2.21 (s, 6 H, NCH_3), 2.24 (s, 3 H, CH_3), 2.34 (s, 6 H, CH_3), 3.34 (s, 2 H, CH_2N), 6.82 (s, 2 H, Ar).

N,N-Dimethylbenzylamine-d_8 was prepared by the $LiAlD_4$ reduction[45] of N,N-dimethylbenzamide-d_6 in dry ether: bp 180-182 °C (743 mm); ^1H NMR δ 7.31 (s, 5 H, Ph); ^{13}C NMR (^{13}C-^2H couplings) δ 45.4 (sp, J = 23 Hz, NCD_3), 64.4 (p, J = 22 Hz, CD_2), 127.0 (s, C-4), 128.2 (s, C-3 and C-5), 129.1 (s, C-2 and C-6), 138.9 (s, C-1); EIMS (40 eV) m/z 143 (M^+, 10), 107 ([M - $2CD_3$]$^+$, 13). N,N-Dimethylbenzamide-d_6 was prepared[46] by heating a mixture of benzoyl chloride and N,N-dimethylformamide-d_7 (Aldrich) at 150 °C for 4 h, followed by extraction of the reaction mixture with ether, evaporation of the ether layer, and fractional distillation under reduced pressure: bp 135-137 °C (15 mm); ^1H NMR δ 7.39 (s, 5 H, Ph).

N,N-Dibenzylmethylamine-α,α-d_2 was prepared[47] by reduction of N-methyl-N-benzylbenzamide[48] with $LiAlD_4$ in dry ether: bp 135-136 °C (4 mm); ^1H NMR δ 2.15 (s, 3 H, NCH_3), 3.94 (s, 2 H, CH_2N), 7.23-7.36 (m, 10 H, Ph); EIMS (40 eV) m/z 213 (M^+, 8).

dl-erythro-2-(1-Piperidino)-1,2-diphenylethanol and *dl-threo*-2-(1-piperidino)-1,2-diphenylethanol were prepared according to the published procedure[49] in 56% and 51% yields, respectively.

Kinetics. Buffer solutions were prepared weekly in doubly distilled water. A solution of the $(batho)_2Cu^{II}$ complex was prepared using the appropriate quantities of $CuSO_4$ and batho. A solution of the amine was prepared separately in phosphate buffer, and the pH was adjusted to the desired value with KOH. Following equilibration of 2.9 mL of the latter solution in the spectrometer at 25 °C, 0.1 mL of $(batho)_2Cu^{II}$ solution was added, and the cuvette was shaken. The reactions were followed by monitoring the formation of $(batho)_2Cu^{I}$ spectrophotometrically at 483 nm (water),[23] 478 nm (30% aqueous MeOH), or 474 nm (50% aqueous MeOH). To complete the reduction of Cu(II) and to determine the infinity absorbance, 5 μL of 10% sodium dithionite solution was added. The pH values were obtained at 25.0 °C using a Fisher Accumet Model 810 meter. The "apparent" pH values in 30% and 50% aqueous MeOH (v/v) were converted to operational pH values by subtraction of 0.04 and 0.10, the appropriate values of "δ" for these solvent mixtures.[50] The pK_w values used for these same solvent mixtures were 14.219 and 14.362, respectively.[51]

Determination of Stoichiometry. The number of equivalents of Cu(II) reduced per equivalent of the various amines was determined by adding 0.1 mL of an aqueous or methanolic solution of 0.02 mmol of amine to a mixture of 2 mL of an aqueous solution of 0.2 mmol of $(batho)_2Cu^{II}$, 1 mL of 0.30 M KH_2PO_4, and 1 mL of 0.60 M KOH and keeping the resulting mixture in the dark at 25 °C. Aliquots were removed at periodic intervals over a 7-day period and diluted by a factor of 150 with water for determination of A_{483}.

Product Analysis. To a solution of batho (3.34 g, 5.90 mmol) and 0.74 g (2.95 mmol) of $CuSO_4$ in 10 mL of water was added a solution of 1.5 mmol of amine in 5 mL of 0.3 M potassium phosphate buffer at pH 8. After remaining at 25 °C for 24 h, the reaction mixture was brought to pH 12.5 and extracted with five 10-mL portions of ether. The ether layer was back-extracted with three 15-mL portions of 10% HCl and then treated with a slight excess of 2,4-DNP reagent, and the resulting (2,4-dinitrophenyl)hydrazone was removed by filtration, dried, and weighed for determination of the yield of aldehyde products. A weighed amount of fumaric acid disodium salt was added to the aqueous layer (containing the amine products in HCl salt form), which was then evaporated to dryness in vacuo and analyzed by ^1H NMR spectroscopy. The yield of amine product was determined by integration relative to the fumaric acid singlet. Both the aldehyde and amine were analyzed by ^1H NMR for determination of the product distribution in the case of the N,N-dibenzylmethylamine-α,α-d_2 reaction.

