lation afforded 18.8 g (93%) of **4**, bp 48–50 °C (10 mm). A run carried out at 25 °C was complete in 50 h and afforded a 97% yield of **4**.

Methyl Trifluoromethanesulfonate (5).[17] A flask provided with magnetic stirrer, reflux condenser, and addition funnel was flame-dried and charged with trifluoromethanesulfonic anhydride (100 g, 355 mmol). Dry methanol was then added dropwise at 25 °C (exothermic) until GLPC (50 °C) indicated complete consumption of the anhydride. This point was reached after 45 min, at which time 13.0 g (407 mmol) of methanol had been added. A Vigreux distillation head was attached, and volatiles were condensed in a −78 °C receiver at 25 °C (10 mm) (59.7 g). Redistillation from P_2O_5 afforded 56.8 g (98%) of **5**, bp 27 °C (33 mm). (*Caution: powerful alkylating agent; inhalation may cause pulmonary edema.*)

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. **1**, 14704-14-4; **2**, 4206-67-1; **3**, 18243-41-9; **4**, 64035-64-9; **5**, 333-27-7; chloromethyl methyl ether, 107-30-2; chlorotrimethylsilane, 75-77-4; trifluoromethanesulfonic anhydride, 358-23-6.

Effect of Transition-Metal Complexation on the Stereodynamics of 1,2-Dineopentyl-3,4,5,6-tetramethylbenzene

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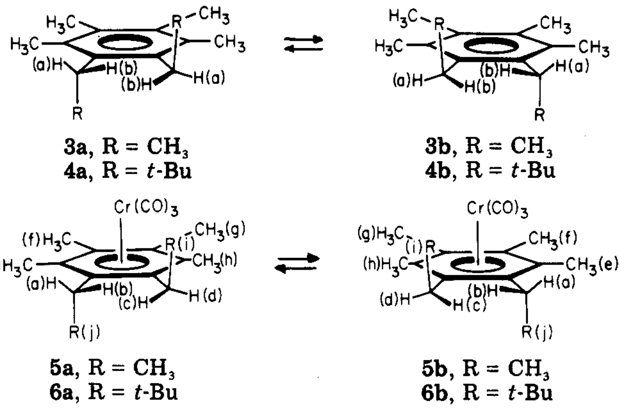
Variable-temperature ^1H NMR measurements have yielded $\Delta G^{\ddagger}$ values of 16.2 and 12.0 kcal mol^{-1} for the barriers to enantiomerization, by aryl–alkyl bond rotation, of 1,2-dineopentyl-3,4,5,6-tetramethylbenzene (**4**) and tricarbonyl(1,2-dineopentyl-3,4,5,6-tetramethylbenzene)chromium(0) (**6**), respectively. Empirical force field calculations on **4** have provided mechanistic details of this process. Starting from the C_2 ground state, in which the *tert*-butyl groups are on opposite sides of the benzene ring, the rearrangement proceeds in stepwise fashion through an achiral intermediate in which both *tert*-butyl groups are located on the same side of the ring and which is 6.4 kcal mol^{-1} less stable than the ground state. The calculated barrier height for the enantiomerization is 14.7 kcal mol^{-1}. The substantially lower barrier for **6** is assumed to be due to an increase in ground-state energy resulting from nonbonded interactions between the tricarbonylchromium fragment and the proximal *tert*-butyl group.

A recent dynamic NMR (DNMR) study[1] of tricarbonyl(hexaethylbenzene)chromium(0) and -molybdenum(0) yielded values of 11.5 ± 0.6 and 11.6 ± 0.2 kcal mol^{-1} for the barriers ($\Delta G^{\ddagger}_{300}$) to ethyl group rotation about the aryl–alkyl bonds. In the observed topomerization process, the methyl groups which project toward the complexed (proximal) side of the ring undergo site exchange with those pointing toward the uncomplexed (distal) side. Although observation of similar site-exchange phenomena in the uncomplexed arene is precluded by the symmetry (D_{3d}) of the molecule, simulation of ethyl group rotation in hexaethylbenzene by the empirical force field (EFF) method yielded a value of 11.8 kcal mol^{-1} for the topomerization barrier,[1] in excellent agreement with the experimentally determined barriers for the π complexes.

