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An X-ray Crystallographic and High-Field NMR Study of $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$ and $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$: Steric Inhibition of Tripodal Rotation

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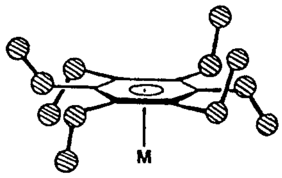
Abstract: Treatment of $(C_6Et_6)Cr(CO)_3$ (**1**) or $(C_6Et_6)Cr(CO)_2CS$ (**3**) with $NO^+BF_4^-$ yields $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$ (**9**) and $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$ (**10**), respectively. Crystals of **9** are orthorhombic, of space group $P2_12_12_1$, with a = 8.995(3) Å, b = 14.144(6) Å, c = 17.825 Å, and V = 2268(1) Å^3, for Z = 4. For **10**; a = 9.164(4) Å, b = 15.007(4) Å, c = 16.876 Å, and V = 2321(2) Å^3, for Z = 4 in the orthorhombic space group $P2_1nb$. The hexaethylbenzene ligand in **9** and in **10** adopts the 1,3,5-*proximal*-2,4,6-*distal* arrangement and the tripodal ligands eclipse the distal ethyl groups; the structures closely resemble those of **1** and **3**. Variable-temperature NMR data on **9** and **10** reveal that each molecule exists as a single conformer with the same structure as in the solid state. In particular, the chiral tripod in **10** renders nonequivalent every carbon in the molecule and the six different ethyl substituents are unambiguously assignable to three proximal and three distal environments. These observations, together with data on $(C_6Et_6)Cr(CO)_2CS$ (**3**), are rationalized in terms of two independent fluxional mechanisms. The higher energy process, for which $\Delta G^‡ \approx 11.5$ kcal mol^{-1}, involves uncorrelated rotation of the ethyl groups; the lower activation energy ($\Delta G^‡ \approx 9.5$ kcal mol^{-1}) represents the barrier to tripodal rotation. These results are in complete accord with the fluxional behavior of the closely analogous $(C_6Et_5COMe)Cr(CO)_3$ system in which the cessation of tripodal rotation on the NMR time scale has been unequivocally established.

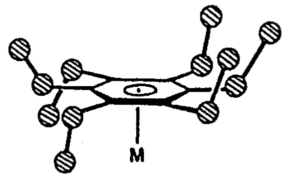
Introduction

Some years ago, in the course of our studies on the effects of π complexation of organometallic fragments on arene ring currents,[1] we measured the solid-state ^{13}C NMR chemical shift tensor elements of the complexed ring carbons of a series of (arene)-$Cr(CO)_3$ complexes.[2] To our surprise, however, the isotropic shift tensors for the molecule $(C_6Et_6)Cr(CO)_3$ (**1**) showed two environments for the methyl carbons, the methylene carbons, and also the aromatic carbon nuclei. The conclusion drawn was that the sixfold symmetry of the ring had been broken to C_3, thus making three alternating ring positions inequivalent to the intervening ones. Since a preliminary X-ray structure[3] of noncomplexed hexaethylbenzene (HEB) indicated that the ethyl groups projected alternately above and below the plane of the arene ring (giving a molecular point group of D_{3d}), we proposed[2] that the arene adopted the same conformation in $(HEB)Cr(CO)_3$ (**1**). Thus, the methyl carbons positioned *proximal* and *distal* to the $Cr(CO)_3$ group are rendered magnetically nonequivalent. Similarly, the methylene and arene ring carbons would be split in accordance with the overall C_{3v} symmetry of the complex.

Subsequently, we obtained the low-temperature ^{13}C NMR spectra of $(HEB)Cr(CO)_3$ in solution;[4] again, the methyl, methylene, and arene ring carbons are each split into two equally intense resonances. Contemporaneously, in an independent study prompted by our solid-state results, Mislow, Hunter, and their colleagues also investigated the solution NMR behavior of a series of HEB complexes.[5] They not only established the validity of our assumption that $(HEB)Cr(CO)_3$ (**1**) in the solid state adopts the alternating proximal–distal arrangement of ethyl groups but they also showed that the organometallic tripod is oriented such that the metal carbonyl ligands lie directly beneath the distal ethyls so as to minimize any steric interactions with the proximal alkyl chains. Furthermore, the authors of this important paper discussed the relative energies of the numerous conformers of HEB and showed the 1,3,5-distal-2,4,6-proximal isomer (a) to be favored over those structures which place adjacent ethyls on the same face of the arene. The highest energy conformation (h) is that in which all six ethyls are oriented the same way and the molecule has C_{6v} symmetry; of course, in a metal π complex of type h these six ethyls must all be distal with respect to the organometallic moiety. (The labeling of the conformers of HEB follows the notation introduced in ref 5.)



(a)



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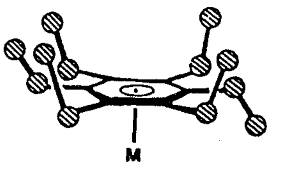

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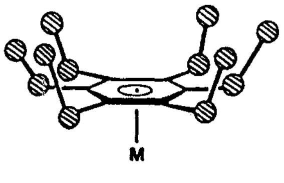

(h)

For a number of years, the question of the possibility of stopping the rotation of a $Cr(CO)_3$ tripod on the NMR time scale had been a somewhat contentious issue.[6] The experimental data were open

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Table I. ^{13}C NMR Data for Hexaethylbenzene–Metal Complexes[a]

		distal ethyl groups			proximal ethyl groups			
		CH_3	CH_2	CAr	CH_3	CH_2	CAr	ref
	(HEB)	15.5 [6]	21.6 [6]	137.2 [6]	–	–	–	5
1	(HEB)Cr$(CO)_3$	14.2 [3]	22.8 [3]	117.2 [3]	20.1 [3]	19.4 [3]	108.8 [3]	5
4	(HEB)Mo$(CO)_3$	14.4 [3]	22.8 [3]	121.6 [3]	23.4 [3]	19.5 [3]	114.7 [3]	5
7	(HEB)W$(CO)_3$	14.6 [3]	22.6 [3]	117.5 [3]	24.6 [3]	19.6 [3]	111.4 [3]	16
2	(HEB)Cr$(CO)_2$$PPh_3$	15.9 [6]	22.4 [6]	108.0 [6]	–	–	–	5
3	(HEB)Cr$(CO)_2$CS[b]	13.6 [2]	21.7 [3]	121.7 [2]	17.8 [2]	19.2 [2]	113.4 [2]	9
		13.2 [1]		119.9 [1]	18.5 [1]	20.7 [1]	112.8 [1]	
9	[(HEB)Cr$(CO)_2$NO]$^{+}$[c]	13.4 [2]	22.9 [2]	130.9 [2]	18.4 [2]	20.3 [2]	122.4 [2]	
		13.1 [1]	21.8 [1]	129.1 [1]	20.3 [1]	19.4 [1]	120.4 [1]	
10	[(HEB)Cr(CO)(CS)NO]$^{+}$	12.8 [1]	21.7 [1]	130.6 [1]	17.0 [1]	20.1 [2]	122.2 [1]	
		13.2 [1]	22.5 [1]	131.5 [1]	18.2 [1]	21.1 [1]	124.0 [1]	
		13.4 [1]	23.2 [1]	131.7 [1]	19.0 [1]		124.1 [1]	
11	(PEAP)Cr$(CO)_3$[d]	14.7 [1]	23.0 [1]	118.6 [1]	20.8 [2]	19.3 [2]	109.1 [2]	19

[a] Numbers in brackets give peak intensity. [b] Tripodal ligand shifts: **1**, CO, 235.4; **3**, CO, 234.7, CS, 347.1; **9**, CO, 226.2; **10**, CO, 223.6, CS, 351.5. [c] In the solid state, **9** exhibits resonances at 18.6 22.9 (CH_3); 24.9, 28.5 (CH_2); 125.5, 134.8 (C_{ar}); and 232 (CO). This deshielding of ≈5 ppm relative to the shifts in methylene chloride solution is entirely typical for such systems.[9] [d] PEAP, pentaethylacetophenone.

to conflicting interpretations, but the theoretical evidence was rather clear;[7] in the absence of strong electronic[8] or steric effects the barrier to tripodal rotation was calculated to be small—almost certainly too low to be detectable by NMR line-broadening techniques. We therefore set out to build molecules that might cast some new light on this problem.