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Registry No. 1, 1126-71-2; **2**, 589-08-2; **3**, 64-04-0; **4**, 103-83-3; **5**, 103-67-3; **6**, 100-46-9; **7**, 34274-10-7; **8**, 40393-99-5; **9**, 6304-27-4; **10**, 38222-85-4; **11**, 43071-19-8; **12**, 3179-63-3; **13**, 108-01-0; **14**, 109-83-1; **15**, 141-43-5; **16**, 3030-44-2; **17**, 109-85-3; **18**, 927-62-8; **19**, 109-02-4; **20**, 110-91-8; **21**, 120-94-5; **22**, 123-75-1; **23**, 626-67-5; **24**, 110-89-4; **25**, 1192-95-6; **26**, 7365-45-9; **27**, 5625-37-6; **29**, 4432-31-9; $(batho)_2Cu^{II}$, 14875-92-4; D_2, 7782-39-0; *dl-erythro*-2-(1-piperidino)-1,2-diphenylethanol, 19640-37-0; *dl-threo*-2-(1-piperidino)-1,2-diphenylethanol, 19640-36-9.

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Effect of Transition-Metal Complexation on the Stereodynamics of Persubstituted Arenes. Evidence for Steric Complementarity between Arene and Metal Tripod

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Contribution from the Department of Chemistry, University of California at San Diego, La Jolla, California 92093-0314. *Received February 4, 1991*

Abstract: The stereodynamics in 1,4-dimethoxy-2,3,5,6-tetraethylbenzene (**5**), 1,4-bis(methoxymethyl)-2,3,5,6-tetraethylbenzene (**6**), and 1,4-dineohexyl-2,3,5,6-tetraethylbenzene (**7**) and their respective tricarbonylchromium complexes, **5(Cr)**, **6(Cr)**, and **7(Cr)**, have been studied by variable-temperature NMR techniques. Barriers to rotation about the sp^2-sp^3 bonds for **5-7** and **5(Cr)-7(Cr)** have been determined using the Gutowsky-Holm approximation to be 7.7, 9.4, 11.2, 6.6, 8.9, and 11.8 kcal/mol, respectively. Unlike previous studies in this area, the stereodynamics of the arene do not change demonstrably upon metal complexation. This observation is attributed to a lock-and-key complementarity between the metal tripod and the arene. The possibility of correlated dynamics between the metal tripod rotation and the ethyl group rotation is discussed.

The use of transition-metal complexation as a method for studying the stereodynamics of alkylbenzenes has recently been demonstrated.[1] This method desymmetrizes a π system (e.g., an arene) by rendering the faces of the π system nonequivalent. The utility of the method is limited by the degree to which the presence of the metal disturbs the parent compound's stereodynamics. These limits can be probed through systems where the symmetry allows one to observe the stereodynamics of both the free and the metal-complexed arene. Investigations of this type

† American Cancer Society Junior Fellow 1990-1993; NSF-PYI 1988-1993.

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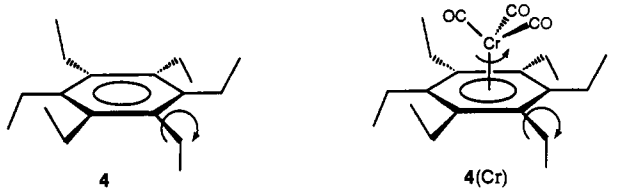
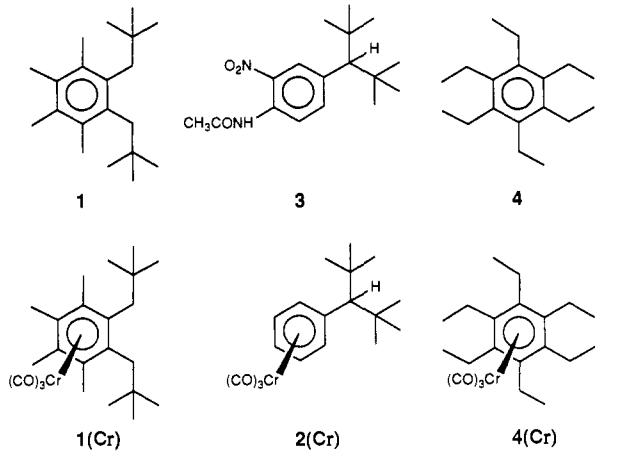


Figure 1. The alternating up–down ground-state conformation of **4** and **4(Cr)**.

provide information about the steric complementarity between the metal fragment and the arene. This information, in turn, applies to the design of transition-metal complexes where control of the steric environment around the metal modifies the reactivity of the complex.

Few experiments have been performed to assess the interference of a transition metal on the dynamic stereochemistry of a sterically crowded arene.[2] Past studies have concluded that the presence of a metal strongly perturbs the stereodynamics of the arene. This probably occurs through raising the energy of the ground state and thus lowering the barrier to rotation about the alkyl–aryl bond. Such behavior indicates a poor complementarity between the arene and the metal tripod.

