state, as measured by the Z1–C1–C8–Z2, C1/8–C9–C10–C4/5, and Z1/2–C1/8–C4/5 angles.[17] Although the magnitudes of the calculated barriers prove to be force field dependent, the direction of the trend is unambiguous: the barriers decrease in the order **1** $\gg$ **2** $>$ **3** $>$ **4**, i.e., in the same order as the skeletal deformations in the ground state.[9]

Our calculations indicated that enantiomerization of **2**–**4** takes place on the NMR timescale, in marked contrast to **1**, which should be resolvable. To test this prediction, we undertook a variable temperature NMR study of **5**, a derivative of **3**. The synthesis of this compound was accomplished by the following route.[18] Conversion of 1,8-diamino-4-methylnaphthalene[19] under Sandmeyer conditions[5] gave **6a** (25%), mp 55–57 °C, after column chromatography on silica (hexane). Bromination with purified NBS (1 equiv in refluxing CCl_4, 3 h) to **6b** (mp 111–113 °C) followed by methanolysis (5.0 equiv of $NaOCH_3$ in refluxing methanol, 3 h) yielded **6c** (70%, mp 43–45 °C). Reaction of freshly sublimed **6c** with n-C_4H_9Li (3 equiv, 0 °C, 1 h) followed by addition of trimethylchlorogermane (3 equiv, room temperature, 3 h) afforded **5** as a yellow oil (62%) after column chromatography on silica (ether/petroleum ether). The product was further purified by high-pressure liquid chromatography: ^{1}H NMR δ ($CDCl_3$) 0.4 (s, 18 H, CH_3Ge), 3.5 (s, 3 H, CH_3O), 4.8 (s, 2 H, CH_2), 7.3–8.0 (m, 5 H, aromatic); $^{13}C\{^1H\}$ NMR δ ($CDCl_3$) 3.2 (CH_3Ge), 58.4 (OCH_3), 73.5 (CH_2), 123.9, 124.6, 124.9, 134.6, 135.0 (aromatic CH).

The 396 MHz ^{1}H NMR spectrum of **5** in a 2:1 mixture of CHF_2Cl/CF_2Cl_2 containing 5% benzene-d_6 features a single line in the methylene region which broadens below ca. −100 °C and gives a clearly resolved AB quartet at −133 °C. The coalescence temperature for the central two lines is −122 °C. The chemical shift difference between the methylene protons at −133 °C is 17 Hz (0.043 ppm), and $|J_{AB}| = 10.5$ Hz. The rate constant for exchange at −122 °C was calculated[20] to be 30 s^{-1}, and $\Delta G^{\ddagger}$ for enantiomerization of **5** is therefore 7.5 ± 0.1 kcal/mol. It is noteworthy that attempts to observe this dynamic NMR effect at a frequency of 270 MHz failed since only line broadening could be observed.[21]

The value of $\Delta G^{\ddagger}$ found for **5** falls between the barrier heights of 5.0 and 9.5 kcal/mol calculated for **3** (Figure 1). That the presence of the 4-methoxymethyl group in **5** leads to a slight increase in $\Delta G^{\ddagger}$ relative to **3** is suggested by enantiomerization barriers of 6.7 and 11.8 kcal/mol calculated for 1,8-bis(trimethylgermyl)-4-ethylnaphthalene, using BIGSTRN and MMPI, respectively. Calculated and experimentally determined barriers are thus in satisfactory agreement.

The present study demonstrates once again the usefulness of EFF calculations in the prediction of stereodynamic timescale domains, and hence in the selection of appropriate methods and conditions for the measurement of barrier heights.[22]

Acknowledgments. We thank the National Science Foundation (CHE 77-07665 and CHE 78-23858) for support of this work and the Swedish Natural Research Council for a postdoctoral fellowship to one of us (U.S.).