Results and Discussion

(HEB)M$(CO)_2$L Complexes, L = CO, PPh_3, or CS. As first reported by Mislow, Hunter, and their colleagues the most favored conformation, i.e., the 1,3,5-distal-2,4,6-proximal arrangement of ethyls, is not always the one found in the solid state and in solution.[5] Thus, when **1** was allowed to react with triphenylphosphine, the resulting complex (HEB)Cr$(CO)_2$$PPh_3$ (**2**) exhibited a ^{13}C NMR spectrum that was essentially temperature-independent. The room temperature singlets for the methyl, methylene, and arene ring carbons remained unsplit at low temperature. This result is in accord with the X-ray crystal structure of **2**, which reveals that the bulky triphenylphosphine ligand causes all six ethyl groups to occupy distal positions and the HEB ligand itself maintains essentially C_{6v} symmetry, as in h.[5] At this point we reported the synthesis, X-ray crystal structure, and variable-temperature ^{13}C NMR spectra of (HEB)Cr$(CO)_2$CS (**3**).[9] The HEB ligand in **3** adopts a conformation almost identical with that in **1**; even the small angular perturbations within the ethyl groups (distal C_{ar}–CH_2–CH_3 112.1°; proximal C_{ar}–CH_2–CH_3 115.5°) are evident in **3** as they are in **1**. The ring centroid—chromium distance has increased from 1.725 Å in **1** to 1.774 Å in **3** but is, of course, shorter than the value of 1.911 Å in the molybdenum analogue **4**. Overall, these three molecular structures are remarkably similar.

At low temperature the ^{13}C NMR spectrum of **3** exhibits a 2:1:2:1 pattern for each of the ring carbon, methylene, and methyl environments. We chose to interpret this result in terms of slowed tripodal rotation since such a scenario would impose C_s symmetry on the molecule, i.e., a single mirror plane which would break the threefold degeneracy of the proximal and distal ethyl groups. This claim was challenged by Hunter and Mislow, who raised the possibility of a conformer of type (c) in which the hexaethylbenzene ligand itself possessed C_s symmetry and thus removed the necessity to invoke slowed rotation of the Cr$(CO)_2$CS tripod.[10]

Since that time, numerous HEB–metal complexes that do not adopt conformation a have been characterized crystallographically: [(HEB)Fe(C_5H_5)]$^{+}$$PF_6^{-}$ (**5**) (c);[11] (HEB)Cr$(CO)_2$$PMe_3$ (**6**) (c);[12] (HEB)Cr$(CO)_2$$PEt_3$ (e and h);[13] and [(HEB)Fe(C_5H_5)]$^{+}$$BPh_4^{-}$ (e).[14] Moreover, it has been reported that the corresponding ruthenium sandwich complex of **5**, i.e., [(HEB)Ru(C_5H_5)]$^{+}$$BF_4^{-}$, probably adopts conformation a at low temperature.[15]

The choice was thus clearly delineated: if (HEB)Cr$(CO)_2$CS (**3**) could be unequivocally shown to adopt conformation a in solution, then the assertion of restricted tripodal rotation would be on firm ground; for a it is only by freezing out the Cr$(CO)_2$CS rotation that one can generate a molecule possessing a single mirror plane. On the other hand, if it could be shown that the predominant isomers of **3** present in solution were c and/or e, then the cessation of tripodal rotation would remain an open question; the arene conformation itself would impose C_s symmetry on the molecule, and there would be no necessity to invoke slowed rotation of the tripod.

Subsequently we reported not only that the solid-state and low temperature solution ^{13}C data for (HEB)Cr$(CO)_2$CS (**3**) were remarkably similar but also that one could examine the trends in ^{1}H and ^{13}C NMR chemical shift data on the whole series of HEB complexes for which the structures were secure.[16] A particularly crucial piece of information was the assignment of the methyl and methylene carbon environments in (HEB)Cr$(CO)_2$$PPh_3$ (**2**); as clearly demonstrated by Hunter and Mislow, all the ethyl groups in this complex are distal with respect to the

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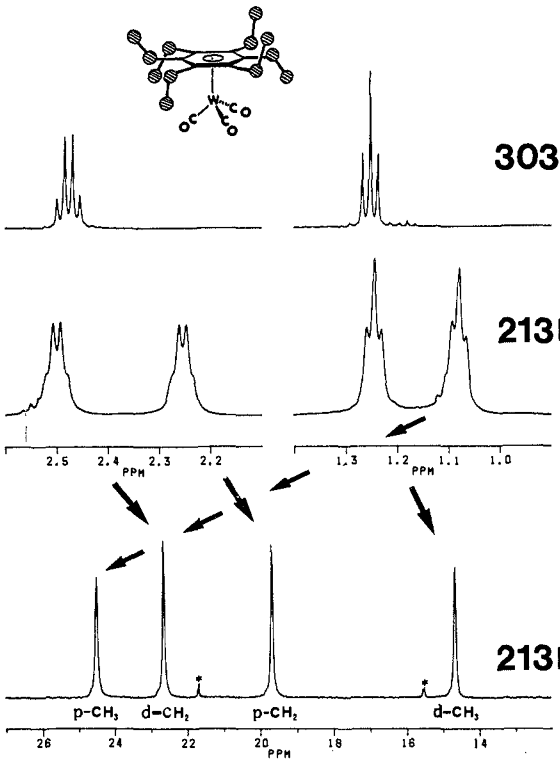


Figure 1. 500-MHz ^1H and 125.7-MHz ^{13}C NMR spectra of (HEB)W$(CO)_3$ (**4**) showing the proton–carbon connectivities established at 213 K. The proximal (p) and distal (d) environments are shown. The small peaks marked with an asterisk are hexaethylbenzene resonances.

organometallic moiety and so the ^{13}C resonance positions for the CH_3 (δ 15.9) and CH_2 (δ 22.4) units of a distal ethyl group are evident. Similarly, the complexes (HEB)M$(CO)_3$, where M = Cr (**1**), Mo (**4**), and W (**7**), exhibit methyl resonances at δ 14.2, 14.4, and 14.6, respectively, at low temperature;[5,16] we assign these relatively constant shifts to the distal methyl groups. In contrast, the proximal methyls fall in quite a different region (Cr, δ 20.1; Mo, δ 23.4; W, δ 24.6) and are to some extent affected by the identity of the nearby M$(CO)_3$ moiety. Analogously, the chemical shift ranges appropriate for methylene carbons in proximal and distal environments are readily assigned, as shown in Table I.

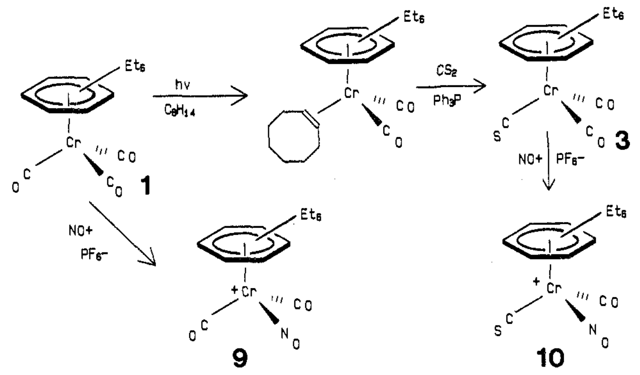
It has long been assumed that arene ring carbons which can be considered directly bonded to an octahedrally coordinated metal are shielded relative to their ring partners.[17] However, this assumption was only verified very recently when Pomeroy observed scalar coupling between the more shielded ring carbon and a *trans*-carbonyl ligand in [1,4-bis(*tert*-butyl)benzene]Ru(CO)$(SiCl_3)_2$—a molecule in which tripodal rotation has certainly stopped on the NMR time scale.[18] We follow this trend in assigning the directly bonded ring carbons, i.e., those attached to proximal ethyl groups, to the lower frequency (higher field) resonances, as in Table I.

Table II. ^1H NMR Data for Hexaethylbenzene-Metal Complexes[a]

		distal ethyl groups		proximal ethyl groups		
		CH_3	CH_2	CH_3	CH_2	ref
1	(HEB)Cr$(CO)_3$	1.16 [9]	2.49 [6]	1.12 [9]	2.24 [6]	6
4	(HEB)Mo$(CO)_3$	1.21 [9]	2.47 [6]	1.07 [9]	2.25 [6]	6
7	(HEB)W$(CO)_3$	1.23 [9]	2.49 [6]	1.06 [9]	2.24 [6]	16
3	(HEB)Cr$(CO)_2$CS	1.23 [9]	2.47 [6]	1.07 [9]	2.29 [6]	11
9	[(HEB)Cr$(CO)_2$NO]$^+$	1.28 [9]	2.58 [6]	1.13 [9]	2.44 [6]	
11	(PEAP)Cr$(CO)_3$[b]	1.30 [3]	2.60 [2]	1.28 [6]	2.36 [4]	19

[a] Numbers in brackets give peak intensity. [b] PEAP, pentaethylacetophenone.

Scheme I. Synthetic Routes to **9** and **10**



The low-temperature ^1H NMR spectra of the complexes (HEB)M$(CO)_3$, where M = Cr, Mo, or W, likewise show methyl and methylene resonances assignable to proximal and distal environments. It is, of course, obvious that proximal (distal) methyl protons will show scalar couplings to the neighboring methylene protons in the same proximal (distal) ethyl group and such connectivities are trivial to ascertain via double-resonance experiments or by two-dimensional techniques; such experiments have been carried out for the molecules **1**, **3**, and **7**–**9**. Furthermore, the corresponding carbon–proton connectivities are also unambiguously obtainable [as shown for (HEB)W$(CO)_3$ (**7**) in Figure 1], and the resulting assignments are collected in Table II.

