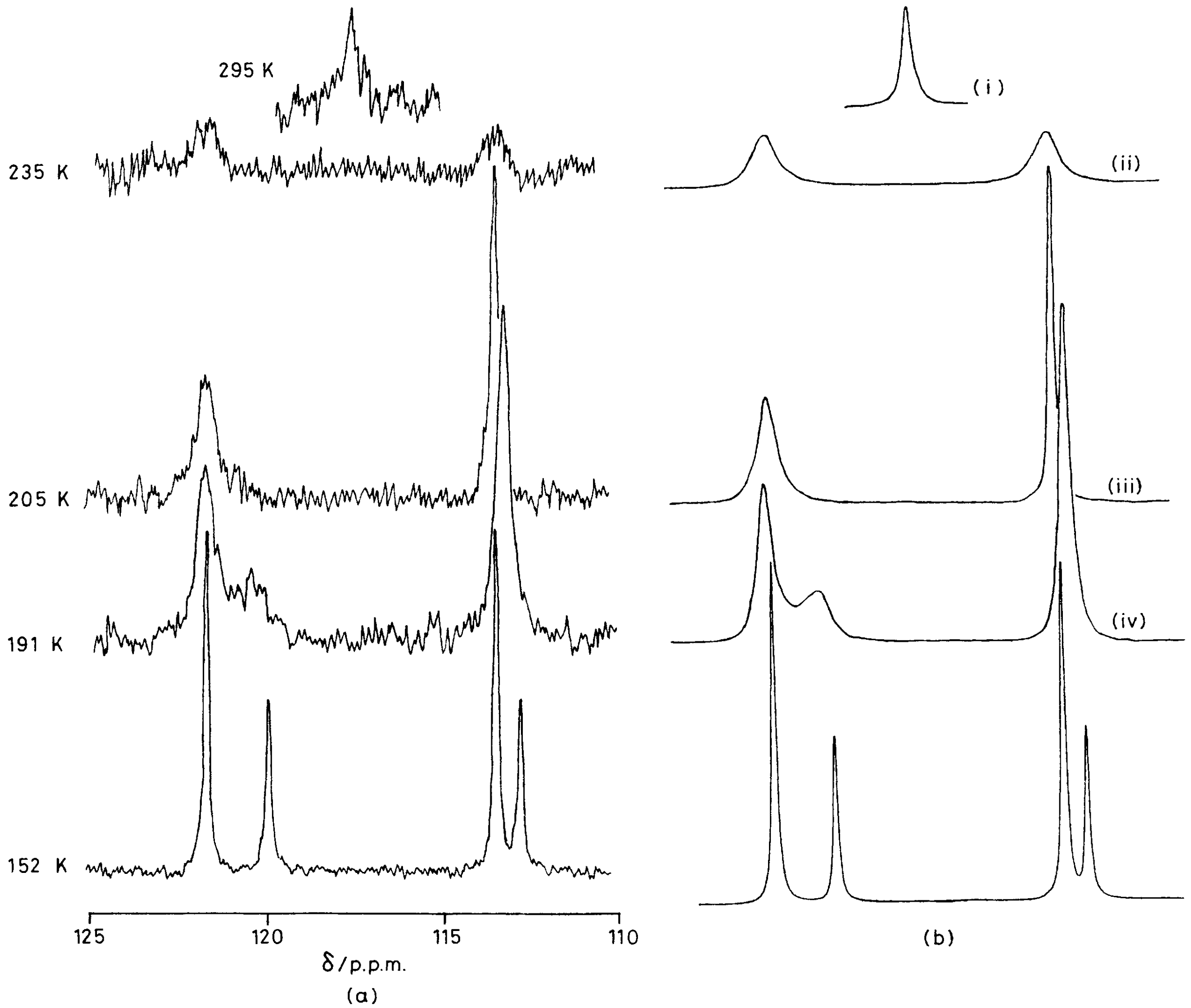

Figure 2. The variable-temperature 90.1 MHz ^{13}C–$\{^{1}H\}$ n.m.r. subspectrum of the arene carbon atoms of (**1**) in CD_2Cl_2; (a) observed; (b) simulated. (i) k_2 = 700000 s^{-1}, (ii) k_2 = 40000 s^{-1}, (iii) k_2 = 1000 s^{-1}, (iv) k_2 = 200 s^{-1}.

rotation in *c* can be considered meaningful. This value is consistent with the corresponding value obtained for (**3**). We therefore consider it plausible that for (**I**) the major stereoisomer in solution (*c*) is different from that found in the crystal (*a*) and that the variable-temperature ^{13}C n.m.r. spectrum is entirely explicable without the need to invoke slowed tripodal rotation.

A coalescence phenomenon is also observed in the 90.1 MHz ^{13}C–$\{^{1}H\}$ spectrum of (**2**) in $CHFCl_2$ (Figure 3). At 140 K the subspectrum assigned to the cyclopentadienyl carbon atoms appears as three well resolved resonances, although those assigned to the arene and ethyl carbon atoms are not apparently fully decoalesced. Tripling of the cyclopentadienyl resonance can conceivably arise from either (i) slowed rotation of the cyclopentadienyl moiety about the iron atom, or (ii) slowed ethyl group rotation resulting in multiple co-existing heb stereoisomers. Both possibilities were carefully examined but only simulations based on (ii) fitted the experimental cyclopentadienyl carbon subspectrum. The presence of three heb stereoisomers (*c*, *e*, *h*)[‡] was assumed and the same interconversion scheme used as for (**1**). $\Delta G^{\ddagger}_{200}$ values obtained were: $c \rightarrow e$, 35.2 ± 1.7, $e \rightarrow c$, 36.4 ± 1.7; $e \rightarrow h$, 36.8 ± 1.7, $h \rightarrow e$ 38.5 ± 1.7 kJ mol^{-1}. Contrary to other reports concerning (**2**),[1,2] we conclude that ethyl group rotation is slowed at accessible temperatures and that the apparently incomplete decoalescences observed for the arene and ethyl subspectrum are due to the numerous overlapping resonances resulting from multiple coexisting heb stereoisomers.

