

Stopping a Chromium Carousel: X-Ray Crystallographic and Variable-temperature ^{13}C N.M.R. Studies on Dicarboxyl(hexaethylbenzene)-thiocarbonylchromium(0) and Related Complexes

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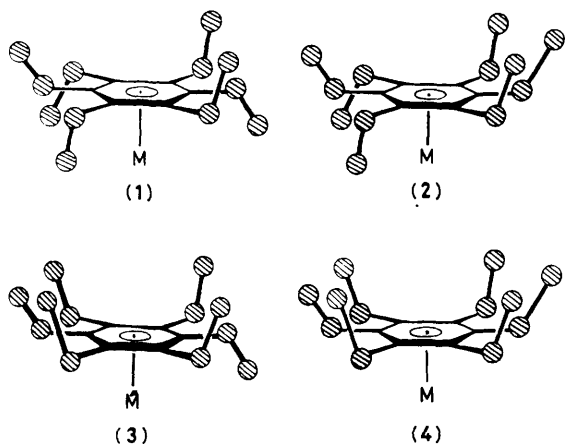
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The low temperature ^{13}C n.m.r. spectrum of $(\text{C}_6\text{Et}_6)\text{Cr}(\text{CO})_2\text{CS}$ shows the molecule to have C_s symmetry as it does in the solid state; this result provides the first clear evidence of cessation of tripodal rotation in a neutral half-sandwich compound of Cr.

Some years ago, we measured the solid state ^{13}C n.m.r. spectrum of (hexaethylbenzene)tricarbonylchromium(0), $(\text{heb})\text{Cr}(\text{CO})_3$. Since the methyl, methylene, and ring carbon resonances were all doubled, we proposed¹ a C_{3v} structure (1) with a fixed $\text{Cr}(\text{CO})_3$ tripod and ethyl groups projecting alternately

above and below the arene plane. Subsequently crystallographic and dynamic n.m.r. data were also compatible with this structure.^{2,3} In an attempt to stop tripodal motion on the n.m.r. time scale, Mislou examined a series of molecules $(\text{heb})\text{Cr}(\text{CO})_2\text{L}$, where $\text{L} = \text{CO}$, PEt_3 , and PPh_3 , and also



enumerated the various rotamers that might reasonably be expected to occur. These elegant studies revealed a correlation between the bulk of *L* and a tendency for the ethyl groups to remain on the distal (non-complexed) face of the arene. Thus, when *L* = PEt_3 and PPh_3 , respectively, the 1,2,3,4,5-distal-6-proximal (3) and all-distal (4) structures have been observed.^{2,4}

We now report that incorporation of a thiocarbonyl group⁵ yields the required 1,3,5-distal-2,4,6-proximal conformer which allows us to probe the rate of tripodal rotation.⁶

Photolysis of $(\text{heb})\text{Cr}(\text{CO})_3$ in cyclo-octene and subsequent treatment with CS_2 and PPh_3 gave $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$ in 84% yield. Recrystallisation from CH_2Cl_2 -hexane gave golden yellow cubes, m.p. 190 °C, ν_{CO} 1957 and 1900, ν_{CS} 1220 cm^{-1} . The crystal structure[†] (Figure 1) closely resembles that of (heb)

[†] Crystal data: $\text{C}_{21}\text{H}_{30}\text{CrO}_2\text{S}$, $M = 398.25$, monoclinic, $P2_1/c$, $a = 13.766(4)$, $b = 9.927(3)$, $c = 15.768(3)$ Å, $\beta = 100.57(2)^\circ$, $U = 2118(1)$ Å³, $Z = 4$, $D_c = 1.248$ g cm^{-3} , $D_m = 1.27(1)$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 6.60$ cm^{-1} . 4216 Unique reflections were recorded on a Syntex P3 diffractometer of which 2023 were considered observed [$I > 3\sigma(I)$]. The residuals are $R = 0.053$ and $R_w = 0.060$. The structure was solved by a combination of Patterson and Fourier difference techniques, and 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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