Our original strategy for resolving the problem of arene–metal rotation was to split the threefold symmetry of the tripod and then detect this lowered symmetry by monitoring the chemical shifts of the methyl, methylene, and ring carbons of the HEB ligand. Our second approach involved the use of $(C_6Et_5COMe)Cr(CO)_3$ (**8**), in which the highest possible symmetry is C_s; this molecule adopts a conformation which closely mimics that of (HEB)Cr$(CO)_3$ (**1**). The 2:1 splitting of the $Cr(^{13}CO)_3$ signal in the solid state and in solution at −100 °C unequivocally demonstrated the cessation of tripodal rotation on the NMR time scale.[19] Furthermore, the X-ray structure of **8** together with the striking correspondence between the ^{13}C NMR data in both phases left no doubt that the arene ring substituents adopted the alternating proximal–distal arrangement.

We note particularly the ^{13}C NMR chemical shifts of the distal 4-ethyl substituent in **8**. The assignments are rendered completely unambiguous in this case since these resonances are only half as intense as those of the other ethyl groups. As shown in Table I, these methyl, methylene, and ring carbons are found at δ 14.68, 22.96, and 118.62, respectively. The corresponding values for the distal ethyl environments in (HEB)Cr$(CO)_3$ (**1**) are δ 14.2, 22.8, and 117.2, respectively. The analogous proximal ethyl chemical shifts for **8** (**1**) are δ 20.8 (20.1), 19.3 (19.4), and 109.1 (108.8). The assignment of the proximal and distal ethyl substituents in these closely related systems is quite unequivocal.[19] There is simply no evidence to support the suggestion[10] that any conformer other than a is present.

[(HEB)Cr$(CO)_2$NO]$^+BF_4^-$ and [(HEB)Cr(CO)(CS)(NO)]$^+$$BF_4^-$. Having established unequivocally not only that tripodal rotation can be slowed on the NMR time scale when proximal ethyl groups are present but also that distal and proximal environments can be readily distinguished, we chose to return to the original concept of using a hexaethylbenzene ligand and then systematically lowering the symmetry of the tripodal moiety. Clearly, it is necessary to incorporate sterically nondemanding ligands since bulky phosphines complicate the situation by generating mixtures of stereoisomers.[20] To this end, we chose to

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Table III. Bond-Length Data (Å) for Nitrosyl and Thiocarbonyl Complexes

	Cr–CO	C–O	Cr–CS	C–S[a]	Cr–NO	N–O	CTRD–Cr	ref
$(C_6H_5CO_2Me)Cr(CO)_2CS$	1.847	1.159	1.797	1.570	–	–	1.730	22b
	1.850	1.156						
$(\eta^5$-fluorenyl$)Cr(CO)_2NO$	1.864	1.145	–	–	1.687	1.169	1.883	22a
$(HEB)Cr(CO)_3$ (**1**)	1.818	1.162						
	1.823	1.164	–	–	–	–	1.725	5
	1.828	1.155						
$(HEB)Cr(CO)_2CS$ (**3**)	1.833	1.155	1.789	1.589	–	–	1.774	9
	1.820	1.169						
$[(HEB)Cr(CO)_2NO]^{+b}$ (**9**)	1.831*	1.178*	–	–	1.793*	1.165*	1.795	
	1.798*	1.157*						
$[(HEB)Cr(CO)(NO)CS]^+$ (**10**)	1.802	1.218	1.846	1.515	1.743	1.188	1.803	

[a] Cr···S distances: in $(C_6H_5CO_2Me)Cr(CO)_3$, 3.367; in **3**, 3.378; in **10**, 3.361. [b] In **9** the nitrosyl and carbonyl ligands are disordered; the assignments marked with an asterisk are arbitrary.

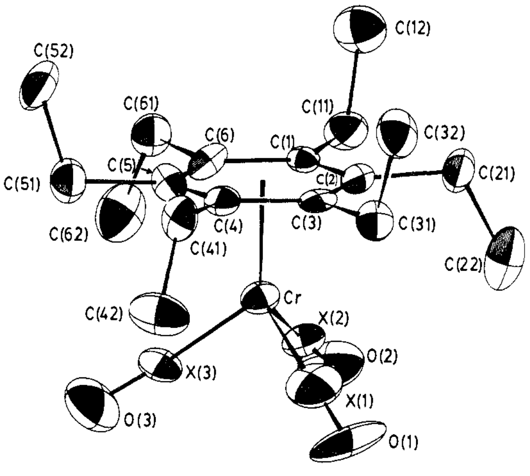

Figure 2. View of $[(C_6Et_6)Cr(CO)_2NO]^+$ cation.

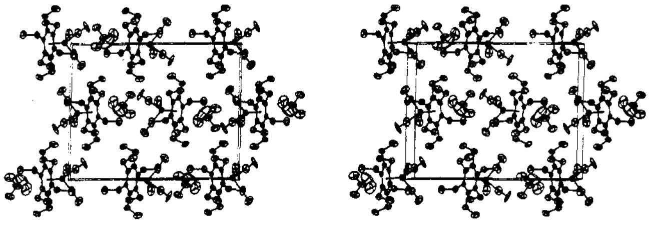

Figure 3. Stereoview of the unit cell of **9**; projection is [1 0 0].

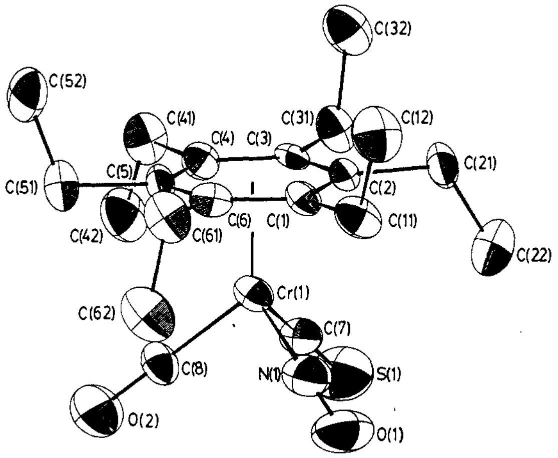

Figure 4. View of $[(C_6Et_6)Cr(CO)(CS)NO]^+$ cation.

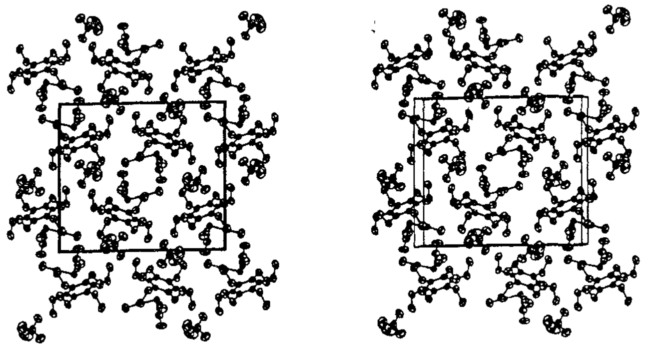

Figure 5. Stereoview of the unit cell of **10**.

synthesize other molecules in the $(HEB)Cr(CO)_2L$ series in which the new ligand is a small cylindrical one possessing essentially the same steric properties as the carbonyl group.

It has been shown that treatment of polyalkylated (arene)-$Cr(CO)_3$ complexes with a source of the nitrosonium ion yields the corresponding $[(arene)Cr(CO)_2NO]^+$ salt.[21] Accordingly, as shown in Scheme I, $(HEB)Cr(CO)_3$ (**1**) and $NO^+BF_4^-$ yielded orange crystals of $[(HEB)Cr(CO)_2NO]^+BF_4^-$ (**9**), suitable for structural determination by using X-ray diffraction techniques. Analogously, treatment of $(HEB)Cr(CO)_2CS$ (**3**) with $NO^+BF_4^-$ gave maroon crystals of $[(HEB)Cr(CO)(CS)(NO)]^+BF_4^-$ (**10**). Views of the $[(C_6Et_6)Cr(CO)_2NO]^+$ and $[(C_6Et_6)Cr(CO)(CS)(NO)]^+$ cations appear in Figures 2–5. In each case, the stereochemistry of the coordinated hexaethylbenzene moiety is remarkably similar to that found for the complexes $(HEB)Cr(CO)_3$ (**1**),[5] $(HEB)Mo(CO)_3$ (**4**),[5] and $(HEB)Cr(CO)_2CS$ (**3**),[9] with the ethyl groups adopting the 1,3,5-distal-2,4,6-proximal conformation, i.e., stereoisomer a. The $Cr(CO)_2NO$ and Cr(CO)(CS)(NO) tripods in **9** and **10**, respectively, adopt an eclipsed orientation with respect to the hexaethylbenzene such that the carbonyl, thiocarbonyl, and nitrosyl ligands are located almost directly below the distal ethyl groups; the torsional angles C(1)-Ctrd-Cr-X(1), C(3)-Ctrd-Cr-X(2), and C(5)-Ctrd-Cr-X(3) are ≤2.0°, where X is CO, CS, or NO and Ctrd is defined as the centroid of the ring given by averaging the coordinates of atoms C(1)–C(6).