Iverson and Mislow[2a] found that the barrier to rotation of a neopentyl group dropped from 16.2 kcal/mol in 1,2-dineopentyl-3,4,5,6-tetramethylbenzene (**1**) to 12 kcal/mol in its tricarbonylchromium complex, **1(Cr)**. Earlier work on tricarbonyl(2,2,4,4-tetramethyl-3-phenylpentane)chromium(0) (**2**) vs 2-nitro-4-(2,2,4,4-tetramethyl-3-pentyl)acetanilide (**3**) showed a similar result. Van Meurs et al.[2b] found a barrier to rotation about the C(ar)–C(methine) bond of 22.2 kcal/mol for the noncomplexed arene, as compared to 16.9 kcal/mol for the complexed arene. Thus, the existing studies betray only interactions of poor complementarity.[3]



In a different study, Iverson et al.[1a] make a direct comparison between the barrier derived from data obtained on tricarbonyl(hexaethylbenzene)chromium (**4(Cr)**) by dynamic NMR spectroscopy and the barrier found for hexaethylbenzene (**4**) by empirical force field calculations. They find an experimentally determined barrier for ethyl group rotation of 11.5 kcal/mol in **4(Cr)** and claim good agreement with the calculated barrier of 11.8 kcal/mol for **4**.

On the basis of the results obtained from **1**/**1(Cr)** or **2**/**3(Cr)**, one would expect a barrier in **4** as high as 16–17 kcal/mol. Therefore, either the chromium plays a particularly innocuous role in the stereodynamics of **4(Cr)** or EFF calculations significantly underestimate the barrier to rotation for the free **4**. Unfortunately, the symmetry of **4** does not allow the observation of the ethyl group rotation in the free arene. No gauge of the disturbance caused by chromium complexation is possible without an alternate mode of desymmetrization.

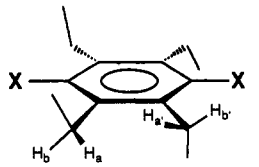


Figure 2. Diastereotopic protons in 1,4-disubstituted 2,3,5,6-tetraethylbenzene.

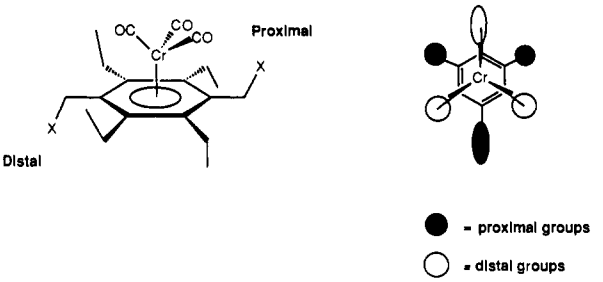


Figure 3. Stereochemical regions in the tricarbonylchromium complexes.

Examination of appropriately modified CPK models[4] suggests that the tricarbonylchromium fragment may bind to **4** with an exceptionally good lock-and-key fit. Data derived from the crystal structure[5] of **4(Cr)**[1a] show that the carbonyl groups sit at van der Waals distances from the proximal methyl and methylene groups of the arene (Figure 1).[6] Here we present experimental evidence to quantify the effect of tricarbonylchromium complexation on the stereodynamics of compounds related to **4**.

Experimental Design. As mentioned above, the symmetry of **4** is too high to permit measurement of the ethyl group barrier to rotation. Therefore, we chose to look at isosteric derivatives of **4** that have the symmetry necessary to observe the ethyl group dynamics.

4 has symmetry D_{3d} in the up–down conformation. A subsymmetry of D_{3d} appropriate to this problem is C_{2h}; the h mirror includes ring carbons 1 and 4 as well as the heavy atoms of the 1,4 substituents. The static symmetry of this C_{2h} conformer increases to $C_{2h} \times C_2$ (isomorphic to D_{2h}) in the dynamic limit. The ethyl groups are chirotopic (site symmetry C_1) in the static structure, and the H's of the methylene must be diastereotopic. The dynamic symmetry indicates that each ethyl group is achirotopic at the dynamic limit; the exchange of the environment of the methylene hydrogens renders them enantiotopic. From this analysis, the methylene hydrogens are seen to be an ideal probe for the dynamics of the free ligand (Figure 2).

The molecular structures chosen in this case are 1,4-dimethoxy-2,3,5,6-tetraethylbenzene (**5**), 1,4-bis(methoxymethyl)-2,3,5,6-tetraethylbenzene (**6**), and 1,4-dineohexyl-2,3,5,6-tetraethylbenzene (**7**). The ground states of **5**, **6**, and **7** are calculated by EFF[7,8] methods to be the insect-like alternating up–down conformer analogous to **4**.

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(4) We have prepared metal–arene CPK models by milling out the π cloud of a normal CPK arene so that a CPK transition metal sits at a distance, metal center to arene centroid, analogous to that found in benzenechromium tricarbonyl. These models give insight to the problems at hand, but we are cautious about drawing any conclusions on the basis of aspects of the model.

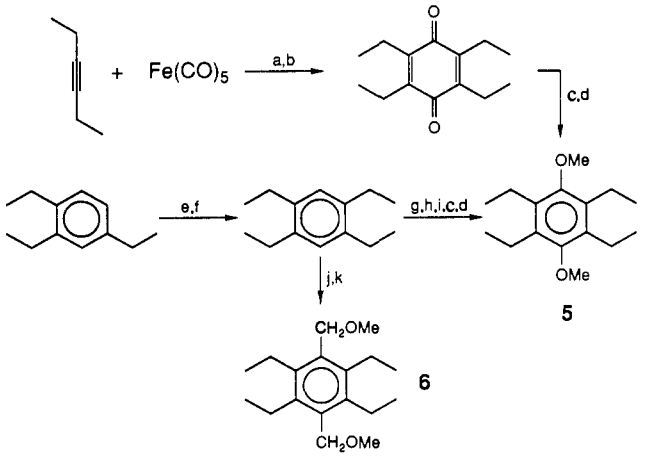
(5) Pauling L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(6) The crystal data was evaluated using the MacMoMo program as distributed by Max Dobler at the ETH-Zurich.