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Received May 12, 1980

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[17] The three parameters reflect the pyramidality at the C1/8 center and the twist about the C9–C10 axis.[9] The notation C1/8–C9–C10–C4/5 represents the average of the symmetry-related angles C1–C9–C10–C4 and C8–C9–C10–C5; similarly, Z1/2–C1/8–C4/5 represents the average of Z1–C1–C4 and Z2–C8–C5 (the numbering scheme is as given in ref 9).

[18] All new compounds gave elemental analyses, NMR, and mass spectra consistent with the assigned structures.

[19] Thompson, H. W. *J. Chem. Soc.* **1932**, 2310.

[20] The rate constant at coalescence was calculated by means of a computer program based on the equations for a mutually exchanging AB system: Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967. The line width in the absence of exchange increases as the temperature is lowered and was estimated to be about 3 Hz at −122 °C. The uncertainty in $\Delta G^{\ddagger}$ includes the uncertainty in this line width and in the temperature (±1 °C).

[21] The calculated AB spectrum at 270 MHz has the two inner lines separated by only 5.1 Hz (vs. 9.5 Hz at 396 MHz), and the intensity ratio of inner to outer lines is 5 (vs. 3 at 396 MHz). As a result, the exchange rate constant which leads to coalescence is smaller at 270 MHz than it is at 396 MHz. Since the line width in the absence of exchange increases steadily as the temperature is decreased, it is not surprising that a resolved AB spectrum is not observed at 270 MHz.

[22] For another recent example, see: Hayes, K. S.; Nagumo, M.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 2773.

Conformational Variability in Hexaethylbenzene π-Complexes. Crystal and Molecular Structure of Tricarbonyl(hexaethylbenzene)chromium(0) and Dicarbonyl(hexaethylbenzene)(triphenylphosphine)chromium(0)

Sir:

Although much interest in the stereochemistry of arene transition metal π-complexes has focused on studies of rotational barriers and conformational preferences about the metal–arene bond,[1] little consideration has been given to possible conformational changes in the coordinated arene. We now report evidence for a remarkable change in the conformation adopted by the hexaethylbenzene ligand in $(C_6Et_6)Cr(CO)_3$ (**1**) upon substitution of one of the carbonyl ligands by triphenylphosphine.

Crystals of **1**, grown from heptane solution, are monoclinic, space group $P2_1/n$. Ultraviolet irradiation of a heptane solution of **1** in the presence of an excess of triphenylphosphine yields an orange-yellow precipitate of $(C_6Et_6)Cr(CO)_2PPh_3$ (**2**). Crystals of **2**, grown from benzene/heptane solution, are triclinic, space group $P\bar{1}$. Stereoviews of the X-ray structures of **1** and **2** are shown in Figures 1 and 2.[2]

The ligated hexaethylbenzene in **1** closely resembles the ground state conformation of the free arene (which has D_{3d} symmetry[3]), including the alternation of the ethyl groups above and below the mean plane of the benzene ring.[4,6] In striking contrast, all six ethyl groups in **2** are on the side of the benzene ring remote from the metal; a maverick ethyl group is found on the other side in roughly one third of the molecules, as a disorder in the crystal.

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[1] See: Albright, T. A.; Hofmann, P.; Hoffman, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546, and references therein.

[2] Crystallographic data for **1**: $a = 14.156$ (6), $b = 16.734$ (4), $c = 9.103$ (3) Å; $\beta = 106.21$ (2)°; $Z = 4$; $R = 0.045$, $R_w = 0.051$ for 2417 reflections with $I > 2.5\sigma(I)$. **2**: $a = 8.911$ (3), $b = 9.489$ (3), $c = 21.665$ (7) Å; $\alpha = 81.06$ (2), $\beta = 80.33$ (2), $\gamma = 65.89$ (2)°; $Z = 2$; $R = 0.052$, $R_w = 0.061$ for 3877 reflections with $I > 2.5\sigma(I)$. Intensity data were measured on a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). Reflections were measured for $\theta < 57°$, and data were corrected for absorption. The structures were solved by the heavy atom method and were refined by full matrix least squares, with anisotropic thermal parameters for the heavier atoms and isotropic temperature factors for hydrogen atoms.