Other structural features of **9** (**10**) also mimic those found in the aforementioned HEB complexes **1**, **3**, and **4**. The C_{ar}–CH_2–CH_3 bond angles of the proximal (noneclipsed) ethyl groups have increased relative to those found in free hexaethylbenzene.[5] The mean values are C_{ar}–CH_2–CH_3 distal 110.3° (110.9°) and C_{ar}–CH_2–CH_3 proximal 114.7° (115.4°); concomitantly, the terminal methyl carbons of the proximal ethyls are approximately 0.25 Å (0.22 Å) closer to the plane of the arene ring than are the corresponding carbon atoms of the distal ethyl groups. The ring centroid–chromium distance in **9** is 1.795 Å (1.803 Å in **10**), slightly longer than the value of 1.725 Å found in **1**; this lengthening is perhaps rationalizable in terms of enhanced back-donation from the chromium to the tripodal ligands in **9** and **10**. The stronger π-accepting ability of CS or NO^+ relative to CO presumably weakens the metal–arene interaction and so slightly lengthens the Cr–ring carbon bonds. Other $Cr(CO)_2L$ complexes that have been crystallographically characterized in-

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(20) Hunter, G.; Weakley, J. R.; Mislow, K.; Wong, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 577.

(21) Connelly, N. G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2334.

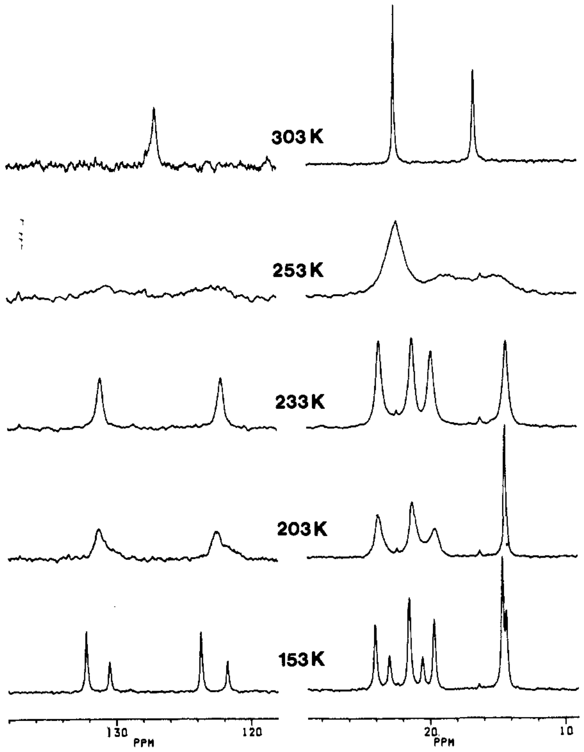

Figure 6. 125.7-MHz variable-temperature ^{13}C NMR spectra of $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$, (**9**).

clude $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$, $(\eta^5\text{-}C_{13}H_9)Cr(CO)_2NO$, and $(C_6H_5CO_2CH_3)Cr(CO)_2CS$.[22] The bond lengths and bond angles within the $Cr(CO)_2NO$ tripod of **9** are comparable to those found in the $(\eta^5\text{-}C_5H_5)$ complex, where disorder within the tripod exists.[22a] In contrast, in **10** the carbonyl and nitrosyl ligands can be differentiated, as shown in Table III. The related chiral system $[(C_5H_5)Mn(CS)(CO)NO]^+$ has been synthesized by Efraty,[23] but we are unaware of any crystallographic data on this cation.

The bond lengths and bond angles of the tetrafluoroborate anions are all normal and need not be further discussed. Stereoviews of the unit cell contents are given in Figures 3 and 5. The crystal packing appears to be determined by van der Waals forces, and no close intermolecular contacts are observed. The overall picture emerging from the X-ray structure determinations of **3**, **9**, and **10** is one in which one or more carbonyl ligands in $(HEB)Cr(CO)_3$ (**1**) have been replaced by isoelectronic CS or NO^+ fragments with essentially no change in the molecular geometry; indeed, one cannot with certainty differentiate crystallographically between the CO and NO sites in **9**.

The variable-temperature ^{13}C NMR spectra of **9** (see Figure 6) reveal that the methyl, methylene, and ring carbon sites undergo decoalescence such that each room temperature singlet exhibits a 2:1:2:1 pattern at 153 K. As with the other $(HEB)M(CO)_2L$ systems in which L is a cylindrical ligand with minimal steric requirement (i.e., CO or CS), the spectra are readily rationalizable in terms of the 1,3,5-distal-2,4,6-proximal conformation for the arene. Again, we see resonances (at δ 13.4 and 13.1) attributable to three methyls in distal positions and at δ 20.3 and 18.4 which are assignable to the three proximal methyl groups. As shown in Table I, there is always a clear distinction such that the ring carbons attached to proximal ethyl substituents are shielded by 6–8 ppm relative to those bearing distal ethyls. This pattern is also found in the solid-state CPMAS ^{13}C NMR spectrum of **9**, thus reinforcing the assignment of the conformation of the HEB ligand as being of type a.

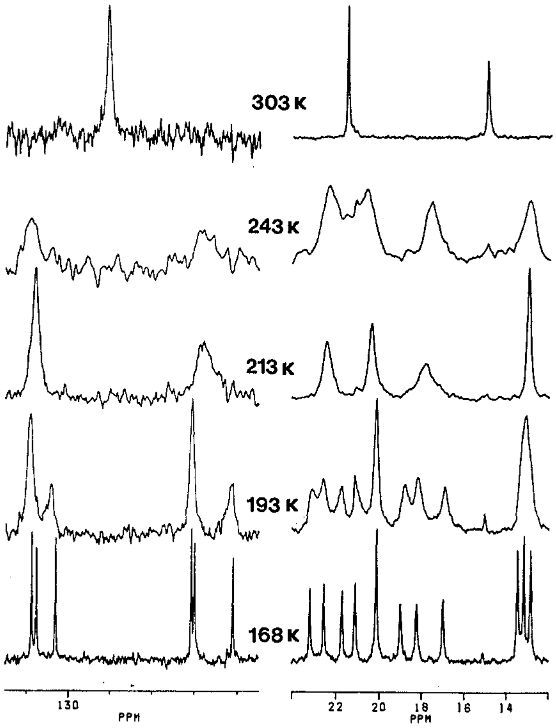

Figure 7. 125.7-MHz variable-temperature ^{13}C NMR spectra of $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$ (**10**).

We have seen that replacement of a carbonyl group in $(HEB)Cr(CO)_3$ (**1**) by either a thiocarbonyl or a nitrosyl ligand leaves the molecular geometry essentially unchanged but leaves the HEB ligand attached to a tripod possessing C_s symmetry; the molecule now possesses only a single mirror plane, and the arene resonances are each split into 2:1:2:1 peak patterns for the CH_3, CH_2, and C_{ar} environments. In principle, one could generate a chiral molecule (and thus render all the ethyls inequivalent) by replacement of one of the remaining carbonyls in either **3** or **9**. As described above, treatment of $(HEB)Cr(CO)_2CS$ (**3**) with $NO^+BF_4^-$ yielded the desired molecule $[(HEB)Cr(CO)(CS)NO]^+BF_4^-$ (**10**), which adopts conformation a in the solid state. Now, if **10** were to maintain this alternating proximal–distal orientation of ethyl groups and if tripodal rotation were to become slow on the NMR time scale, one would expect to see six methyl, six methylene, and six ring carbon resonances; moreover, in each case three of these six peaks should be found at chemical shifts appropriate for proximal ethyls and three for distal substituents.[24]

The ^{13}C NMR spectrum of $[(HEB)Cr(CO)(CS)NO]^+BF_4^-$ (**10**) at room temperature revealed, as one would have expected, singlets for the methyl, methylene, and ring carbon resonances. The onset of decoalescence is apparent at −30 °C and reveals two peaks for each of the CH_3, CH_2, and C_{ar} sites entirely analogous to that previously noted for $(HEB)Cr(CO)_3$, (**1**). The limiting NMR spectrum at −105 °C is shown in Figure 7 and can only be described as spectacular. Not only are the distal and proximal resonances clearly separated, but also they show three carbon environments for each case; i.e., all 18 carbons are readily differentiated. Even at 500 MHz we have not been able to unravel the six overlapping methyl and six methylene resonances in the ^1H NMR spectrum of **10**. Moreover, within each proximal and distal set we cannot definitively assign which CH_3, CH_2, and C_{ar} peaks are associated with the CO, CS, and NO ligands. For the molecules $(HEB)Cr(CO)_2L$, where L = CS or NO^+, the 2:1 peak intensities make such attributions obvious, but in **10** there are no

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[22] (a) (Cyclopentadienyl)Cr(CO)₂NO complexes: Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P.; Alt, H. G. *J. Organomet. Chem.* **1979**, *165*, 65. (b) (Arene)Cr(CO)₂CS complex: Saillard, J-Y.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409.

