Evidence for Gated Stereodynamics in [1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethyl-benzene]chromium Tricarbonyl

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addition, our results suggest that Fischer–Tropsch methylene coupling may lead to new ways of making close to monodisperse poly(ethylene).[11]   We are currently checking to see if such a merging interest of the objectives of Fischer–Tropsch and Ziegler–Natta type chemistry can be experimentally realized.

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Evidence for Gated Stereodynamics in [1,4-Bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6-tetraethyl-benzene]chromium Tricarbonyl

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Networks of cooperative nonbonded interactions often lead to restricted motions in molecules.[2] Cascades of such networks in which the stereodynamics of one network gate that of another present especially tough stereochemical problems; unique observation of gated behavior among several processes in the same system places strong constraints on the allowable relationships between the static and dynamic symmetries of the molecule. One molecule in which this type of gated stereochemistry has been disputed for some time is (hexaethylbenzene)chromium tricarbonyl (1-Cr).[3] We now present clear evidence for a cascade of processes in 2-Cr, a system analogous to 1-Cr.
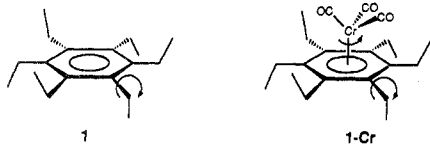
Shortly after the use of metal complexation had been shown to be an effective method for desymmetrizing hexaethylbenzene (1), in order to study the ethyl group dynamics,[4] speculations appeared suggesting that the barrier to ethyl group rotation was interrelated with the rotational barrier for the chromium tricarbonyl tripod.[5] Recently, McGlinchey[6] and others[7] showed that the tripod rotation was hindered in sterically encumbered alkyl aromatics. 2-Cr represents the first system designed to allow the

(1) American Cancer Society Junior Faculty Fellow, 1990–1993; NSF-P-YI, 1988–1993.

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(3) Although Mislow and co-workers[4] believed the barrier to chromium tricarbonyl rotation to be no greater than ca. 5 kcal/mol, McGlinchey and co-workers[5] estimated the barrier to rotation of the chromium tripod at ca. 11 kcal/mol, which would rival the ethyl group rotational barrier.

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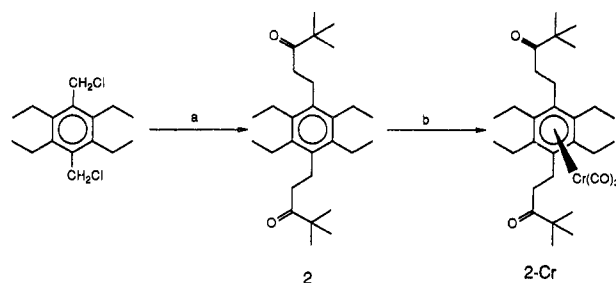
Scheme I[a]

[a](a) TiCl₄, (CH₃)₃CCH=CHOTMS, –45 °C, CH₂Cl₂, 30 min. (b) Cr(NH₃)₃(CO)₃, dioxane, reflux, 5 h.
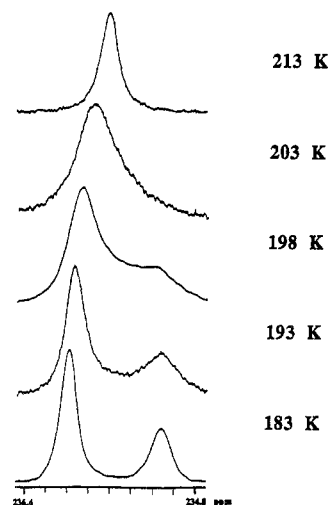

