

Stereodynamics of Ethyl Group Rotation in Co-ordinated Hexaethylbenzene: X-Ray Crystallographic and Dynamic N.M.R. Spectral Studies on Dicarbonyl(hexaethylbenzene)trimethylphosphinechromium(0)

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The co-ordinated hexaethylbenzene (heb) of (heb)Cr(CO)₂(PMe₃) adopts a 1,2,3,5-distal-4,6-proximal methyl conformation, with an additional distal methyl found as a disorder in the crystal in approximately one molecule in five; the low-temperature n.m.r. spectra of (heb)Cr(CO)₂(PMe₃) (³¹P and ¹³C) are satisfactorily explained by slowed ethyl group rotation resulting in multiple heb stereoisomers coexisting in equilibrium, and without invoking slowed rotation about the metal-arene bond.

The up-down alternation of ethyl groups actually observed in hexaethylbenzene (heb) is only one of eight possible arrangements in which the methyl groups are located on one side or other of the benzene ring plane.^{1b} We have, however, postulated that only the four heb stereoisomers shown in Figure 1 are favoured for (η⁶-heb)ML₃ complexes and have further postulated that compensatory destabilisation will tend to equalise the internal energies of the stereoisomeric heb complexes, thus leading to their probable coexistence in comparable quantities in both the crystal and in solution.^{1c} Examples of three stereoisomeric types have been reported: *a* [(heb)Cr(CO)₃]^{1a,b}, (heb)Mo(CO)₃,^{1a,b} (heb)Cr(CO)₂(CS)^{2a}, *e* [(heb)Cr(CO)₂(PEt₃)]^{1c}, (heb)Cr(CO)₂(PPh₃)^{1a,b}, and *h* [(heb)Cr(CO)₂(PEt₃)]^{1c}, (heb)Cr(CO)₂(PPh₃)^{1a,b}.

We now report that the crystal structure[†] of (heb)Cr(CO)₂(PMe₃) (**1**) crystallised from heptane solution (Figure 3) shows it to be the first example of a *tripodal* complex[‡] in which heb occurs as stereoisomer *c*. In approximately one molecule in five, a 'maverick' methyl [C(36A)] is found on the distal side (*i.e.* stereoisomer *e*) as a disorder in the crystal and (**1**) therefore joins (heb)Cr(CO)₂(PEt₃) and (heb)Cr(CO)₂(PPh₃) as examples of the almost isoenergetic nature of heb stereoisomeric complexes in the crystal.

We also observe that there is a coalescence phenomenon involving four resonances resolved at 153 K in the 145.79 MHz ³¹P-¹H spectrum of (**1**) in CD₂Cl₂, thus providing the first evidence that all four favoured heb stereoisomers can coexist in equilibrium in solution. As the sequence in which the phosphorus atom visits each chemical environment is dependent on the ethyl group rotational sequence, the ³¹P spectrum provides a probe of the ethyl group stereodynamics. For heb bound to a rapidly rotating tripodal moiety there are a total of

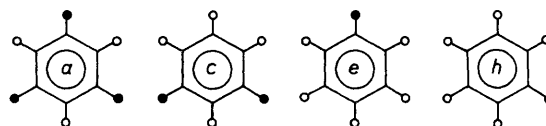


Figure 1. The four favoured heb stereoisomers for (η⁶-heb)ML₃ complexes. The metal atom is the point of reference and should be viewed as residing over the ring and above the plane of the paper. The filled (open) circles represent proximal (distal) methyl groups projecting toward (away from) the observer. We retain the previously introduced^{1b} conformational descriptors (*a-h*) for the eight possible heb stereoisomers.

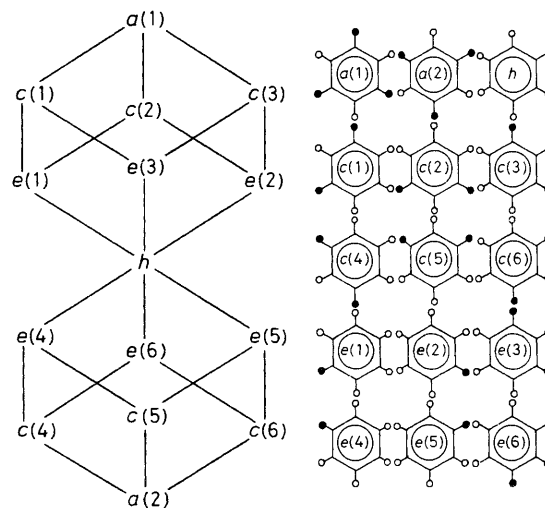


Figure 2. The 'siamese cubes' interconversion scheme and the 15 'label' isomers of the four favoured stereoisomers for (η⁶-heb)ML₃ complexes.