(7) Calculations using the EFF method were done with the programs MODEL and PC MODEL as distributed by Kosta Steliou (U. of Montreal) and Kevin Gilbert (Serena Software), respectively.

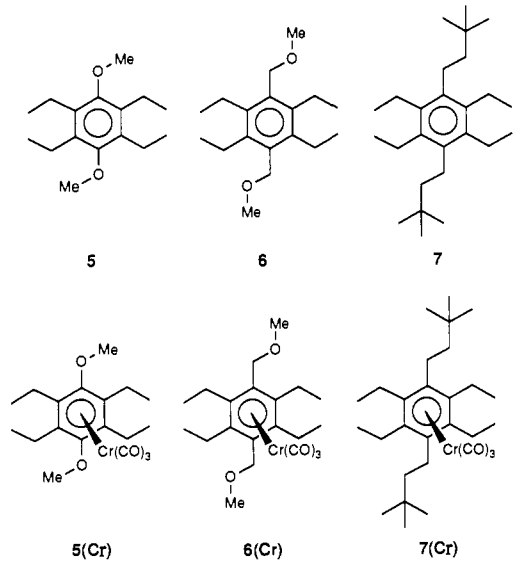
(8) For applications and limitations of this method, see: Burkert, U.; Allinger, N. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

Scheme I. Synthetic Path to **5** and **6**[a]



[a](a) *hν*, room temperature, 36 h, CH_2Cl_2. (b) $(NH_4)_2Ce(NO_3)_6$, CH_3CH_2OH. (c) HOAc, Zn, room temperature. (d) NaH, DMF, Me_2SO_4, reflux, 6 h. (e) CH_3COCl, $AlCl_3$, CS_2, room temperature, 18 h. (f) N_2H_4(aq), NaOH, triethylene glycol, reflux, 4 h. (g) HNO_3, H_2SO_4, $CHCl_3$, 0 °C, 0.5 h. (h) HOAc, $SnCl_2$, HCl, reflux, 1 h. (i) $FeCl_3$(aq), 12 h. (j) CH_3OCH_2Cl, $SnCl_4$, CH_2Cl_2, 0 °C, 1 h. (k) CH_3OH/H_2O, NaOH, reflux, 18 h.

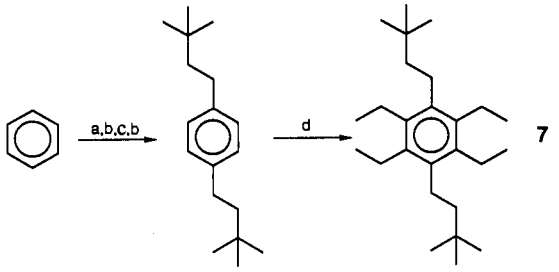
Assuming the up–down conformation of the arene is retained,[7,8] the tricarbonylchromium complexes of **5**, **6**, and **7** have C_s symmetry in the absence of ethyl group rotation. Under conditions



of rapid ethyl group rotation this symmetry increases to $C_s \times C_2$ (isomorphic to C_{2v}). In this system the ethyl group remains chirotopic; thus, the geminal hydrogens never become equivalent, and they are not useful to monitor the dynamics. The hydrogens of the methyl groups at positions 1 and 4 on the arene are diastereotopic at the static limit and become homotopic through side-group rotation (Figure 3). Therefore, in the metal complex the probe to be monitored is the methyl resonance. Having established the probes for our systems,[9] we are ready to approach the synthesis of the molecules to be studied.

Synthesis. **5** is, to our knowledge, previously unreported in the literature. This was much to our surprise as one might imagine that **5** could be trivially synthesized from 1,4-dimethoxybenzene by exhaustive Friedel–Crafts alkylation. We were unable to effect this route so we turned to two others.

Scheme II. Synthetic Path to **7**[a]



[a](a) $(CH_3)_3CCH_2COCl$, $AlCl_3$, reflux, 18 h. (b) N_2H_4(aq), NaOH, triethylene glycol, reflux, 4 h. (c) $(CH_3)_3CCH_2COCl$, $AlCl_3$, CS_2, reflux, 12 h. (d) CH_3CH_2Cl, $AlCl_3$, 5 °C, 18 h.

The first route involved nitration of tetraethylbenzene by nitric acid, reduction of the nitro compound to the diamine, and oxidation of the diamine with aqueous ferric chloride to the quinone.[10] The quinone was then reduced and O-methylated to give **5**. The second route differs in its approach to the quinone but ends similarly. It begins with a variation of the Reppe reaction;[11] 3-hexyne plus pentacarbonyliron are mixed together neat under an inert atmosphere and irradiated for 3 days, followed by oxidation of the crude product with ferric nitrate or ceric ammonium nitrate in ethanol. This reaction yields pure tetraethylquinone.[12,13]

Synthesis of **6** proceeds through chloromethylation[14] of tetraethylbenzene by chloromethyl methyl ether and stannic chloride, followed by solvolysis of the resulting bis(chloromethyl) compound in methanol/water (Scheme I). The tetraethylbenzene was produced from the commercially available triethylbenzene by Friedel–Crafts acylation and Wolff–Kischner reduction.