Scheme I



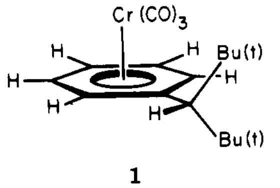
3a, R = CH_3
4a, R = *t*-Bu

3b, R = CH_3
4b, R = *t*-Bu

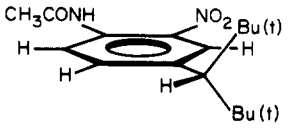
5a, R = CH_3
6a, R = *t*-Bu

5b, R = CH_3
6b, R = *t*-Bu

The present work was undertaken in order to provide data for an experimental comparison between aryl–alkyl rotation barriers in an uncomplexed alkyl-substituted arene and in the corresponding η^6-arene transition-metal complex. To the best of our knowledge, no such comparison has previously been described in the literature. The closest example is found in the work of van Meurs et al.,[2a] who reported a barrier ($\Delta G^{\ddagger}$) of 16.9 kcal mol^{-1} for rotation about the aryl–alkyl single bond in tricarbonyl(2,2,4,4-tetramethyl-3-phenylpentane)chromium(0) (**1**), as compared to 22.2 kcal mol^{-1} for the corresponding barrier in 2-nitro-4-(2,2,4,4-tetramethyl-3-pentyl)acetanilide (**2**).[2b]



1



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Experimental Design. To remain faithful to our objective, a system had to be chosen with the same arene in

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[1] Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

[2] (a) van Meurs, F.; Baas, J. M. A.; van der Toorn, J. M.; van Bekkum, H. *J. Organomet. Chem.* **1976**, *118*, 305. (b) Baas, J. M. A. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1287.

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complexed and uncomplexed form, and with the capability of having site exchanges experimentally monitored in both. In addition, our design called for a system which would bear some resemblance to the structural type studied before,[1] i.e., a hexaalkylbenzene with rotating alkyl groups of the type C_{ar}–CH_2R.

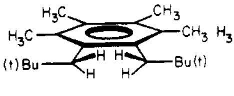
All of the above conditions are met by the 1,2-dialkyl-3,4,5,6-tetramethylbenzenes (alkyl = CH_2R), exemplified by 1,2-diethyl-3,4,5,6-tetramethylbenzene (**3**) and 1,2-dineopentyl-3,4,5,6-tetramethylbenzene (**4**). As shown by EFF calculations (see below), both molecules adopt a ground state of approximate C_2 symmetry, in which the two R groups are located on opposite sides of the benzene ring (see Scheme I). The geminal methylene protons in sites a and b are therefore not related by symmetry, and an AB spin pattern is expected. Enantiomerization (Scheme I: **3a** ⇄ **3b**, **4a** ⇄ **4b**) by rotation about the C_{ar}–CH_2R bonds results in site exchange of H(a) and H(b), observable by collapse of the AB system. Complexation with chromium tricarbonyl (**3** → **5**, **4** → **6**) destroys the C_2 axis and renders the molecules asymmetric; at the slow-exchange limit one would therefore expect anisochrony of all signals. Enantiomerization (Scheme I: **5a** ⇄ **5b**, **6a** ⇄ **6b**) by rotation about the C_{ar}–CH_2R bonds now results in pairwise site exchanges of H(a) and H(c), H(b) and H(d), H(i) and H(j), H(e) and H(h), and H(f) and H(g). Because of molecular asymmetry, site exchange in the π complexes can also be monitored by ^{13}C NMR spectroscopy.

Accordingly, variable-temperature NMR studies on **3** and **5**, or **4** and **6**, are capable in principle of leading to the desired comparison of experimentally determined rotation barriers.

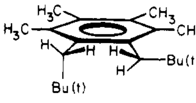
Results and Discussion

While the effect of metal complexation on the barrier to ethyl group rotation in hexaethylbenzene is more appropriately modeled by **3**,[3] no NMR decoalescence of the methylene protons could be observed down to −140 °C at 100 MHz, and we therefore directed our attention to **4**.