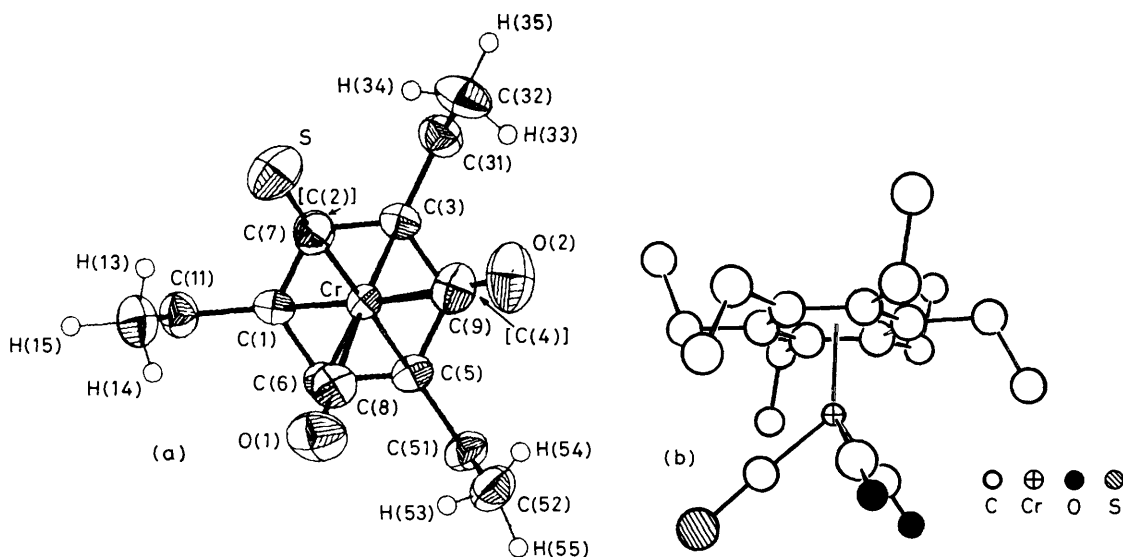


Figure 1. (a) View of the molecule $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$ showing the tripodal eclipsing (the distal ethyl groups have been omitted). (b) View showing the up-down alternation of the ethyl groups. (The atoms are represented by circles of arbitrary size.)

$\text{Cr}(\text{CO})_3$, except that the Cr atom is displaced slightly from the ring centre.

The 100.613 MHz ^{13}C n.m.r. spectra[‡] over the temperature range 163–308 K are shown in Figure 2 and exhibit 2:1:2:1 patterns of methyl, methylene, and aromatic ring carbons at 163 K entirely consistent with a molecule of C_s symmetry. Upon raising the temperature the small chemical shift differ-

[‡] Spectra were obtained on a Bruker WH 400 spectrometer; the solvent was CD_2Cl_2 , with Me_4Si as standard. The spectra can be simulated assuming a single process with ΔG ca. 48 kJ mol^{-1} ; at 163 K the peaks appear at δ 347.1 (CS); 234.7 (CO); 121.7, 119.9, 113.4, and 112.8 (C_{Ar}); 21.7, 20.7, and 19.9 (CH_2); 18.5, 17.8, 13.6, and 13.2 p.p.m. (CH_3).

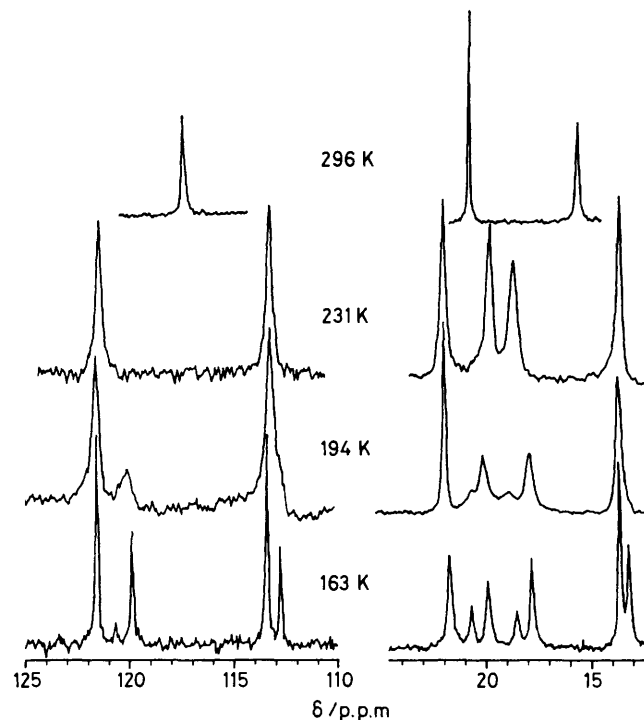


Figure 2. The variable-temperature 100.613 MHz ^{13}C n.m.r. spectra of $(\text{heb})\text{Cr}(\text{CO})_2\text{CS}$.

ence attributable to the proximity of the ethyl groups to either CO or CS is lost; thus at 231 K the spectrum resembles that of (heb)Cr(CO)₃ in which only the proximal and distal ethyls can be differentiated. Finally, when proximal-distal interconversion of the ethyls is rapid, only a single environment is seen for the methyl, methylene, and ring carbons. Mirror symmetry could arise either from conformation (1) with a static Cr(CO)₂CS tripod, as in the solid state structure, or conceivably from a conformation in which tripod rotation was rapid but the arene itself adopted C₈ geometry as in (2). However, even in such a 4-up-2-down structure, tripod rotation could not occur without turning the proximal ethyl-C(Ar) bond through about 50° towards the ring plane. Furthermore, in the only known example⁷ of such a geometry, viz., [(heb)Fe(C₅H₅)⁺][PF₆]⁻, the ethyl rotation cannot be stopped even at 153 K on a 400 MHz spectrometer.

The obvious inference is that ethyl rotation and/or tripod rotation can only be made slow on the n.m.r. time scale when there are steric constraints as in the molecules discussed here or when there is a strong electronic factor operating as in [(C₆H₅CR₂)Cr(CO)₃]⁺.⁸ We have observed similar behaviour in the molecules (heb)W(CO)₃, (heb)Mn(CO)₂CN, and (heb)-Fe(C₅Me₅)⁺ and have also encountered steric problems with (heb)₂Cr.

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