7 was synthesized starting from benzene and *tert*-butylacetyl chloride. Repetitive acylation and reduction yielded the 1,4-dineohexylbenzene. This was then exhaustively ethylated using ethyl chloride and aluminum chloride to form **7** (Scheme II).

The synthesis of the chromium complex of **5** differs slightly from that of **6** and **7**. **5** is reacted with triamminetricarbonylchromium,[15] whereas **6** and **7** are reacted with hexacarbonylchromium. All complexations were done in dry dioxane.

Results and Discussion

Variable-temperature NMR studies on **5** showed that the barrier to ethyl group rotation was quite low compared to **4**. Even at −60 °C and 500 MHz the AB pattern for the methylene hydrogens did not mannifest itself. Switching to a deuterated freon,[16] we were able to observe the AB pattern below −100 °C and to measure a barrier of 7.7 kcal/mol. [Note: For **5**, **6**, and **7**, the methyl of the ethyl group was decoupled to simplify the spectra.] The result on the free ligand raised doubt about the experimental accessibility of the ethyl group barrier in the chromium complex. By analogy to the existing studies,[2] the barrier would be around 5–6 kcal/mol. However, the variable-temperature NMR study on **5**(Cr) in CCl_2FD showed two methyl signals from the methoxy

(9) A study based on substitution of the 1,3 or 1,2 ethyl groups would have also been possible. The 1,4 pattern was chosen because of the simplicity of resulting NMR spectra. In the 1,3 pattern the two faces of the ring are diastereotopic and would lead to diastereomeric conformations after complexation with chromium. The 1,2 pattern has two different types of ethyl groups, and the chance of accidental signal overlap makes it an undesirable candidate.

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Table I. Data for Estimation of the Barriers to Rotation About the C(aromatic)–C(methylene) Bond by the Gutowsky–Holm Approximation [$k_c = \pi/2(\Delta\nu_{ab}^2 + 6J_{ab}^2)^{1/2}$; $\Delta G^{\ddagger}_c = 4.576T_c(10.319 + \log T_c/k_c)$ cal/mol; See Text for Error Analysis]

compd	R (obsd)[a]	T_c (K)	$\Delta\nu$ (Hz)	J_{ab} (Hz)	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
5	CH_2CH_3	166 ± 5	120 ± 2	14 ± 1	277 ± 12	7.7 ± 0.3
5(Cr)	OCH_3	140 ± 5	54 ± 2		128 ± 4	6.6 ± 0.3
6	CH_2CH_3	193 ± 5	23 ± 2	14 ± 1	92 ± 14	9.4 ± 0.3
6(Cr)	OCH_3	179 ± 5	25 ± 2		56 ± 4	8.9 ± 0.3
7	CH_2CH_3	229 ± 5	24 ± 2	14 ± 1	94 ± 14	11.2 ± 0.3
7(Cr)	$(CH_3)_3C$	228 ± 5	11 ± 2		24 ± 4	11.8 ± 0.3
4						11.8[b,c]
4(Cr)	CH_2CH_3	243 ± 5	70 ± 2		156 ± 5	11.7 ± 0.3 (11.5 ± 0.6)[c]
1						16.2 ± 0.3[d]
1(Cr)						12.0 ± 0.3[d]
3						22.2 ± 0.4[e]
2(Cr)						16.9 ± 0.2[f]

[a] Signals observed through coalescence. [b] EFF calculation. [c] Reference 1a. [d] Reference 2a. [e] Reference 2c. [f] Reference 2b.

groups at −140 °C. These coalesced at −133 °C. Using the Gutowsky–Holm approximation (GHA)[17] the barrier was found to be 6.6 kcal/mol, almost identical to that of the free arene.

The variable-temperature NMR of **6** showed a doublet of doublets for the methylene protons at −120 °C. The coalescence temperature was assigned at −80 °C, and by GHA a barrier was calculated of 9.2 kcal/mol. The complex, **6**(Cr), showed two methyl signals from the diastereotopic methoxy groups at −120 °C. They coalesced at −94 °C, and the barrier was found to be 8.9 kcal/mol, again close to that of the free ligand. On the basis of the earlier work[2] and the barrier in **6**(Cr), one would predict a barrier as high as 15 kcal/mol for the noncomplexed arene (Figures 4 and 5).

The results for **7** were consistent with the first two examples. The variable-temperature NMR of **7** showed a doublet of doublets at −80 °C. Coalescence of the AB signals was found at −44 °C, and the barrier was then calculated to be 11.2 kcal/mol. In the case of **7**(Cr), two signals are seen for the methyls of the *tert*-butyl groups at −70 °C. Warming the sample one arrives at coalescence at −45 °C. The calculated barrier is 11.8 kcal/mol (Table I).