[3] Pal, H. K.; Guha, A. C. *Z. Kristallogr.* **1935**, *A92*, 392. Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338.

[4] This result was anticipated by solid-state NMR studies on **1**, which led to an assignment of C_{3v} symmetry.[5]

[5] Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902.

[6] In the conformation of the isoelectronic tricarbonyl(hexaethylborazine)chromium(0), the alternation described for **1** is interrupted by one of the N-ethyl groups, presumably as a result of borazine ring puckering in the complex.[7]

[7] Huttner, G.; Krieg, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 512. *Chem. Ber.* **1972**, *105*, 3437.

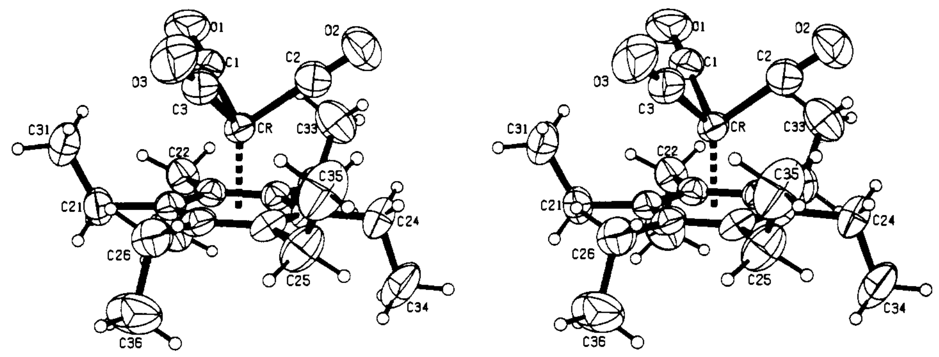

Figure 1. Stereoview of the X-ray structure of tricarbonyl(hexaethylbenzene)chromium(0) (1).

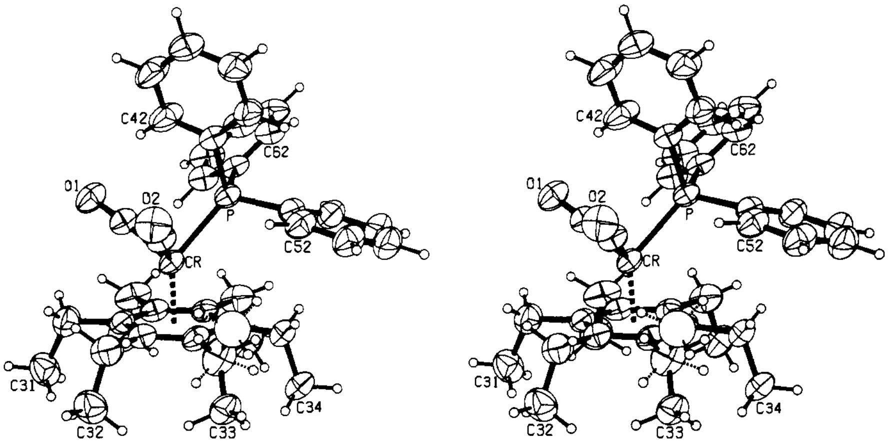

Figure 2. Stereoview of the X-ray structure of dicarbonyl(hexaethylbenzene)(triphenylphosphine)chromium(0) (2). The maverick ethyl group is shown by dashed bonds and by an open circle representing the methyl carbon.