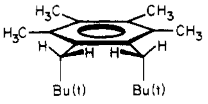
The variable-temperature ^1H NMR spectrum of **4** was first reported in 1966 by Dix et al.,[4] who observed coalescence of the diastereotopic methylene protons and who interpreted their results as described in Scheme I. A concerted conrotatory motion of the neopentyl groups through a transition state resembling **7** was thought to be responsible for the enantiomerization. In a trenchant critique, Martinson[5] subsequently argued that the internal rotations of the neopentyl groups in **4** should be reinterpreted in terms of a stepwise motion, implying transition states resembling **8a** and its enantiomer **8b**, and the intervention of an intermediate (**9**) in which both *tert*-butyl groups are located on the same side of the benzene ring.[5-7] However, attempts to observe this proposed intermediate by use of low-temperature ^{13}C NMR spectroscopy have thus far proven unsuccessful.[6]



7



8a



9

Support for the stepwise mechanism comes from EFF calculations. The AM force field[11,12] was used within the framework of the previously described[1] BIGSTRN-2 program.[13] Energy minima (**4** and **9**) were calculated by the full relaxation technique, and the preferred rearrangement pathway of the neopentyl groups was simulated by use of the incremental group-driving technique.[14] Our calculations indicate an enantiomerization pathway, **4a** ⇄ **8a** ⇄ **9** ⇄ **8b** ⇄ **4b**, with **8** and **9** lying 14.7 and 6.4 kcal mol^{-1}, respectively, above the ground state.[15] By contrast, the transition state for the concerted pathway, **7**, lies 23.4 kcal mol^{-1} above **4**,[16] and this mechanism may therefore be safely ruled out of consideration.

The ^1H NMR (100-MHz) spectrum of **4** in 1,1,2,2-tetrachloro[1,2-$^2H_2$]ethane (Table I) at −2.6 °C displays an AB quartet for the methylene protons which reversibly collapses at elevated temperatures. Rate constants for exchange were obtained in the temperature range −2.6 to +121.5 °C by a line-shape analysis using the program DNMR3.[17,18] A least-squares fit of the rate data to the Eyring equation[20] yielded a value of $\Delta G^{\ddagger}_{298} = 16.2 \pm 0.3$

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(3) Newman, M. S.; LeBlanc, J. R.; Karnes, H. A.; Axelrad, G. *J. Am. Chem. Soc.* **1964**, *86*, 868.

(4) Dix, D. T.; Fraenkel, G.; Karnes, H. A.; Newman, M. S. *Tetrahedron Lett.* **1966**, 517.

(5) Martinson, P. *Acta Chem. Scand.* **1972**, *26*, 3568.

(6) Nilsson, B.; Martinson, P.; Olsson, K.; Carter, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 3190.

(7) Evidence adduced in support of this mechanism was taken from studies on the internal dynamics of substituted neopentylbenzenes.[5,8,9,10] Martinson[5] and Nilsson et al.[9] also concluded that the magnitude of rotational barriers in neopentylbenzenes is determined largely by the size of the smaller ortho substituent. The proposed stepwise rearrangement of the neopentyl groups in **4** is therefore further supported by the similarity of the reported[6] rotation barrier in **4** ($\Delta G^{\ddagger}_{298}$ = 16.3 kcal mol^{-1}) to that in related systems ($\Delta G^{\ddagger}$ = 15.0 to 15.5 kcal mol^{-1}).[6]

(8) Mårton, J.; Martinson, P. *Acta Chem. Scand.* **1969**, *23*, 3187. Carter, R. E.; Mårton, J.; Dahlqvist, K.-I. *Ibid.* **1970**, *24*, 195. Reuvers, A. J. M.; Sinnema, A.; Nieuwstad, Th. J.; van Rantwijk, F.; van Bekkum, H. *Tetrahedron* **1971**, *27*, 3713.

(9) Nilsson, B.; Carter, R. E.; Dahlqvist, K.-I.; Mårton, J. *Org. Magn. Reson.* **1972**, *4*, 95.