Thus, in all three of the systems we examined, we found only a minor perturbation of the barrier to ethyl group rotation when the metal tripod was introduced onto the arene. These results would indicate that for these systems the use of transition metals as desymmetrizing units for the study of such stereodynamics provides data that is an accurate assessment of the parent–ligand dynamics. This lock-and-key fit is also of importance to the design of arene ligands which modify the steric environment around a transition metal; 1,3,5-substituted hexaalkylbenzenes should be capable of enshrouding the metal without strongly altering the strength of the metal–arene bond.

We attribute our observations to an unusual complementarity between the steric demands of the arene template and the metal tripod. Another view would be that the metal tripod is not interacting at all with the alkyl groups of the arene and that lock-and-key fitting has nothing to do with it. This highlights the question of whether there is a dynamic correlation between the rotation of the ethyl groups and the rotation of the tripod in such compounds. If nestling of the carbonyls among the proximal ethyls is an important aspect of the stereochemistry in **4**(Cr), then one would expect an increase in the barrier to metal tripod rotation as compared to hexamethylbenzene. This question has generated some controversy in the literature due to the lack of a definitive system that had been designed on rigorous symmetry principles and at the same time served as an accurate model for **4** and **4**(Cr).[18]

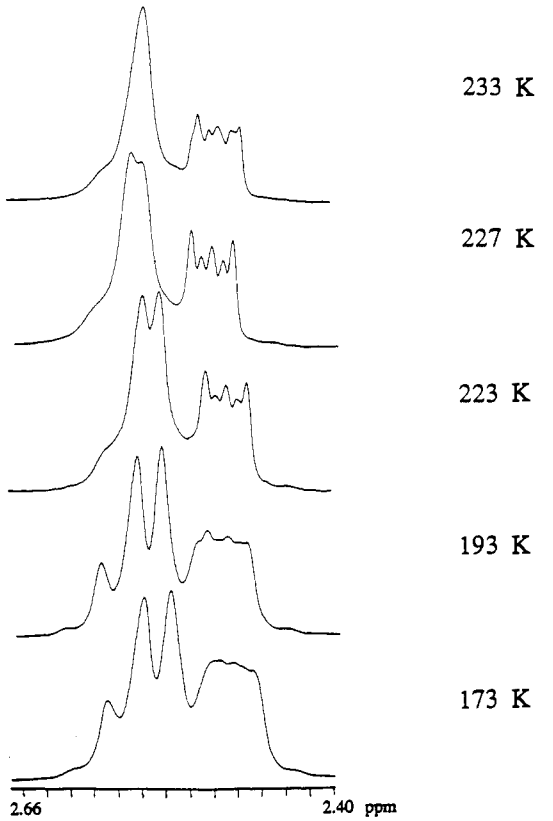

Figure 4. 500-MHz ^{1}H NMR spectra of the methylene region of **7** at 233, 227, 223, 193, and 173 K.

It should be noted that the desymmetrization scheme employed here applies directly to the question of dynamic correlation. The above analysis includes the fact that **6**(Cr) has a symmetry of C_s at the slow motion limit. Tripod rotation in the absence of ethyl group rotation imparts a dynamic symmetry of $C_s \times C_3$. Thus, the ^{13}C NMR spectrum of the complex should exhibit two different carbonyl carbons at the static limit, and these two signals should coalesce at the dynamic limit. In suitably substituted systems, both ethyl group rotation and tripod rotation can be monitored

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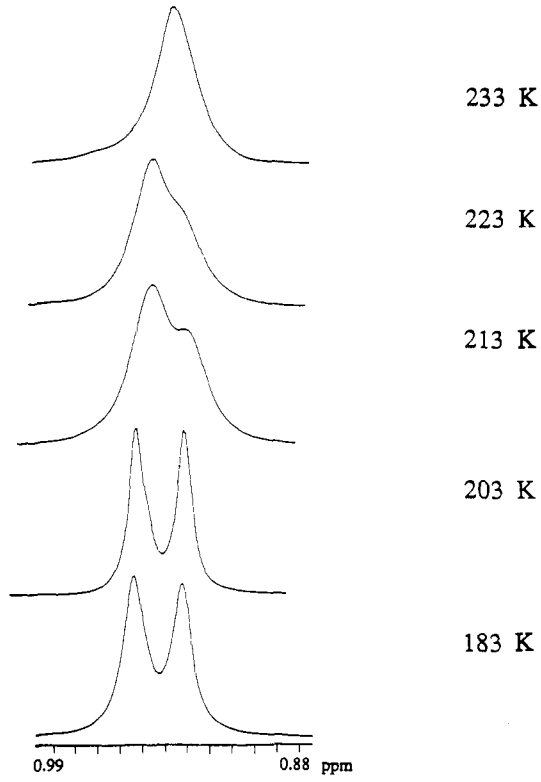

Figure 5. 500-MHz ^1H NMR of the *tert*-butyl region of **7(Cr)** at 233, 223, 213, 203, and 183 K.

independently yet concomitantly. This permits investigation of the dynamic correlation. We have addressed this question in a separate study and have found that the barrier to metal tripod rotation increases from 0.3 kcal/mol in hexamethylbenzene to 9.5 kcal/mol in an analogue of **4(Cr)**.[23]