The disparity between the arene conformations in **1** and **2** persists in solution, as shown by a comparison of the 25.2 MHz $^{13}C\{^1H\}$ NMR spectra of the two complexes. The spectra of **1** in CD_2Cl_2 in the temperature range -71 to -30 °C exhibit pairs of singlets of equal intensity for the methyl [δ_{Me_4Si} 14.2, 20.1], methylene [δ_{Me_4Si} 19.4, 22.8], and aromatic [δ_{Me_4Si} 108.8, 117.2] carbons. With increasing temperature, the pairs of signals coalesce, and above 10 °C sharp singlets are observed for the methyl [δ_{Me_4Si} 17.0], methylene [δ_{Me_4Si} 21.6], and aromatic [δ_{Me_4Si} 114.4] carbons.[8,9] This coalescence phenomenon reflects the topomerization of conformations with C_3 (or C_{3v}) symmetry[10] and is ascribable to the onset of rapid rotation of the ethyl groups.[12,13]

The variable temperature spectra of **2** in CD_2Cl_2 are markedly different from those observed for **1**. At -84 °C, **2** displays only single resonances for the methyl [δ_{Me_4Si} 15.9], methylene [δ_{Me_4Si} 22.4], and aromatic [δ_{Me_4Si} 108.0] carbons,[14] and a weak carbonyl signal [δ_{Me_4Si} 243.6 ($^2J_{CP}$ = 22.3 Hz)]. It is noteworthy that the intensity of the carbonyl doublet at ambient temperature is substantially lower in **2** than in **1**; this may be indicative of a longer spin-lattice relaxation time due to an increase in the average distance between these carbons and the methyl hydrogens in **2**, relative to **1**.[15] On the timescale of rapid rotation about the metal-arene bond, and barring accidental isochrony, these observations are consistent with a ground-state conformation of **2** in which the arene moiety effectively exhibits local C_{6v} symmetry[12,16] and provide strong evidence that the conformational disparity between **1** and **2** is not merely the result of crystal packing forces.

We assume that the arene ligand in **2** adopts the observed conformation in response to the steric requirements of the bulky triphenylphosphine group. Work is under way to explore the generality of the observed phenomenon.

Acknowledgments. We thank the National Science Foundation (CHE77-07665) for support of this work.

Supplementary Material Available: Final positional and thermal parameters with standard deviations for **1** and **2** (5 pages). Ordering information is given on any current masthead page.

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[8] Resonances at the high- and low-temperature limits were assigned with the use of single frequency off-resonance decoupled ^{13}C NMR.

[9] The carbonyl resonance remains a sharp singlet throughout this temperature range [δ_{Me_4Si} 235.4].

[10] A least-squares fit of the rate data[11] to the Eyring equation (assuming a transmission coefficient of unity) yielded a value for $\Delta G_{300}^{\ddagger}$ = 11.5 ± 0.6 kcal mol^{-1}.

[11] Obtained by line-shape analysis by using DNMR3: Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

[12] A site exchange process involving arene-metal bond dissociation was ruled out by the observation of separate resonances in a mixture of complexed and free arene at ambient temperatures.

[13] At the slow exchange limit for ethyl group rotation, the torsional motion of the chromium tricarbonyl fragment is still fast on the NMR timescale: a variable temperature T_1 study of **1** yields a reorientation barrier of 2.7 kcal mol^{-1} for this process.

[14] At -125 °C in $CHFCl_2/C_6D_6$, the methyl and methylene resonances of **2** still appear as singlets; the aromatic resonance is obscured by solvent peaks. At 32 °C, changes in relative intensities and temperature-dependent chemical shifts are observed for these signals.

[15] The carbonyl doublet in **2** may be readily observed on material prepared from ^{13}CO enriched **1**.

[16] Dicarbonyl(1,3,5-tri-*tert*-butylbenzene)(triphenylphosphine)chromium(0), presumably a more sterically hindered system, shows no sign of slowed rotation about the metal-arene bond at -60 °C: Jackson, W. R.; Pincombe, C. F.; Rae, I. D.; Rash, D.; Wilkinson, B. *Aust. J. Chem.* **1976**, *29*, 2431.

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Received March 17, 1980