(10) The internal dynamics of neopentylbenzene systems have been a subject of continuing interest. See: (a) Ris, C.; Schaasberg-Nienhuis, Z. R. H.; Cerfontain, H. *Tetrahedron* **1973**, *29*, 3165. (b) Nilsson, B.; Martinson, P.; Olsson, K.; Carter, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 5615. (c) Nilsson, B. *Mol. Phys.* **1974**, *27*, 625. (d) Nilsson, B.; Drakenberg, T. *Org. Magn. Reson.* **1974**, *6*, 155. (e) Carter, R. E.; Nilsson, B.; Olsson, K. *J. Am. Chem. Soc.* **1975**, *97*, 6155. (f) Dahlberg, E.; Nilsson, B.; Olsson, K.; Martinson, P. *Acta Chem. Scand., Ser. B* **1975**, *B29*, 300. (g) Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, *98*, 7515. (h) Andersson, S.; Carter, R. E.; Drakenberg, T. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 661.

(11) Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168. Mislow, K.; Dougherty, D. A.; Hounshell, W. D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 555.

(12) A corrected value of −25.9 kcal mol^{-1} was used for the C_{ar}–C_{ar}–C_{ar}–C_{ar} torsional constant.

(13) Iverson, D. J.; Mislow, K. *QCPE* **1981**, *13*, 410.

(14) The torsion angle ϕ (defined by the quaternary, methylene, aryl, and ortho-methylated aryl carbon atoms) was fixed at increasing values while all other internal parameters were minimized with respect to energy.

(15) Similar calculations indicate that enantiomerization of **3** proceeds by the same stepwise mechanism. The corresponding transition and intermediate states, analogous to **8** and **9**, are calculated to lie 6.4 and 1.3 kcal mol^{-1}, respectively, above the ground state.

(16) Calculated by minimizing the energy of **7** under the constraint of maintaining $\phi = 0$ for both *tert*-butyl groups. The transition state for the concerted pathway in **3**, which was similarly calculated, lies 11.6 kcal mol^{-1} above the ground state.

(17) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165. The site exchange was treated as a single-step permutation; i.e., the presence of an intermediate species was formally ignored in our analysis.

(18) A temperature dependent chemical shift difference ($\Delta\nu$) of ca. 0.027 Hz deg^{-1} was observed in the temperature range −2.6 to +45.4 °C. The values used for $\Delta\nu$ at higher temperatures were obtained by linear extrapolation. We also noted a slight but distinct asymmetry in the methylene line shape at intermediate rates of exchange; this type of asymmetry may be expected[19] if the exchange proceeds via a chemically shifted low-population isomer such as **9**. This evidence is, of course, far from conclusive, and we therefore prefer to withhold further comment.

Table I. NMR Properties of 4 and 6

			resonance frequencies[a]					
compd	nucleus	temp, °C	CH_2	$C_q(CH_3)_3$	C_{ar}-CH_3	C_q	C_{ar}	CO
4	^1H[b]	−2.6	2.74 (d),[c] 2.95 (d)[c]	0.83	2.20, 2.23			
	^1H[b]	121.5	2.88	0.84	2.20, 2.24			
	$^{13}C\{^1H\}$[d]	30 to 35	41.5	30.1	17.0, 19.5	34.4	132.0, 132.7, 135.0	
6	^1H[e]	−76	2.49 (d),[f] 2.75 (d),[f] 2.64 (d),[g] 2.97 (d)[g]	1.03, 1.20	2.12, 2.20, 2.22, 2.37			
	^1H[e]	35	2.73	1.13	2.22, 2.24			
	$^{13}C\{^1H\}$[e]	−70 to −75	39.7, 39.7	30.5, 31.1	16.8, 17.0, 18.9, 20.5	33.2, 34.5	102.0, 103.7, 107.9, 113.2, 114.0, 117.9	235.5
	$^{13}C\{^1H\}$[e]	30 to 35	41.3	32.0	17.6, 20.2	34.6	108.2, 108.6, 113.9	235.7

[a] Chemical shifts are in parts per million downfield from internal tetramethylsilane. Resonances are singlets unless specified otherwise. For $^{13}C\{^1H\}$ spectra, assignments were aided by use of single frequency off-resonance decoupling. [b] In 1,1,2,2-tetrachloro[1,2-$^2H_2$]ethane. [c] $^2J_{HH}$ = 14.5 Hz. [d] In [^{2}H]chloroform. [e] In dichloro[$^2H_2$]methane. [f] $^2J_{HH}$ = 15.0 Hz. [g] $^2J_{HH}$ = 15.0 Hz.

kcal mol^{-1} for the enantiomerization barrier, in excellent accord with the values of 16.2 and 16.3 kcal mol^{-1} estimated[6] from the original work of Dix et al. (CCl_4 solution)[4] and measured by Nilssen et al. ($CDCl_3$ solution),[6] respectively,[21] and in good agreement with the calculated (EFF) value of 14.7 kcal mol^{-1}.

