

Solid State ^{13}C and High Resolution ^1H and ^{13}C N.M.R. Spectra of Dicarbonyl(hexaethylbenzene)thiocarbonylchromium(0): A Reaffirmation of Slowed Tripodal Rotation

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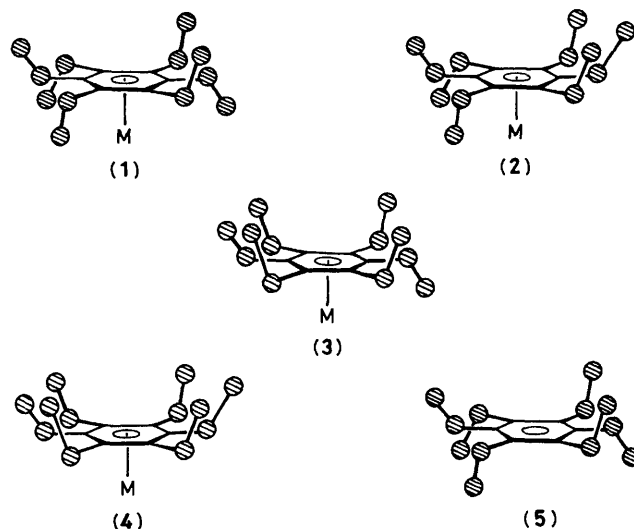
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The high resolution and solid state n.m.r. spectra of the title compound indicate that the arene has alternating proximal and distal ethyl groups both in the solid and in solution: this not only requires slowed tripodal rotation on the n.m.r. time scale but also militates against the recent proposal that the major stereoisomer found in solution is different from that established crystallographically.

Recently we reported the synthesis, crystal structure, and variable-temperature ^{13}C n.m.r. spectrum of $(\text{C}_6\text{Et}_6)\text{Cr}(\text{CO})_2\text{CS}$.¹ In the solid state, the molecule adopts structure (1) in which the ethyl groups project alternately above and below the plane of the arene ring with the tripodal ligands eclipsing the three distal ethyls while the three proximal ethyls lie between the thiocarbonyl and carbonyl groups. This approximate C_3 symmetry is reflected in the low-temperature ^{13}C n.m.r. spectrum in which the methyl, methylene, and ring carbons exhibit 2:1:2:1 patterns. This result was rationalised in terms of slowed rotation of the tripodal moiety on the n.m.r. time scale, *viz.*, 'stopping a chromium carousel'.

An ingenious alternative explanation has since been advanced by Hunter and Mislow² in which they claim that the major stereoisomer in solution is different from that in the solid state. In particular, it is proposed that the 1,2,3,5-distal-4,6-proximal isomer, (2), is the sole conformer detectable in solution and that this stereoisomer (which also possesses C_3 symmetry even with rapid tripodal rotation) can account for the observed limiting spectrum. However, they advance no experimental evidence for this postulate; they arbitrarily assign the n.m.r. peaks to structure (2), assume that stereoisomers (3) and (4) are present in undetectable concentrations, and that (1) is completely absent. Nevertheless, one cannot simply dismiss their proposal without careful consideration since both ourselves³ and they⁴ have crystallographically characterized hexaethylbenzene (heb) complexes with such a 4-up-2-down arrangement of ethyl groups.

We report here data establishing that the only detectable stereoisomer in solution is indeed the 1,3,5-distal-2,4,6-proximal one, *as in the solid state*. Let us consider first the ^{13}C chemical shift data for the structurally characterised molecules collected in Table 1. It is immediately apparent that the distal methyl resonances are but little affected by the identity of the metal and can readily be distinguished from the proximal ones. This gains convincing support from the earlier elegant work of the Mislow group in which it was shown that incorporation of a bulky triphenylphosphine ligand, as in (4) $\text{M} = \text{Cr}(\text{CO})_2\text{PPh}_3$, forces all the methyls into a distal environment.⁵ This result also establishes the resonance position of a proximal methylene moiety. Likewise, the chemical shift ranges for ring carbons bearing proximal or distal ethyls are straightforward to assign. The low-temperature ^{13}C n.m.r. spectrum of $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$, (1) $\text{M} = \text{Cr}(\text{CO})_2\text{CS}$, reveals clearly that we have three carbons in the proximal range and three in the distal positions for the methyl, methylene, and ring environments. For Hunter and Mislow to be correct in their assignment of $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$ as the 4-up-2-down isomer, it would be necessary (a) to have distal methyls at 13.2, 13.6, and 18.5 with proximal methyls at 17.8, (b) to have proximal methylenes at 21.7 and 20.7 with distal methylenes at 19.9, and (c) to have distal arene carbons at 112.8, 113.4, and 119.9 with the proximal ones at 121.7; such assignments are untenable in view of the values already established in Table 1.



The identities of the CH_3 and CH_2 resonances have been confirmed by the '*J*-resolved' technique to sort the carbons according to the number of attached protons. Furthermore, the ^1H - ^{13}C two-dimensional correlations show that we have correctly assigned the proximal and distal environments. (It is obvious that the protons of a proximal methyl group couple to the contiguous distal methylene protons, and *vice versa*.) The proton assignments[†] also show that the $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$ adopts conformation (1) in solution as do $(\text{heb})\text{M}(\text{CO})_3$, $\text{M} = \text{Cr}, \text{Mo}, \text{W}$.