213 K

203 K

198 K

193 K

183 K

Figure 1. Variable-temperature ¹³C NMR spectra of 2-Cr in the region of the carbon monoxide (bound) carbons. The exchange barrier for the carbon monoxide carbons (chromium tripod rotation) is 9.5 kcal/mol.
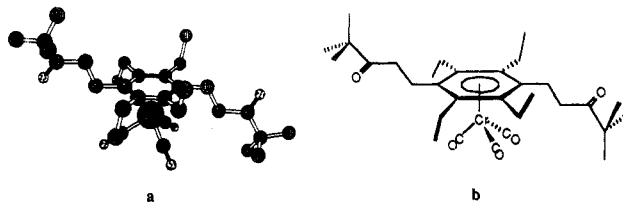

a   b

Figure 2. Structure of 2-Cr as predicted from empirical force field calculations (MXX): (a) picture from Chem-3D and (b) ChemDraw.

observation of both processes concomitantly and thereby uniquely answer this question of gated dynamics.

Synthesis of 2 is effected by the Reetz reaction[8] of the trimethylsilyl enol ether of pinacolone[9] and 1,4-bis(chloromethyl)-2,3,5,6-tetraethylbenzene[10] with titanium tetrachloride in dichloromethane.[11,12] The reaction of 2 with triamminetricarbonylchromium[13] in refluxing dioxane produced 2-Cr in 35% yield[11,14] (Scheme 1).

The static symmetry of 2-Cr is C_s and should give rise to two types of carbon monoxide sites in a ratio of 2:1 as well as two ketone carbon sites in a ratio of 1:1. Tripod rotation produces

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(11) Full experimental details are in the supplementary material.

(12) Spectral data on 2: mp 151–153 °C; ¹H NMR (CDCl₃, 360 MHz) δ 1.17 (18 H, s), 1.19 (12 H, t, *J* = 7.6 Hz), 2.58 (8 H, q, *J* = 7.6 Hz), 2.77 (4 H, m), 2.85 (4 H, m); ¹³C[¹H] NMR (CDCl₃, 75 MHz) δ 15.7, 22.4, 23.5, 26.4, 38.0, 44.1, 135.6, 138.4, 215.6; IR (KBr) 1690 cm⁻¹; FABMS (high resolution) found 414.3462 (calcd for C₂₈H₄₆O₂ (M⁺) 414.3498).

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a dynamic symmetry of $C_s \times C_3$, rendering the carbon monoxide sites equivalent but leaving the ketone sites nonequivalent. Ethyl group rotation introduces yet greater dynamic symmetry and renders the ketone sites equivalent. Thus independent probes for the tripod and for the ethyl group motion are established. Furthermore, the free arene is of a symmetry wherein the methylene protons of the ethyl groups are diastereotopic at the static limit and enantiotopic under dynamic exchange; they serve as a probe of the ethyl group motion in the free arene.

Observation of the ^1H NMR spectrum of **2** at room temperature reveals a singlet for the methylene protons of the ethyl group, methyl decoupled. The spectrum at -100 °C shows a clear AB pattern with $^2J_{H-H} = 14.5$ Hz and $\delta\nu = 128$ Hz. Coalescence occurs at -32 °C. The ^{13}C NMR spectrum of **2-Cr** shows one signal each for the ketone and carbon monoxide carbon at room temperature. At -60 °C the ketone carbon signal has split into two peaks ($\delta\nu = 151$ Hz) of equal intensity whereas the carbon monoxide carbon signal remains a sharp singlet. At -90 °C in $CDCl_2F$[15] the carbon monoxide signal also splits into two peaks ($\delta\nu = 108$ Hz), now of intensity 2:1. The coalescence temperatures for the ketone and carbon monoxide signals are -20 °C and -70 °C, respectively. On the basis of the above data and the Gutowsky–Holm approximation,[16] the barriers for the various processes in the cascade are as follows: free arene ethyl group = 11.3 kcal/mol; complexed arene ethyl group = 11.8 kcal/mol;[17] chromium tricarbonyl tripod = 9.5 kcal/mol (Figure 1).

The signal pattern and intensities of the ^1H and ^{13}C NMR spectra of **2-Cr** are consistent with the existence of only one isomer, the alternating up–down conformer, in solution at low temperature. Empirical force field calculations[18,19] on both **2** and **2-Cr** predict this same conformation to be the most stable by at least 3 kcal/mol (Figure 2).