The ^{1}H NMR (100-MHz) spectrum of 6 in dichloro[$^2H_2$]methane at −76 °C displays two methylene AB quartets, four ring–methyl singlets, and two *tert*-butyl singlets; as discussed above, reversible pairwise collapse of ^{1}H (and also ^{13}C) signals reflects the onset of rapid rotation of the neopentyl groups (Scheme I and Table I).[23] Rate constants for exchange were obtained from the ring–methyl signals in the temperature range −76 to +35 °C by a line-shape analysis using the program DNMR3.[17] Representative experimental spectra and calculated line shapes are shown in Figure 1. A least-squares fit of the rate data to the Eyring equation[20] yielded a value of $\Delta G^\ddagger_{298}$ = 12.0 ± 0.3 kcal mol^{-1} for the enantiomerization barrier.

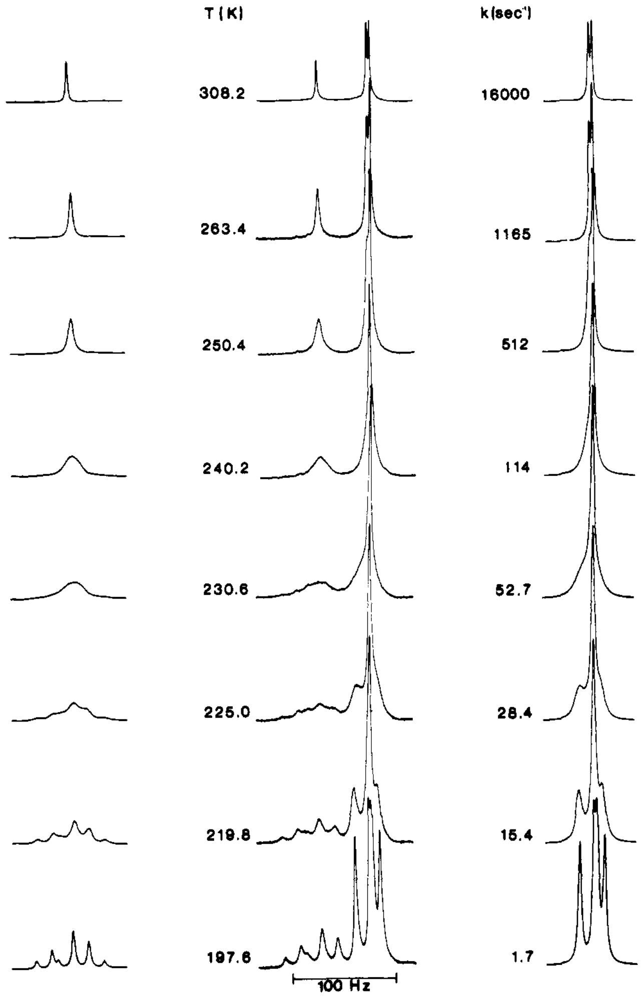

Figure 1. Center: variable-temperature ^{1}H NMR spectrum (C_{ar}–CH_3 and methylene region) of tricarbonyl(1,2-dineopentyl-3,4,5,6-tetramethylbenzene)chromium(0) in dichloro[$^2H_2$]methane. Right: calculated C_{ar}–CH_3 line shapes and enantiomerization rate constants. Left: calculated methylene proton line shapes.