[23] Efraty, A.; Arneri, R.; Sikora, J. *J. Organomet. Chem.* **1975**, *91*, 65.

[24] We emphasize that the mere observation of six different ethyl resonances is insufficient to show unequivocally that tripodal rotation has slowed. In conformer c the 1,3-distal and the 2,4-proximal groups would be diastereotopic even when the chiral tripod is rotating. The crucial requirement is that the 1,3,5-distal-2,4,6-proximal peak pattern be retained.

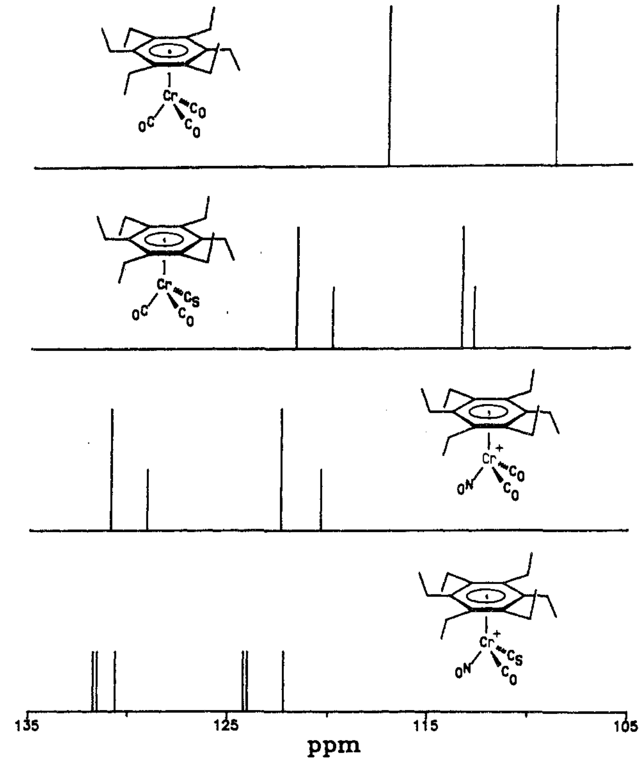

Figure 8. ^{13}C NMR chemical shift patterns for the aromatic ring carbons of complexes **1**, **3**, **9**, and **10**.

degeneracies to help resolve such problems. Nevertheless, as shown in Figure 8, it is clear that for molecules **3** and **9** the lower frequency (more shielded) carbon resonances are associated with those ligands which are the better π acceptors. Tentatively, therefore, we assign the most shielded resonance in each of the proximal sets as being trans to the nitrosyl ligand; however, in the absence of carbon-carbon coupling data such as could be obtained in an INADEQUATE[25] experiment, these assignments must remain speculative.

Simulation of the variable-temperature spectra of **10** was carried out, as shown in Figure 9. It is necessary to invoke two separate rate processes: the first involves interconversion **within** distal and **within** proximal environments. By use of the methyls as an example, the distal methyls at δ 12.8, 13.2, and 13.4 exchange among themselves while mutual interchange among the proximal methyls at δ 17.0, 18.2, and 19.0 is also occurring. The activation energy barrier for this low-energy process is $\approx$9.5 kcal mol^{-1}. The second and higher energy process brings about exchange **between** proximal and distal sites and has a barrier of $\approx$11.5 kcal mol^{-1}. These results are in excellent accord with other NMR spectral simulations in (HEB)CrL^{1}L^{2}L^3 systems where the tripodal ligands are CO, CS, or NO$^+$. Thus, in (HEB)Cr(CO)$_3$ (**1**) only proximal-distal exchange can be detected, and it has a barrier of $\approx$11.5 kcal mol^{-1}. In contrast, in (HEB)Cr(CO)$_2$CS (**3**), [(HEB)Cr(CO)$_2$NO]$^+$ (**9**), and [(HEB)Cr(CO)(CS)NO]$^+$ (**10**), there are two detectable processes, the first (viz. tripodal rotation) requires that one overcome an activation energy barrier of $\approx$9.5 kcal mol^{-1}, while the second process (ethyl rotation) is somewhat more difficult and requires $\approx$11.5 kcal mol^{-1}. We note also that the barrier to tripodal rotation in (C_6Et_5COMe)Cr(CO)$_3$ (**8**) is estimated to be $\approx$9 kcal mol^{-1}.[19] It is now apparent that the careful line-shape calculations of Hunter and Mislow on (HEB)Cr(CO)$_2$CS (**3**), which provided a reliable value of 9.4 kcal mol^{-1} for the lower energy process,[20] are in fact measuring the barrier to tripodal rotation, not ethyl rotation. This is no way invalidates their major conclusion that proximal-distal exchange proceeds via uncorrelated ethyl rotations. Indeed, we have also carried out simulations that involve correlated motion to interchange all six ethyls simultaneously; however, they give very poor agreement with the experimental spectra.

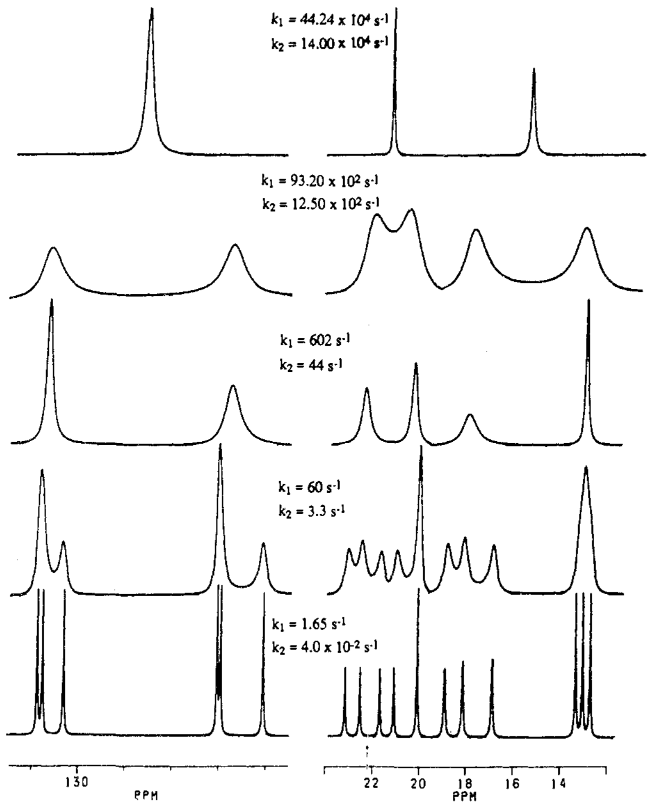

Figure 9. Simulations of the variable-temperature ^{13}C NMR spectra of **10**. Rate constant k_1 is for the mutual exchange within proximal and within distal environments. Rate constant k_2 describes exchange between proximal and distal sites. These data yield activation energies of 9.5 ± 0.4 and 11.4 ± 0.4 kcal mol^{-1}, respectively.

Since it is now established that the low-temperature ^{13}C NMR spectra of the complexes **1**, **3**, **4**, and **7**–**10** are of molecules in which tripodal rotation of the ML$_3$ moiety can become slow on the NMR time scale, one can directly evaluate the influence of a given ligand, CO, CS, or NO$^+$, on the ring carbon trans to it. A particularly noteworthy observation is that incorporation of a thiocarbonyl or nitrosyl ligand in place of a carbonyl group in (arene)Cr(CO)$_3$ complexes leads to a marked deshielding of the ring carbon nuclei.[21,26] The logical deduction might well have been that in a normal system, in which tripodal rotation is unhindered, the carbons trans to the CS or NO$^+$ ligands experience relatively large shifts to high frequency, resulting in an overall deshielding effect on the time-averaged ring carbon shift. We can now see that such a deduction would have been erroneous. In (HEB)Cr(CO)$_2$CS (**3**) and [(HEB)Cr(CO)$_2$NO]$^+$ (**9**), the carbons situated trans to the CS or NO$^+$ ligands are clearly the more shielded! In each case the spectra exhibit 2:1 patterns such that the unique ring carbon (which must be one associated with the non-carbonyl ligand) resonates at lower frequency than its doubly intense partners, as shown schematically in Figure 8. Thus, although the *overall* effect of substituting a CO by a CS or NO$^+$ ligand in an (arene)Cr(CO)$_3$ complex is to deshield the ring carbons, the *isolated* effect of a thiocarbonyl or nitrosyl ligand is to shield the carbon trans to it relative to the situation when the trans ligand is CO. The strong π-accepting ability of a CS or NO$^+$ ligand relative to that of CO results in decreased π back-donation from the metal to the remaining carbonyl ligands and is reflected in increased ν_{CO} frequencies in the infrared and also the shielding of the ^{13}CO NMR resonances.[21,26] This phenomenon must have the secondary effect of deshielding the ring

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[25] Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.