Experimental Section

General Data. Proton NMR spectra were recorded on a ^1H NMR spectrometer equipped with a Nicolet 1180E computer interfaced with an Oxford magnet operating at 360 MHz, a Varian 500 MHz, or a GE/Nicolet QE300 spectrometer. Carbon NMR were recorded on a QE300 spectrometer operating at 75 MHz, a Varian Unity 500 spectrometer operating at 125.7 MHz, or a Nicolet NT200 spectrometer operating at 50 MHz. Infrared spectra were recorded on a Perkin-Elmer 1420 IR spectrometer. Unless otherwise stated, commercial chemicals were used as supplied. Starting materials can be obtained from the following sources: 1,2,4-triethylbenzene (Fluka); 3-hexyne (Albany/Farchan/Wiley); iron pentacarbonyl and chromium hexacarbonyl (Strem); chloromethyl methyl ether and *tert*-butylacetyl chloride (Aldrich). Dioxane was distilled from calcium hydride and then sodium. Benzene was distilled from sodium.

2,3,5,6-Tetraethylquinone (8) was synthesized according to the procedure of Sternberg et al.[12] 3-Hexyne (11.2 mL, 0.110 mol), iron pentacarbonyl (14 mL, 0.110 mol), and dichloromethane (100 mL) were placed in a 200-mL Kjeldahl flask under argon. The red-brown solution was irradiated for 36 h at room temperature. After that time period, the solution turned black and the solvent was removed under vacuum. The resulting black solid was dissolved in ethanol (150 mL) and oxidized using ceric ammonium nitrate[13] until gas evolution ceased. Then the volume was reduced in half, and a dilute HCl solution (2 mL of concentrated HCl in 100 mL of water) was added until cloudiness occurred. The product mixture was cooled, filtered, and dried, yielding the bright yellow quinone **8** (6.0 g, 0.028 mol, 50%). The tetraethylquinone was recrystallized using water/acetone: mp 57–58 °C [lit. mp 60–62,[24a] 56–58,[24b] 58–59[24c] °C]; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.07 (12 H, t, ^3J = 9 Hz), 2.48 (8 H, q, ^3J = 9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 14.3, 19.2, 144.5, 187.0.

1,4-Dihydroxy-2,3,5,6-tetraethylbenzene (9) was synthesized by a procedure adapted from the work of Nef.[10] The tetraethylquinone (5.00 g, 22.7 mmol) was dissolved in glacial acetic acid (60 mL). Zinc dust (2.98 g, 45.4 mmol) was added to the swirling yellow solution until the color disappeared. The reaction was quenched in ice. The precipitate was collected by filtration and dissolved in acetone. The residual particulates (zinc) were filtered off and the remaining solution was evaporated, yielding white crystals of **9** (3.28 g, 14.8 mmol, 65%).[26] The product was recrystallized using water/acetone: mp 110–112 °C; ^1H NMR (DMSO, 360 MHz) δ 1.2 (12 H, t, ^3J = 7.6 Hz), 2.7 (8 H, q, ^3J = 7.6 Hz), 7.35 (4 H, s); $^{13}C\{^1H\}$ NMR (DMSO, 75 MHz) δ 14.9, 19.4, 127.3, 145.2.

1,4-Dimethoxy-2,3,5,6-tetraethylbenzene (5). To a stirred solution of dihydroxytetraethylbenzene (3.5 g, 15.8 mmol), dry dimethylformamide (75 mL), and sodium hydride (1.01 g, 42.0 mmol) was added 4 equiv (6 mL, 8 g, 63.2 mmol) of freshly distilled dimethyl sulfate. The reaction mixture was heated at reflux for 6 h. The reaction was monitored by TLC on silica gel eluting with chloroform. The product mixture was added to ice in order to precipitate **5** (3.20 g, 12.8 mmol, 81%) as a white solid. The solid was recrystallized from water/acetone or absolute ethanol: mp 115–117 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.18 (12 H, t, ^3J = 7.6 Hz), 2.64 (8 H, q, ^3J = 7.6 Hz), 3.75 (6 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 15.7, 19.4, 61.7, 134.0, 153.2; MS (high resolution) found 250.1930 (calcd for $C_{16}H_{26}O_2$ (M^+) 250.1933).

(1,4-Dimethoxy-2,3,5,6-tetraethylbenzene)chromium Tricarbonyl (5(Cr)). To a stirred solution containing **5** (2.0 g, 8.0 mmol) and dry dioxane (75 mL) was added 1.5 equiv of triamminechromium tricarbonyl (2.24 g, 12 mmol).[15] The reaction mixture was heated to reflux, and the reaction was monitored by TLC (20% ethyl acetate/hexanes, silica). After approximately 3 h, the solution was cooled, filtered, and evaporated to give a yellow-green solid. The chromium complex, **5(Cr)**, was isolated by column chromatography on silica gel. Initial elution with hexanes yielded starting material and a yellow band which was *not* **5(Cr)**. Further elution with 20% ethyl acetate/hexanes yielded a yellow band which was identified as **5(Cr)** (0.81 g, 2 mmol, 25%): mp 82–83 °C; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.26 (12 H, t, ^3J = 7.6 Hz), 2.52 (8 H, d of q, ^3J = 7.2 Hz), 3.79 (6 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 16.2, 20.6, 65.1, 108.5, 136.8, 234.4; IR (KBr) 1940, 1855 cm^{-1}; FABMS (high resolution) found 386.1166 (calcd for $C_{19}H_{26}O_5Cr$ (M^+) 386.1185).