Added in proof: Professor McGlinchey has drawn our attention to an argument, based on detailed chemical shift assignments within the aliphatic carbon subspectrum, in favour of (**1**) adopting the same heb conformation in solution as in the crystal. However, we consider that neither this argument nor that based on apparent similarities in the low-temperature solution and room-temperature solid-state ^{13}C n.m.r. spectra[8] can be regarded as being conclusive, and therefore contend that the case for slowed tripodal rotation in (**1**) remains not proven.

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[‡] Although heb is not bound to a tripodal moiety it seems plausible that similar criteria[3] can be applied to predict relative stereoisomer stability for (**2**). Stereoisomer *a* now becomes disfavoured on steric grounds.

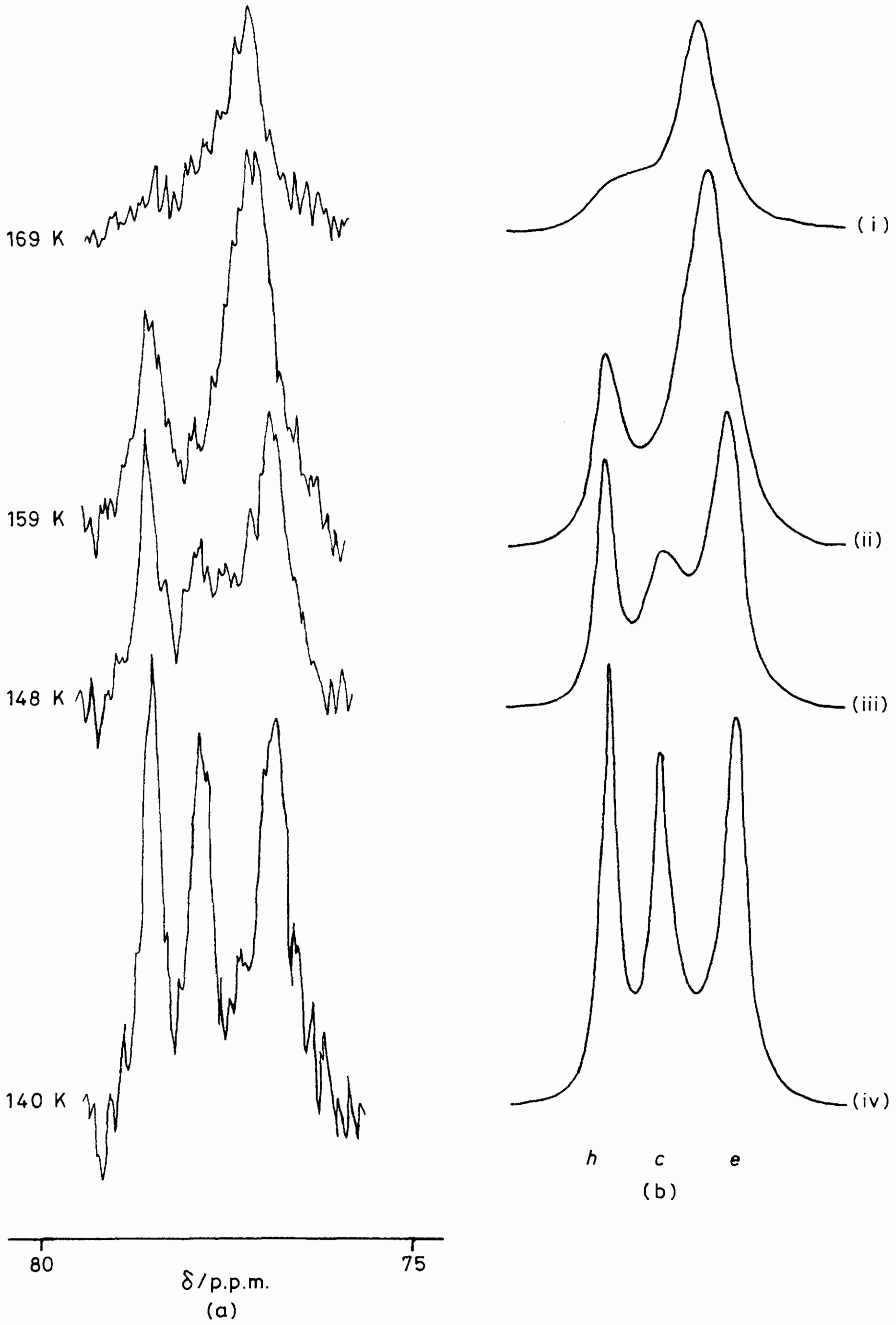

Figure 3. The variable-temperature 90.1 MHz $^{13}C-\{^1H\}$ n.m.r. subspectrum of the cyclopentadienyl carbon atoms of (**2**) in $CHFCl_2$; (a) observed; (b) simulated. (i) $k_2 = 300$, $k_3 = 100$, $k_4 = 30$, $k_5 = 160\ s^{-1}$; (ii) $k_2 = 120$, $k_3 = 40$, $k_4 = 13$, $k_5 = 75\ s^{-1}$; (iii) $k_2 = 55$, $k_3 = 18$, $k_4 = 6$, $k_5 = 30\ s^{-1}$; (iv) $k_2 = 25$, $k_3 = 8$, $k_4 = 3$, $k_5 = 15\ s^{-1}$.

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