Furthermore, we note that comparisons of solid state ^{13}C n.m.r. and high resolution spectra have been used to support the assertion that a structure is the same in solution and in the crystal,⁶ and gratifyingly we can report that this circumstance holds here.‡ The striking similarity between the solid state and high resolution spectra of (1) $\text{M} = \text{Cr}(\text{CO})_2\text{CS}$ bears testimony to the fact that we are dealing with the *same stereoisomer in both phases*.

[†] Spectra of (1) were obtained on a Bruker WM 400 at -70°C in CD_2Cl_2 : $\text{M} = \text{W}(\text{CO})_3$, δ 1.06 (t, 9H), 1.23 (t, 9H), 2.24 (q, 6H), 2.49 (q, 6H); $\text{M} = \text{Mo}(\text{CO})_3$, δ 1.07 (t, 9H), 1.21 (t, 9H), 2.25 (q, 6H), 2.47 (q, 6H); $\text{M} = \text{Cr}(\text{CO})_3$, δ 1.12, 1.16 (overlapping triplets, 18H), 2.21 (q, 6H), 2.41 (q, 6H); $\text{M} = \text{Cr}(\text{CO})_2\text{CS}$, δ 1.07 (t, 9H), 1.23 (t, 9H), 2.29 (q, 6H), 2.47 (q, 6H). The spectrum of $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$ was obtained at -20°C ; below this temperature the peaks begin to separate towards a 2:1 pattern for each of the methylene and methyl environments. A completely resolved limiting spectrum has not yet been observed and we hope to obtain data at 500 MHz in the near future.

[‡] Solid state ^{13}C spectra were obtained on a Bruker CXP 200 operating at 50.32 MHz; (1) $\text{M} = \text{Cr}(\text{CO})_2\text{CS}$, δ 350.1, 237.0, 123.2, 119.3, 114.8, 110.5, 23.7, 22.8, 20.0, 14.9, 14.4.

Table 1. ^{13}C N.m.r. chemical shift data (δ) in CD_2Cl_2 .

	Methyl		Methylene		Arene ring		Ref.
	Proximal ^a	Distal ^b	Proximal ^c	Distal ^d	Proximal ^e	Distal ^f	
(5) (1)		15.5 (6) ^g		21.6 (6)		137.2 (6)	5
M = W(CO) ₃	24.6 (3)	14.6 (3)	22.6 (3)	19.6 (3)	117.5 (3)	111.4 (3)	
(1)							
M = Mo(CO) ₃	23.4 (3)	14.4 (3)	22.8 (3)	19.5 (3)	121.6 (3)	114.7 (3)	5
(1)							
M = Cr(CO) ₃	20.1 (3)	14.2 (3)	22.8 (3)	19.4 (3)	117.2 (3)	108.8 (3)	5
(4)							
M = Cr(CO) ₂ PPh ₃	—	15.9 (6)	22.4 (6)	—	—	108.0 (6)	5
(1)							
M = Cr(CO) ₂ CS	17.8 (2)	13.2 (1)	21.7 (3)	19.9 (2)	119.9 (1)	112.8 (1)	1
	18.5 (1)	13.6 (2)		20.7 (1)	121.7 (2)	113.4 (2)	

^a CH₃ is near the metal. ^b CH₃ is away from the metal. ^c H's are proximal. ^d H's are distal. ^e Attached ethyl is proximal. ^f Attached ethyl is distal. ^g Numbers in parentheses give peak intensity.

Now that it is clearly established that the low temperature spectrum of (heb)Cr(CO)₂CS is that of the 1,3,5-proximal-2,4,6-distal conformer (1), we must rationalise the fact that the arene itself has approximate D_{3d} symmetry while the complex overall has C_s symmetry; the answer is unavoidable, we have stopped the tripodal rotation on the n.m.r. time scale! As a corollary it is appropriate to point out that, if (heb)Cr(CO)₂CS shows slowed tripodal rotation, then so do (heb)Cr(CO)₃, (heb)Mo(CO)₃, and (heb)W(CO)₃ which have almost identical structures and n.m.r. parameters. This result also allows us to disprove a widely adopted hypothesis,⁷ viz., that the ring carbons bonded to the presumably octahedrally co-ordinated metal atom are the more shielded. We can now see clearly that the directly bonded ring carbons (*i.e.* the proximal ones) are actually deshielded relative to their distal partners.

Finally, it is appropriate to reconcile our establishment of the 3-up-3-down isomer in solution with the convincing line-shape calculations of Hunter and Mislow.² This is not a problem; one need simply assign the ^{13}C n.m.r. peaks to the six label isomers of structure (1). As already pointed out,² if the assumed populations of the other isomers present, viz. (2), (3), and (4), do not exceed 5% of (1) the appearance of the simulated exchange-broadened spectrum is not materially affected. Thus, we reiterate our original statement¹ that (heb)Cr(CO)₂CS exhibits slowed tripodal rotation on the n.m.r. time scale. This in no way contradicts the Hunter-

Mislow proposal of uncorrelated ethyl rotation as the mechanism for interconverting proximal and distal ethyls; once the alkyl groups have rotated out of the path of the carbonyls the tripod can rotate without hindrance.

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