[26] (a) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359. (b) Cozac, D.; Butler, I. S.; Baibich, I. M. *J. Organomet. Chem.* **1979**, *169*, 381. (c) Herberhold, M.; Smith, P. D.; Alt, H. G. *J. Organomet. Chem.* **1980**, *191*, 79.

carbons trans to the remaining carbonyl ligands. Hence, even though the strong π-acceptor ligands shield the ring carbons trans to themselves, the global effect of replacing a CO moiety by CS or NO^+ is to increase the mean resonance frequency of the ring carbons. In **9** and **10** the presence of a formal positive charge seems to have little effect on the absolute chemical shifts of the ethyl carbons, but the shifts of the ring carbons and of the ethyl protons do reflect the lowered electron density in the cation.

The conclusions we have drawn from these experiments must be placed in context with some recent studies concerning other metal π complexes of sterically demanding arenes. In particular, we note that Herrmann has prepared $[(HEB)Mo(CO)_3Cl]^+$-$MoCl_6^-$ (**11**), in which the chlorine and the three carbonyl ligands occupy the vertices of a square-based pyramid capped by the molybdenum atom.[27] In this complex, the hexaethylbenzene exists as yet another stereoisomer, viz., the 1,2,4,5-distal-3,6-proximal conformer (b), which presumably minimizes the interactions between the ethyl substituents and the ligands on the metal without having to resort to the high-energy all-distal arrangement. No variable-temperature NMR data have yet been reported on this fascinating molecule. However, in the closely analogous protonated species $[(HEB)M(CO)_3H]^+$, where M = Cr, Mo, or W, the cation has C_{3v} symmetry since the hexaethylbenzene ligand retains conformation a but the proton attacks along the threefold axis.[28] Another relevant study is that carried out by Pomeroy,[18] who examined the complex (1,4-di-*tert*-butylbenzene)Ru(CO)-$(SiCl_3)_2$. In this and related molecules the tripodal RuL_3 fragment exhibits slowed rotation on the NMR time scale at low temperature. It was suggested that, to stop rotation of the organometallic moiety, it is necessary to incorporate bulky ligands on the metal as well as sterically demanding substituents on the arene. In light of the present observations one might propose that, unlike 1,4-disubstituted arenes bearing bulky substituents, hexaethylbenzene resists ring deformation or ring tilting and thus the steric hindrance to $Cr(CO)_3$ rotation is not removed. We note also some particularly interesting recent reports by Hunter et al. that use of the 1,3,5-tris[(trimethylsilyl)methyl]-2,4,6-triethylbenzene ligand or other very bulky arenes provides very strong evidence for restricted tripodal rotation.[29,30] Finally, we note that Hunter has reported the structure of $(C_6Pr_6)Cr(CO)_2PPh_3$ in which all six *n*-propyl substituents are distal.[31]

To conclude, we believe that we have observed slowed rotation about the arene–metal bond in molecules of the type [1,3,5-distal-2,4,6-proximal-hexaethylbenzene]$Cr(CO)L^1L^2$, where L^1 = CO, L^2 = CS, **3**, L^1 = CO, L^2 = NO^+, **9**, or L^1 = CS, L^2 = NO^+, **10**, and, by implication, in **1**, where $L^1 = L^2$ = CO. The strikingly good correlations between the structural data and the ^{13}C NMR parameters for this set of complexes provide compelling evidence that all of the molecules adopt conformation a, in which the ethyl groups are oriented alternately proximal and distal. Moreover, this series provides an excellent opportunity to examine not only the rotational behavior of the ethyl groups attached to the arene but also the electronic effects brought about at the arene ring carbons by different ligands bonded to the metal. Normally, such localized effects are only detectable by use of techniques such as vibrational spectroscopy or X-ray crystallography for which the time scale of the interaction is very fast. However, in systems such as **3**, **9**, and **10** the ligands are essentially locked in place and so the time scale moves into the NMR regime. In complexes for which tripodal rotation is rapid, one sees only the average shift brought about at the ring carbons by all the groups attached to the metal rather than the specific contributions of each individual ligand. It is now apparent that π complexes of hexaethylbenzene can exhibit great conformational variability and that the orientations of the ethyl groups are a reflection of the steric requirements of the ligands attached to the metal.[20] We are currently extending these ideas to other chiral $(HEB)CrL^1L^2L^3$ systems in which the three ligands are all linear and stereochemically nondemanding, such as C≡O, C≡S, N≡O, N≡N, C≡N, C≡C—R, and C≡N—R; these molecules will be the subject of further papers.

Table IV. Crystal Data for $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$ (**9**) and $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$ (**10**)

	9	**10**
formula	$C_{20}H_{30}O_3NBF_4Cr$	$C_{20}H_{30}O_2NSBF_4Cr$
formula wt	471.26	487.32
system	orthorhombic	orthorhombic
systematic absences	$h00$, $h \neq 2n$	$h0l$, $h + l \neq 2n$, $hk0$, $k \neq 2n$
	$0k0$, $k \neq 2n$	$h00$, $h \neq 2n$, $0k0$, $k \neq 2n$
	$00l$, $l \neq 2n$	$00l$, $l \neq 2n$
space group	$P2_12_12_1$, No-19	$P2_1nb$, No-33
a, Å	8.995 (3)	9.164 (4)
b, Å	14.144 (6)	15.007 (4)
c, Å	17.825 (5)	16.876 (7)
V, Å^3	2268 (1)	2321 (2)
Z	4	4
D_c, g cm^{-3}	1.38	1.39
D_m, g cm^{-3}	1.38	1.39
$F(000)$	985.6 (984)	1018.05 (1016)
μ(Mo Kα), cm^{-1}	5.84	6.12
final R_1, R_2	0.0893, 0.0786[b,d]	0.0763, 0.0683[b,f]
weighting scheme	$w = (\sigma^2F + 0.0013F^2)^{-1}$	$w = (\sigma^2F + 0.0008F^2)^{-1}$
GOF[c]	1.1086	1.2987
highest peak, eÅ^{-3}	0.89[e]	0.40[g]
lowest peak, eÅ^{-3}	−0.64	−0.42

[a] Alternate setting of $Pna2_1$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. [c] $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. m = no. of reflections; n = no. of variables. [d] R_1, R_2 for 1795 reflections with $I > 3\sigma(I)$ 0.0522 and 0.0508, respectively. [e] −0.042, 0.002, −0.480; 1.05 Å from Cr. [f] R_1, R_2 for 1125 reflections with $I > 2.5\sigma(I)$ 0.0489 and 0.0470, respectively. [g] 0.249, 0.438, 0.016; 0.69 Å from H(34).

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[32] ^1H and ^{13}C NMR spectra were recorded at 500 and 125.7 MHz, respectively, by using a Bruker AM500 spectrometer equipped with a 5-mm dual-frequency $^1H/^{13}C$ probe. All spectra were measured in methylene-d_2 chloride, and chemical shifts are reported relative to tetramethylsilane. Solid-state ^{13}C spectra were obtained at 25.18 MHz on a Bruker MSL100 operating at 2.35 T. The CPMAS spectra were obtained by using a 1-ms contact time and a recycle time of 10 s. NMR simulations were carried out by using DNMR3[33] and also the multisite EXCHANGE program generously provided by Professor R. E. D. McClung (University of Alberta at Edmonton). Infrared data were obtained on a Perkin-Elmer 283 spectrometer using either NaCl solution cells or KBr pellets. Fast atom bombardment (FAB) mass spectrometry was performed on a VG Analytical micromass ZAB-SE reversed-geometry double-focusing mass spectrometer with an accelerating potential of 8 kV and equipped with a VG11/250 data system. 3-Nitrobenzyl alcohol was used as the sample matrix and Xe as the bombarding gas. Analytical data are from Guelph Chemical Laboratories, Guelph, ON.

Tricarbonyl(η^6-hexaethylbenzene)chromium(0) (**1**) and dicarbonyl-(η^6-hexaethylbenzene)thiocarbonylchromium(0) (**3**) were prepared according to literature methods.[2,9]

Dicarbonyl(η^6-hexaethylbenzene)nitrosoniumchromium(I) Tetrafluoroborate (9). (HEB)$Cr(CO)_3$ (1.48 g, 3.9 mmol) and nitrosyl tetrafluoroborate (0.49 g, 4.2 mmol) were dissolved in 20 mL of a 50/50 mixture of methanol and toluene at ambient temperature under an at-

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(27) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *Polyhedron* **1988**, *7*, 2027.

(28) Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1990**, *9*, 1089.