On the basis of spectral complexities and the relative barrier heights, we conclude that the dynamics of the ethyl groups in **2** are essentially unaltered through desymmetrization to **2-Cr**.[20] However, forming the chromium tricarbonyl complex does introduce a new dynamic process, tripod rotation, and this process is gated by the motion of the ethyl groups on the arene. Thus both the steric complementarity of the arene and tripod fragments and the gated stereodynamics of the tripod motion are demonstrated rigorously in one simple system.

Supplementary Material Available: Experimental procedures for **2** and **2-Cr** (2 pages). Ordering information is given on any current masthead page.

(14) Spectral data on 2-Cr: mp 147–150 °C; ^1H NMR (CDCl₃, 360 MHz) δ 1.19 (18 H, s), 1.26 (12 H, t, J = 7.2 Hz), 2.33 (8 H, q, J = 7.2 Hz), 2.62 (4 H, m), 2.82 (4 H, m); ^{13}C NMR (CDCl₃, 125.7 MHz, −60 °C) δ 14.4 (q), 19.8 (t), 19.9 (t), 20.3 (q), 22.8 (t), 23.4 (t), 25.9 (q), 26.0 (q), 36.2 (t), 43.5 (t), 43.9 (s), 105.4 (s), 108.7 (s), 115.5 (s), 117.3 (s), 214.2 (s), 215.4 (s), 234.8 (s); IR (KBr) 1945, 1935, 1870, 1855, 1845, 1835 cm⁻¹; FABMS (high resolution) found 683.1856 (calcd for C₃₁H₄₆O₅Cr (M⁺ + Cs) 683.1805).
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(18) Calculations using the EFF method were done with the programs MODEL and PC MODEL as distributed by Kosta Steliou (University of Montreal) and Kevin Gilbert (Serena Software), respectively.
(19) For applications and limitations of this method, see: Burkert, U.; Allinger, N. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.
(20) This is consistent with our findings on a series of 1-Cr analogues.[10]

Chemically Etched Silicon Surfaces Viewed at the Atomic Level by Force Microscopy

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Herein we describe the first atomic force microscopy[1,2] (AFM) studies of Si(111) surfaces that directly address the atomic structure of silicon interfaces produced under a variety of etching conditions. We have shown that the atomic structure of hydrofluoric acid (HF) etched interfaces depends strongly on the pH of the etchant solution. We have also used AFM to study the reactions of atomically ordered Si(111):H interfaces with aqueous solutions and have characterized large pH-dependent changes in the interface structure. Significantly, these results suggest that AFM can be used to characterize with atomic resolution details of chemical reactions at silicon interfaces in situ.

Chemical cleaning and etching of semiconductor interfaces are essential processing steps in the production of microelectronic devices.[3–6] A case in point is HF etching of silicon which produces ultraclean and stable surfaces that can be used directly in the fabrication of high-quality devices.[6,7] Studies of HF-etched Si(111) have indicated that the stability of this interface is due to the passivation of Si dangling bonds with Si–H bonds.[8–13] Recent infrared investigations have shown that the Si(111):H interface may consist of mixtures of mono-, di-, and trihydride species, depending on the etching conditions, although only a pure monohydride termination can yield a defect-free interface.[8,9] It is important for high-quality-device fabrication to understand the microscopic structural details of these etched interfaces and to learn how the interface characteristics vary with reaction conditions; however, very few studies have characterized these interfaces on the atomic scale.[14,15]

Silicon (111 oriented, n type, 4 Ω cm) was etched with HF acid via standard procedures.[8,9,16] Several solutions were examined ranging from 48% HF to pH 9 HF/NH₄F in order to investigate how the atomic structure varies with etching conditions. Images of the surface structure were acquired in air with a commercial AFM instrument (Digital Instruments, Inc., Santa Barbara, CA) operated in the constant-force mode.[2,17] The observed surface

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