The observed 4.2 kcal mol^{-1} decrease in activation energy of 6 relative to 4 is comparable to the previously reported[2a] 5.3 kcal mol^{-1} decrease in activation energy of 1 relative to 2. In both cases the effect may be attributed to an increase in the ground-state energy of the π complex, resulting from nonbonded interactions between the tricarbonylchromium fragment and the proximal *tert*-butyl group.[24-26] By the same token, in the presence of smaller steric interactions one would expect a smaller difference between alkyl rotation barriers in complexed and uncom-

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(19) Kaplan, J. I.; Fraenkel, G. "NMR of Chemically Exchanging Systems"; Academic Press: New York, 1980; pp 120–122.

(20) Assuming a transmission coefficient of unity.

(21) However, the partitioning of $\Delta G^\ddagger$ into $\Delta H^\ddagger$ and $\Delta S^\ddagger$ components is at variance with previous results: we calculate $\Delta S^\ddagger = -1$ cal mol^{-1} K^{-1}, whereas the reported[6] values are −16 and −11.5 cal mol^{-1} K^{-1}. Several factors may be held accountable for this discrepancy,[22] e.g., solvent effects, the asymmetry of the methylene line shape at intermediate rates of exchange,[18] and problems associated with a linear extrapolation of $\Delta\nu$ values to the higher temperature range.[18]

(22) Uncertainties in the values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$ derived from NMR line-shape analyses have been widely discussed. See for example: Shoup, R. R.; Becker, E. D.; McNeel, M. L. *J. Phys. Chem.* **1972**, *76*, 71. Colebrook, L. D.; Giles, H. G.; Granata, A.; Icli, S.; Fehlner, J. R. *Can. J. Chem.* **1973**, *51*, 3635. Bickley, D. G.; Serpone, N. *Can. J. Spectrosc.* **1974**, *19*, 40. Liljefors, T. *Org. Magn. Reson.* **1974**, *6*, 144. Carter, R. E.; Drakenberg, T.; Roussel, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1690.

(23) A site-exchange process involving arene–metal bond dissociation was ruled out by the observation of separate resonances in a mixture of 4 and 6 at the fast-exchange limit of 6.

(24) This interaction is absent in the free arene. In the π-complexed intermediate, both *tert*-butyl groups are presumably distal to the metal atom.

(25) This conclusion is corroborated by an X-ray analysis of 1 which demonstrates molecular distortion: van Meurs, F.; van Koningsveld, H. *J. Organomet. Chem.* **1976**, *118*, 295. von Koningsveld, H.; van Meurs, F. *Tetrahedron* **1977**, *33*, 2699.

plexed arenes. This is what was found[1] for hexaethylbenzene,[27] and it is what we predict for 3.

Experimental Section

Solution 100.1-MHz ^{1}H and 25.2-MHz ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer. The infrared spectrum was obtained on a Perkin-Elmer 283 spectrometer. Mass spectra were measured on an AEI MS-9 high-resolution mass spectrometer, with an ionizing voltage of 70 eV. High-performance liquid chromatography (HPLC) was done on a Waters Associates Prep LC/System 500 instrument. Reagents obtained from the indicated sources were used without further purification: 1,2,3,4-tetramethylbenzene (Aldrich); paraformaldehyde (Aldrich); *tert*-butyllithium in pentane (Alfa); chromium hexacarbonyl (Pfaltz & Bauer). Di-*n*-butyl ether and tetrahydrofuran were distilled from $LiAlH_4$.

1,2-Dineopentyl-3,4,5,6-tetramethylbenzene (4) was synthesized by a procedure adapted from the work of Bassindale et al.[28] and Reuvers et al.[29] 1,2-Bis(chloromethyl)-3,4,5,6-tetramethylbenzene[30] (15.0 g, 64.9 mmol) was dissolved in hexane (300 mL). The magnetically stirred solution was cooled to 0 °C, and a 1.9 M pentane solution of *tert*-butyllithium (68.2 mL, 130 mmol) was slowly added. The resulting pink solution was stirred for 3 h at 0 °C and for an additional 12 h at room temperature. During this time the mixture turned yellow. Finally, the mixture was refluxed for 3 h. After being cooled to room temperature, the mixture was quenched with saturated aqueous NH_4Cl. The organic layer was separated and sequentially washed with water and brine. After the solution was dried over $MgSO_4$, the solvents were stripped under reduced pressure. The resulting gummy yellow residue was initially purified by silica gel chromatography, using pentane as the eluant. This yielded 5.64 g of a mixture of three components, as determined by silica gel TLC. The R_f's, using pentane as the eluant, were 0.69, 0.60, and 0.52. The middle spot was identified as 4 and isolated by HPLC on silica gel, with hexane as the eluant. The yield was 2.07 g, mp 90–91.5 °C (lit.[3] mp 96.0–97.5 °C). Mass spectrum: *m/e* (relative intensity) 274 (M^+, 46), 259 ($M^+ - CH_3$, 8), 217 ($M^+ - C_4H_9$, 89), 187 ($M^+ - C_4H_9 - 2CH_3$, 11), 161 ($217 - C_4H_8$, 100), 119.5 (M^*). Mass spectrum (high resolution): *m/e* 274.2652 (274.2661 calcd for $C_{20}H_{34}$). NMR properties are listed in Table I.