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Table V. Positional Parameters (×10^4) and U_{eq} (Å^2) (×10^4) for $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$ (**9**) with Standard Errors in Parentheses

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cr	8486.6 (12)	9912.6 (8)	5387.7 (6)	304
C(1)	8957 (6)	9642 (5)	6634 (3)	212
C(11)	10336 (9)	9288 (6)	7040 (4)	424
C(12)	10055 (10)	9257 (6)	7877 (5)	564
C(2)	7852 (9)	8992 (5)	6404 (4)	258
C(21)	8011 (9)	7937 (5)	6566 (4)	409
C(22)	8818 (11)	7386 (6)	5935 (5)	655
C(3)	6554 (8)	9325 (5)	6063 (3)	230
C(31)	5338 (8)	8638 (5)	5819 (4)	323
C(32)	4269 (9)	8455 (6)	6468 (5)	485
C(4)	6309 (9)	10328 (5)	5970 (4)	289
C(41)	4808 (8)	10685 (5)	5647 (4)	367
C(42)	4741 (10)	10783 (6)	4812 (4)	564
C(5)	7425 (6)	10968 (5)	6188 (4)	287
C(51)	7158 (9)	12029 (5)	6109 (5)	428
C(52)	6428 (11)	12432 (5)	6826 (5)	554
C(6)	8729 (9)	10645 (5)	6527 (4)	325
C(61)	9918 (9)	11333 (5)	6821 (4)	397
C(62)	11093 (10)	11619 (6)	6253 (6)	649
X(1)	7762 (8)	9193 (5)	4616 (4)	605
X(2)	10349 (9)	9489 (5)	5240 (4)	352
X(3)	8752 (9)	10899 (6)	4770 (4)	407
O(1)	7259 (6)	8746 (5)	4120 (3)	789
O(2)	11555 (6)	9223 (5)	5164 (3)	703
O(3)	8886 (8)	11571 (5)	4398 (4)	811
B	9274 (13)	4504 (8)	1867 (6)	539
F(1)	10532 (10)	4878 (8)	2139 (5)	1739
F(2)	9607 (6)	3752 (3)	1451 (3)	775
F(3)	8632 (10)	5187 (4)	1446 (4)	1361
F(4)	8740 (11)	4293 (6)	2460 (4)	1641

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table VI. Positional Parameters (×10^4) and U_{eq} (Å^2) (×10^4) for $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$ (**10**) with Standard Errors in Parentheses

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cr	0	1548.4 (9)	886.0 (8)	352
C(1)	1914 (10)	2085 (6)	1606 (6)	368
C(11)	3128 (11)	1574 (6)	1992 (5)	442
C(12)	4209 (13)	2187 (8)	2441 (6)	611
C(2)	2073 (11)	2408 (6)	793 (5)	328
C(21)	3508 (12)	2250 (6)	376 (6)	462
C(22)	3635 (13)	1391 (8)	−105 (6)	636
C(3)	935 (11)	2891 (6)	443 (5)	284
C(31)	1125 (12)	3250 (6)	−400 (6)	448
C(32)	1794 (13)	4173 (8)	−366 (6)	586
C(4)	−368 (10)	3064 (6)	861 (5)	340
C(41)	−1579 (13)	3617 (6)	477 (6)	496
C(42)	−2700 (13)	3085 (8)	3 (6)	632
C(5)	−524 (10)	2758 (6)	1656 (5)	341
C(51)	−1912 (12)	2981 (6)	2116 (6)	463
C(52)	−1779 (15)	3893 (8)	2525 (6)	642
C(6)	629 (12)	2287 (6)	2035 (6)	385
C(61)	502 (12)	2026 (6)	2901 (6)	530
C(62)	−172 (16)	1096 (8)	3042 (6)	639
C(7)	−242 (13)	1265 (6)	−170 (6)	441
C(8)	−1829 (12)	1156 (6)	1064 (5)	408
N	719 (11)	489 (6)	1047 (5)	555
S	−406 (5)	1003 (2)	−1033 (2)	800
O(1)	1205 (11)	−232 (5)	1172 (5)	767
O(2)	−3061 (10)	888 (6)	1194 (6)	830
B	−1112 (23)	5345 (11)	−1657 (9)	749
F(1)	−149 (15)	5172 (6)	−2264 (5)	1397
F(2)	−1497 (10)	4586 (5)	−1315 (4)	891
F(3)	−2271 (13)	5740 (6)	−2031 (6)	1518
F(4)	−478 (13)	5935 (5)	−1177 (4)	1160

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

mosphere of nitrogen. The reaction mixture was stirred for approximately 2 h, during which time carbon monoxide evolved. Ether was added to precipitate the salt, and the solid was then collected by suction filtration and washed with ether. Recrystallization from CH_2Cl_2/C_6H_6 yielded **9** as orange crystals (0.61 g, 1.3 mmol; 32%): mp 160 °C dec; FAB mass spectrum *m/z* (%) 384 (100) $C_{20}H_{30}CrNO_3$ $(M - BF_4)^+$, 356 (5) $C_{19}H_{30}CrNO_2$ $(M - BF_4 - CO)^+$, 328 (78) $C_{18}H_{30}CrNO$ $(M - BF_4 - 2CO)^+$, 298 (24) $C_{18}H_{30}Cr$ $(M - BF_4 - 2CO - NO)^+$, 246 (8) $C_{20}H_{30}$ $(HEB)^+$; IR (CH_2Cl_2) ν_{CO} at 2015 and 2062 cm^{-1}, ν_{NO} at 1765 cm^{-1}. ^1H and ^{13}C NMR data are collected in Tables I and II. Anal. Calcd for $C_{20}H_{30}BCrF_4NO_3$: C, 50.98; H, 6.37; N, 2.97. Found: C, 50.69; H, 6.71; N, 2.94.

Table VII. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[(C_6Et_6)Cr(CO)_2NO]^+BF_4^-$ (**9**) with Estimated Standard Deviations in Parentheses

	Chromium Coordination		
Cr–C(1)	2.293 (6)	Cr–X(1)	1.831 (8)
Cr–C(2)	2.303 (7)	Cr–X(2)	1.798 (8)
Cr–C(3)	2.273 (7)	Cr–X(3)	1.793 (8)
Cr–C(4)	2.294 (8)	X(1)–O(1)	1.178 (9)
Cr–C(5)	2.275 (7)	X(2)–O(2)	1.157 (9)
Cr–C(6)	2.290 (7)	X(3)–O(3)	1.165 (9)
Cr–Ctrd	1.795 (3)		
Cr–X(1)–O(1)	178.0 (7)	Ctrd–Cr–X(1)	124.1
Cr–X(2)–O(2)	178.2 (7)	Ctrd–Cr–X(2)	123.2
Cr–X(3)–O(3)	176.2 (7)	Ctrd–Cr–X(3)	124.5
	Hexaethylbenzene		
C(1)–C(2)	1.415 (9)	C(4)–C(41)	1.552 (10)
C(2)–C(3)	1.398 (10)	C(5)–C(51)	1.526 (10)
C(3)–C(4)	1.445 (9)	C(6)–C(61)	1.539 (10)
C(4)–C(5)	1.407 (10)	C(11)–C(12)	1.515 (10)
C(5)–C(6)	1.397 (10)	C(21)–C(22)	1.550 (11)
C(6)–C(1)	1.445 (9)	C(31)–C(32)	1.526 (10)
C(1)–C(11)	1.521 (10)	C(41)–C(42)	1.496 (10)
C(2)–C(21)	1.526 (10)	C(51)–C(52)	1.544 (11)
C(3)–C(31)	1.526 (10)	C(61)–C(62)	1.518 (12)
C(6)–C(1)–C(2)	120.0 (7)	C(3)–C(4)–C(5)	119.4 (7)
C(11)–C(1)–C(2)	119.8 (6)	C(41)–C(4)–C(5)	120.9 (6)
C(11)–C(1)–C(6)	120.1 (7)	C(41)–C(4)–C(3)	119.6 (7)
C(1)–C(11)–C(12)	110.0 (6)	C(4)–C(41)–C(42)	115.7 (7)
C(1)–C(2)–C(3)	119.6 (6)	C(4)–C(5)–C(6)	120.5 (6)
C(21)–C(2)–C(3)	119.4 (7)	C(51)–C(5)–C(6)	119.6 (7)
C(21)–C(2)–C(1)	121.0 (7)	C(51)–C(5)–C(4)	119.7 (6)
C(2)–C(21)–C(22)	113.4 (7)	C(5)–C(51)–C(52)	110.7 (6)
C(2)–C(3)–C(4)	120.5 (7)	C(5)–C(6)–C(1)	119.8 (7)
C(31)–C(3)–C(4)	118.9 (7)	C(61)–C(6)–C(1)	118.6 (7)
C(31)–C(3)–C(2)	120.5 (6)	C(61)–C(6)–C(5)	121.6 (6)
C(3)–C(31)–C(32)	110.1 (6)	C(6)–C(61)–C(62)	115.1 (6)
	Tetrafluoroborate Anion		
B–F(1)	1.340 (13)	F(1)–B–F(2)	109.1 (9)
B–F(2)	1.331 (11)	F(1)–B–F(3)	106.3 (10)
B–F(3)	1.353 (12)	F(1)–B–F(4)	105.2 (10)
B–F(4)	1.316 (13)	F(2)–B–F(3)	111.0 (9)
F(2)–B–F(4)	113.0 (9)		
F(3)–B–F(4)	111.9 (10)		