fifteen individual 'label' isomers of the four favoured stereoisomers (two *a*, six *c*, six *e*, one *h*), all interconvertible by ethyl group rotation. An interconversion scheme can be represented by arranging the fifteen label isomers at the vertices of two cubes sharing a common vertex which is occupied by the unique label isomer *h* ('siamese cubes,' Figure 2). Of the 105 possible interconversion reactions, if only completely uncorrelated ethyl group rotation is significant,[§] only the 24 exchanges represented by the edges of the two cubes will have effective rates. Successful simulation of the experimental spectrum was achieved with these rate constants separated into six groups; $a \rightarrow c$, k_1 ; $c \rightarrow e$, k_2 ; $e \rightarrow h$, k_3 ; $h \rightarrow e$, k_4 ;

[§] Empirical force-field calculations have shown that ethyl group rotation in free heb is completely uncorrelated.^{1b}

[†] Crystal data: C₂₃H₃₀CrO₂P, *M* = 430.53, triclinic, space group *P* $\bar{1}$, *a* = 9.693(1), *b* = 9.848(2), *c* = 13.947(2) Å, α = 79.51(1), β = 81.50(1), γ = 65.03(1)°, *Z* = 2, *D*_c = 1.309 g cm⁻³, 3190 independent reflections were measured on a Hilger-Watts diffractometer (Ni-filtered Cu-K α radiation), of which 3073 were considered observed [*I* > 2.5σ(*I*)]. The residuals are *R* = 0.033 and *R*_w = 0.046. The structure was solved by a multiple-solution procedure and was refined by full-matrix least squares.

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.

[‡] Stereoisomer *c* occurs in the crystal of [(heb)Fe(η⁵-C₅H₅)]PF₆^{2b} where, of course, the heb is not bound to a tripodal moiety, and a stereoisomer analogous to *c* occurs in tricarbonyl(hexaethylborazine)chromium(0),³ presumably as a result of borazine ring puckering.

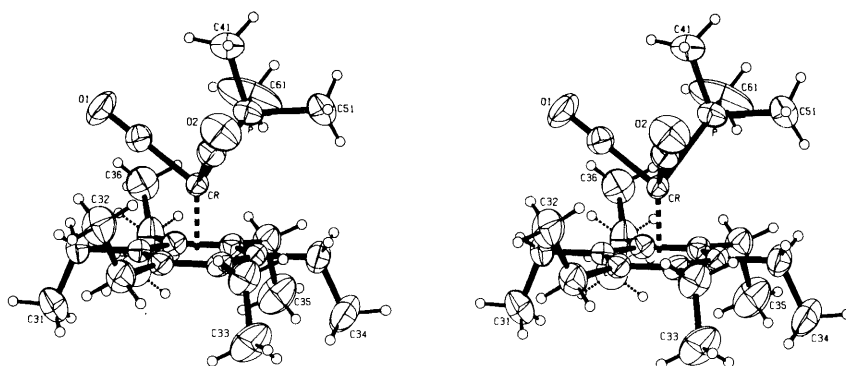


Figure 3. Molecular structure of (1). The maverick ethyl group is shown by dashed bonds.