Tricarbonyl(1,2-dineopentyl-3,4,5,6-tetramethylbenzene)chromium(0) (6) was synthesized according to the procedure of Mahaffy and Pauson.[31] Chromium hexacarbonyl (1.2 g, 5.5 mmol) and 4 (1.0 g, 3.6 mmol) were placed in a nitrogen-purged flask fitted with a reflux condenser and a nitrogen inlet. Di-*n*-butyl ether (30 mL) and tetrahydrofuran (5 mL) were added, and the solution was refluxed under nitrogen for ca. 15 h. The solvents were removed at 60 °C and a pressure of ca. 1 mmHg. Small samples (≤80 mg) of pure 6 were conveniently obtained from this greenish yellow residue by small-scale silica gel chromatography (a 7-in. Pasteur pipette was used as the column). Pentane elutes unreacted 4 and pentane–acetone (5:1) elutes 6. Mass spectrum: *m/e* (relative intensity) 410 (M^+, 14), 395 ($M^+ - CH_3$, 4), 382 ($M^+ - CO$, 2), 354 ($M^+ - 2CO$, 9), 326 ($M^+ - 3CO$, 100), 274 ($M^+ - Cr(CO)_3$, 37). Mass spectrum (high resolution): *m/e* 410.1903 (410.1913 calcd for $C_{23}H_{34}{}^{52}CrO_3$). IR (CCl_4): 1880, 1904 (sh), 1955, 1979 cm^{-1}. NMR properties are listed in Table I.

Variable-Temperature NMR Measurements. All variable-temperature ^{1}H spectra were recorded at 100.1 MHz in the Fourier transform mode on a Varian XL-100 spectrometer. NMR samples were contained in 5-mm o.d. sample tubes. Temperatures were measured with a copper–constantan thermocouple which was inserted, at coil height, into another 5-mm o.d. sample tube containing an equal volume of the NMR solvent. Temperatures are considered to be accurate to ±2 °C. For the measurement of internal line-width parameters, the *tert*-butyl resonance was used for 4 and internal tetramethylsilane for 6.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8009670) for support of this work.

Registry No. 4, 6668-20-8; 6, 78685-96-8.

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[26] It should also be noted that enantiomerization of 4 involves an intermediate (9) in which the two *tert*-butyl groups project with equal probability toward either one of the two faces of the aromatic ring, whereas in 6 only the side distal to the metal is expected to be available for double occupancy by these bulky groups.[24] The probability for enantiomerization of 6 is therefore effectively halved, relative to 4, and, as was previously pointed out[2a] in connection with the study of 1, the $\Delta G^{\ddagger}{}_{298}$ value obtained for 6 should therefore be decreased by $RT \ln 2$ = ca. 0.4 kcal mol^{-1} due to a statistical factor.

[27] The absence of strong steric interactions between the tricarbonylchromium moiety and the ethyl groups of hexaethylbenzene is indicated by the absence of major distortions in the X-ray structure.[1]

[28] Bassindale, A. R.; Eaborn, C.; Walton, D. R. M. *J. Chem. Soc. C* **1969**, 2505.

[29] Reuvers, A. J. M.; Klomp, J.; van Rantwijk, F. *Delft Prog. Rep., Ser. A* **1973**, *1*, 27.

[30] Prepared as previously described.[3]

[31] Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.