Carbonyl(η^6-hexaethylbenzene)thiocarbonylnitrosoniumchromium(I) Tetrafluoroborate (10). $(HEB)Cr(CO)_2CS$ (0.0955 g, 0.24 mmol) was dissolved in 4 mL of a 50/50 mixture of toluene and methanol, and the solution was degassed for 5 min. Nitrosyl tetrafluoroborate (0.03 g, 0.26 mmol, 10% excess) was added and stirred at room temperature for 2 h, during which time the evolution of CO was monitored. Anhydrous ether (60 mL) was added to the reaction flask, which was then allowed to cool in the refrigerator for 1 day. Maroon needle-like crystals deposited upon cooling and were collected by suction filtration to give **10** (0.0116 g, 10%): mp 150 °C dec; FAB mass spectrum (positive ion) *m/z* (%) 400 (100) $C_{20}H_{30}CrO_2NS$ $(M)^+$, 372 (68) $C_{19}H_{30}CrONS$ $(M - CO)^+$, 328 (12) $C_{18}H_{30}CrON$ $(M - CO - CS)^+$, 298 (11) $C_{18}H_{30}Cr$ $(M - CO - CS - NO)^+$; FAB mass spectrum (negative ion) *m/z* (%) 87 (100) BF_4 $(M)^-$; IR (KBr) ν_{CO} at 2015 cm^{-1}, ν_{NO} at 1752 cm^{-1}, ν_{CS} at 1300 cm^{-1}. Anal. Calcd for $C_{20}H_{30}CrO_2NSBF_4$: C, 49.3; H, 6.16; N, 2.88; S, 6.57. Found: C, 49.57; H, 5.96; N, 2.82; S, 6.58.

X-ray Crystallography of 9 and 10. The densities were determined by flotation in aqueous zinc chloride solution. A well-formed orange (maroon) parallelepiped crystal of **9** (**10**) was sealed in a Lindemann capillary tube. Precession photographs revealed the symmetry of the crystals, and unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $15.4° < 2\theta < 21.6°$ ($14.4° < 2\theta < 24.8°$). Data were collected on a Nicolet P3 diffractometer with the use of Mo Kα radiation (λ = 0.71069 Å at 22 °C). Corrections for Lorentz and polarization effects and absorption (ψ scans) were applied to all reflections. Two standard reflections (0,2,−4 1.84% and −1,−1,−2 1.36% for **9**), (1,6,3 1.46% and −1,3,5 1.77% for **10**) monitored every 48 reflections showed no sign of crystal decomposition. Crystal data and other

Table VIII. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[(C_6Et_6)Cr(CO)(CS)NO]^+BF_4^-$ (**10**) with Estimated Standard Deviations in Parentheses

	Chromium Coordination		
Cr–C(1)	2.281 (9)	Cr–C(7)	1.846 (10)
Cr–C(2)	2.302 (9)	Cr–C(8)	1.802 (11)
Cr–C(3)	2.313 (8)	Cr–N	1.743 (10)
Cr–C(4)	2.300 (9)	C(7)–S	1.515 (10)
Cr–C(5)	2.283 (9)	N–O(1)	1.188 (10)
Cr–C(6)	2.307 (10)	C(8)–O(2)	1.218 (12)
Cr–Ctrd	1.803 (4)		
Cr–C(7)–S	177.9 (7)	Ctrd–Cr–C(7)	123.9
Cr–N–O(1)	178.7 (9)	Ctrd–Cr–N	125.8
Cr–C(8)–O(2)	179.2 (9)	Ctrd–Cr–C(8)	126.5
	Hexaethylbenzene		
C(1)–C(2)	1.463 (13)	C(4)–C(41)	1.531 (13)
C(2)–C(3)	1.400 (13)	C(5)–C(51)	1.528 (13)
C(3)–C(4)	1.411 (13)	C(6)–C(61)	1.518 (13)
C(4)–C(5)	1.426 (13)	C(11)–C(12)	1.550 (14)
C(5)–C(6)	1.423 (13)	C(21)–C(22)	1.528 (14)
C(6)–C(1)	1.416 (13)	C(31)–C(32)	1.516 (15)
C(1)–C(11)	1.500 (13)	C(41)–C(42)	1.527 (15)
C(2)–C(21)	1.510 (13)	C(51)–C(52)	1.536 (14)
C(3)–C(31)	1.532 (12)	C(61)–C(62)	1.544 (14)
C(6)–C(1)–C(2)	119.4 (9)	C(3)–C(4)–C(5)	119.7 (8)
C(11)–C(1)–C(2)	120.3 (8)	C(41)–C(4)–C(5)	120.1 (8)
C(11)–C(1)–C(6)	120.3 (9)	C(41)–C(4)–C(3)	120.1 (8)
C(1)–C(11)–C(12)	112.5 (8)	C(4)–C(41)–C(42)	115.2 (9)
C(1)–C(2)–C(3)	119.6 (8)	C(4)–C(5)–C(6)	120.6 (8)
C(21)–C(2)–C(3)	122.3 (8)	C(51)–C(5)–C(6)	119.9 (8)
C(21)–C(2)–C(1)	118.1 (9)	C(51)–C(5)–C(4)	119.4 (9)
C(2)–C(21)–C(22)	116.5 (9)	C(5)–C(51)–C(52)	110.9 (9)
C(2)–C(3)–C(4)	121.0 (8)	C(5)–C(6)–C(1)	119.6 (8)
C(31)–C(3)–C(4)	119.7 (9)	C(61)–C(6)–C(1)	120.1 (8)
C(31)–C(3)–C(2)	119.2 (8)	C(61)–C(6)–C(5)	120.3 (8)
C(3)–C(31)–C(32)	109.4 (8)	C(6)–C(61)–C(62)	114.4 (9)
	Tetrafluoroborate Anion		
B–F(1)	1.376 (20)	F(1)–B–F(2)	109.4 (1.4)
B–F(2)	1.326 (16)	F(1)–B–F(3)	103.7 (1.2)
B–F(3)	1.370 (20)	F(1)–B–F(4)	107.3 (1.5)
B–F(4)	1.335 (16)	F(2)–B–F(3)	111.5 (1.5)
F(2)–B–F(4)	114.9 (1.2)		
F(3)–B–F(4)	109.3 (1.4)		

parameters related to data collection appear in Table IV.

Solution of the Structure. The structure of **9** was solved by direct methods based on 404 reflections $|E| > 1.2$ and 20 sets of starting phases with the use of the program SHELXS-86.[34] **10** was solved by routine heavy atom methods also with use of SHELXS-86.[34] Full-matrix least-squares refinement of the coordinates of chromium followed by three-dimensional electron density difference synthesis revealed all the non-hydrogen atoms. After refinement, the temperature factors of the non-hydrogen atoms which were previously isotropic were made anisotropic and further cycles of refinement revealed the positional parameters for most of the hydrogen atoms. These were included along with the calculated positions for the rest of the hydrogen atoms in subsequent cycles of refinement (U fixed at 0.08 Å^2). From a close examination of the Cr–CO and Cr–NO bond lengths it became evident that the $Cr(CO)_2NO$ tripod in **9** was probably disordered in a similar fashion to that reported for $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$,[22] and a weighted scattering factor $(2/3f_c + 1/3f_n)$ for the disordered atoms was used in subsequent cycles of refinement. Further refinement using full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached 0.018. Alternative refinement where coordinates x, y, and z, were replaced by $-x$, $-y$, and $-z$ gave $R_1 = 0.0554$ and $R_2 = 0.0545$ for 1795 reflections, confirming the assignment for the correct hand for the structure of **9**. Although **10** is an inherently chiral molecule, the unit cell contains two molecules of each enantiomer and the space group itself is achiral. Correction for secondary extinction was not necessary. Scattering curves obtained from ref 35 and anomalous dispersion corrections from ref 36 were applied to the curve for chromium during refinement. All calculations were performed on a VAX 8650 computer. Programs XTAL[37] for data reduction, TAPER[38] for absorption correction, SHELX-86[34] for structure solution, SHELX-76[39] for structure refinement, MOLGEOM[40] for molecular geometry, and SNOOPI[41] for drawing diagrams were used. Atomic positional parameters, selected bond lengths and bond angles appear in Tables V–VIII.

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Supplementary Material Available: Tables listing crystal data, mean planes, dihedral torsional angles, hydrogen positional parameters, bond lengths, bond angles, and temperature factors for **9** and **10** (20 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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