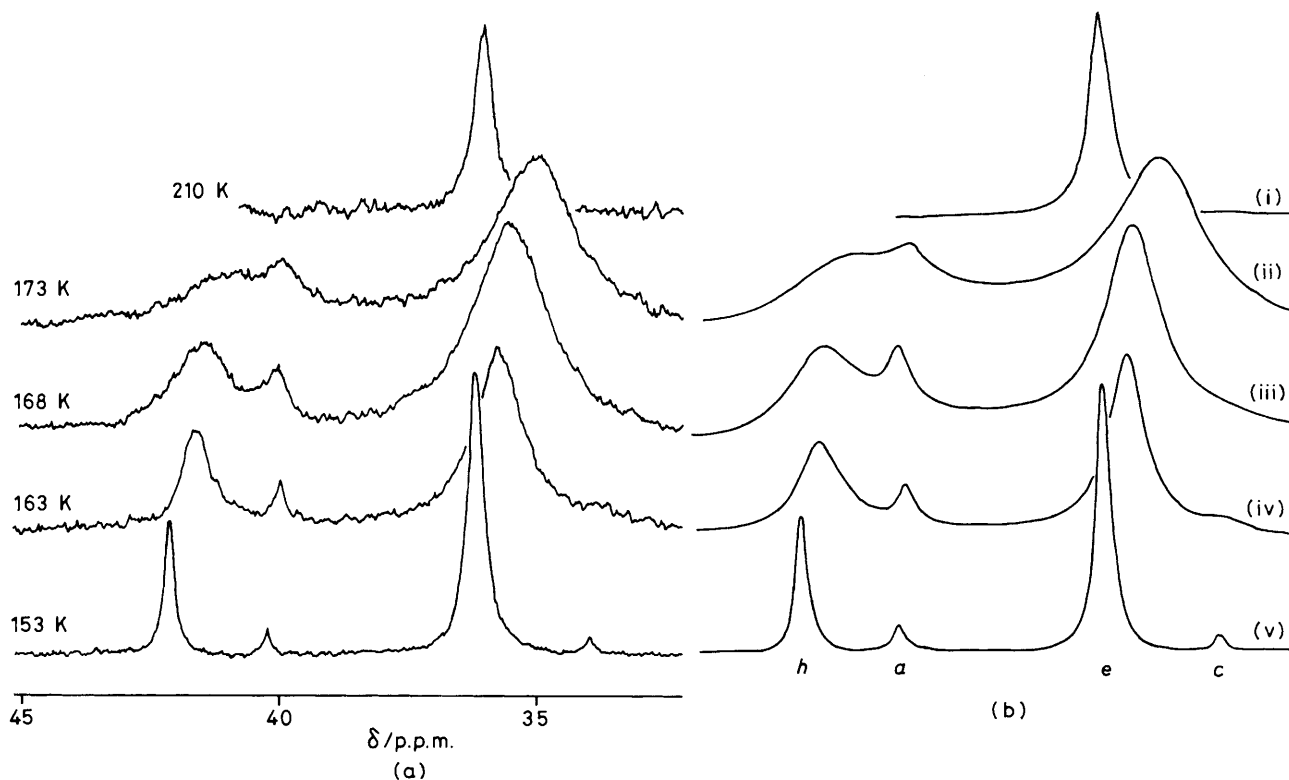


Figure 4. The variable temperature 145.79 MHz $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (1) in CD_2Cl_2 : (a) observed; (b) simulated. All 24 possible permutations of the chemical shift assignments were examined and that which gave the best fit is shown on the figure. (i) $k_1 = 3000, k_2 = 20\,000, k_3 = 27\,000, k_4 = 6800, k_5 = 2000, k_6 = 12\,000\ \text{s}^{-1}$; (ii) $k_1 = 90, k_2 = 600, k_3 = 800, k_4 = 200, k_5 = 60, k_6 = 360\ \text{s}^{-1}$; (iii) $k_1 = 45, k_2 = 300, k_3 = 500, k_4 = 100, k_5 = 30, k_6 = 180\ \text{s}^{-1}$; (iv) $k_1 = 7, k_2 = 175, k_3 = 200, k_4 = 55, k_5 = 13, k_6 = 21\ \text{s}^{-1}$.

$e \rightarrow c, k_5; c \rightarrow a, k_6$ (the pairs $k_1/k_6, k_2/k_5, k_3/k_4$, are related by the relative populations of the exchanging label isomers). ΔG^\ddagger_{200} values obtained were: $a \rightarrow c, 36.4 \pm 2.0$; $c \rightarrow a, 34.3 \pm 2.0$; $c \rightarrow e, 33.5 \pm 2.0$; $e \rightarrow c, 37.3 \pm 2.0$; $e \rightarrow h, 32.7 \pm 1.3$; $h \rightarrow e, 35.2 \pm 1.3\ \text{kJ mol}^{-1}$. These barriers to ethyl group rotation are similar to those reported for (heb)- $\text{Cr}(\text{CO})_3$,^{1b} (heb)- $\text{Mo}(\text{CO})_3$,^{1b} and (heb)- $\text{Cr}(\text{CO})_2(\text{PEt}_3)$,^{1c} and determined for (heb)- $\text{Cr}(\text{CO})_2[\text{P}(\text{OPh})_3]$,⁴ (heb)- $\text{Cr}(\text{CO})_2(\text{C}_4\text{H}_2\text{O}_3)$,⁵ (heb)- $\text{Mo}(\text{CO})_2(\text{C}_4\text{H}_2\text{O}_3)$,⁵ and [(heb)- $\text{Fe}(\text{C}_5\text{H}_5)]\text{PF}_6$.⁶

All 24 possible permutations of the ^{31}P chemical shift assignments were carefully examined and that which gave the best fit is shown in Figure 4. It is of interest to note that for (heb)- $\text{Cr}(\text{CO})_2(\text{PMe}_3)$ the major stereoisomer of the crystal (c) is that least populated in CD_2Cl_2 solution at low temperature.

The 90.1 MHz $^{13}\text{C}\{-^1\text{H}\}$ spectrum of (1) in CD_2Cl_2 displays a spectacular coalescence in the arene subspectrum. No

attempt has been made to assign the individual resonances of this subspectrum but there are enough resolved at 153 K to support further the presence of the four heb stereoisomers (*i.e.* two for *a*, four for *c*, four for *e*, one for *h*). These resonances coalesce to a sharp singlet with increasing temperature. At low temperatures there are numerous overlapping alkyl resonances.

We have found other examples with multiple heb stereoisomers unequivocally co-existing in solution: (heb)- $\text{Cr}(\text{CO})_2(\text{PEt}_3)$, two;^{1c} (heb)- $\text{Cr}(\text{CO})_2[\text{P}(\text{OPh})_3]$, three;⁴ (heb)- $\text{Cr}(\text{CO})_2(\text{C}_4\text{H}_2\text{O}_3)$, two;⁵ (heb)- $\text{Mo}(\text{CO})_2(\text{C}_4\text{H}_2\text{O}_3)$, two;⁵ [(heb)- $\text{Fe}(\text{C}_5\text{H}_5)]\text{PF}_6$, three.⁶ For all the heb complexes we have examined, the n.m.r. spectra can be satisfactorily analysed without the need to invoke hindered rotation about the metal-arene bond.

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