5-Acetyl-1,2,4-triethylbenzene (10). An aliquot of 1,2,4-triethylbenzene (15.3 mL, 13.3 g, 82.0 mmol) was dissolved in 50 mL of carbon disulfide. To the swirling solution were added acetyl chloride (6.5 mL, 7.18 g, 91.0 mmol) and anhydrous aluminum chloride (21.7 g, 163.0 mmol). After the HCl evolution subsided, the flask was fitted with a drying tube. After 18 h of stirring at room temperature, the reaction was quenched by addition to a 0.10 M HCl/ice water solution. The organic layer was extracted with methylene chloride and dried with anhydrous sodium sulfate, yielding 17.3 g of the impure product. The product was purified via vacuum distillation to give **10** (13.4 g, 66.0 mmol, 80%):[26] ^1H NMR ($CDCl_3$, 360 MHz) δ 1.25 (12 H, m), 2.57 (3 H, s), 2.7 (4 H, m), 2.8 (2 H, m), 7.1 (1 H, s), 7.5 (1 H, s).

1,2,4,5-Tetraethylbenzene (11) was synthesized according to the Huang-Minlon modification of the Wolff–Kischner reaction.[25] Sodium hydroxide (7.52 g, 188.0 mmol) and hydrazine hydrate (7.12 mL, 145.0 mmol) were added to a stirred solution of **10** (9.52 g, 47.0 mmol) in 60 mL of triethylene glycol, and the mixture was refluxed for 1 h. Then the condenser was removed, and the mixture was heated to 195 °C. At that point, the condenser was replaced, and the reaction was heated at reflux for an additional 3 h. The solution was cooled, acidified with dilute HCl, and extracted with methylene chloride. The organic layer was dried over sodium sulfate. The solvent was removed on a rotary evaporator yielding an oil, which was recrystallized in absolute ethanol at −20 °C in the freezer. Note: This compound melts at ca. 10 °C, but recrystallization at low temperatures yielded pure crystals [lit. mp 10 °C].[27] The mother liquor can be removed at low temperatures by cannulation, leaving pure tetraethylbenzene (6.48 g, 34 mmol, 73%): ^1H NMR ($CDCl_3$, 360 MHz) δ 1.21 (12 H, t, ^3J = 7.2 Hz), 2.61 (8 H, q, ^3J = 7.2 Hz), 6.96 (2 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 15.4, 25.1, 128.3, 139.0; MS (high resolution) found 190.1720 (calcd for $C_{14}H_{22}$ (M^+) 190.1722).

1,4-Bis(chloromethyl)-2,3,5,6-tetraethylbenzene (12) was synthesized from an adapted procedure of Gambarova for chloromethylation of alkylbenzenes.[14] The tetraethylbenzene (2.0 g, 10 mmol) was dissolved in 20 mL of dry dichloromethane at 0 °C. To the swirling solution were added chloromethyl methyl ether (2.41 g, 30 mmol) and stannic chloride

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(7.80 g, 30 mmol). After approximately 1 h at 0–5 °C, the reaction was quenched with ice water to precipitate a white solid. In some runs, the product precipitated from the chilled reaction mixture, but no change in the workup was made. The product was washed with water and recrystallized in absolute ethanol to give **12** (2.58 g, 9 mmol, 90%):[28] mp 128–9 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.24 (12 H, t, ^3J = 7.6 Hz), 2.78 (8 H, q, ^3J = 7.6 Hz), 4.68 (4 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 16.0, 22.2, 41.2, 134.4, 140.3; MS (high resolution) found 286.1258 (calcd for $C_{16}H_{24}Cl_2$ (M^+) 286.1256).

1,4-Bis(methoxymethyl)-2,3,5,6-tetraethylbenzene (6). The bis(chloromethyl) compound, **12**, (0.50 g, 1.8 mmol) was dissolved in 15 mL of 50% methanol/water. Sodium hydroxide (0.21 g, 5.2 mmol) was added to the swirling solution. The reaction was heated to reflux for 18 h. After the solution was cooled, the methanol was removed on the rotary evaporator yielding **6** (0.44 g, 1.6 mmol, 91%), which was recrystallized from absolute ethanol: mp 73–74 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.17 (12 H, t, ^3J = 7.2 Hz), 2.72 (8 H, q, ^3J = 7.2 Hz), 3.45 (6 H, s), 4.42 (4 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 16.2, 22.2, 58.5, 69.0, 134.0, 140.0; MS (high resolution) found 278.2241 (calcd for $C_{18}H_{30}O_2$ (M^+) 278.2246).

(1,4-Bis(methoxymethyl)-2,3,5,6-tetraethylbenzene)chromium Tricarbonyl (6(Cr)). A mixture containing **6** (0.50 g, 1.8 mmol) and chromium hexacarbonyl (0.59 g, 2.7 mmol) in 25 mL of dry dioxane was heated to reflux under an atmosphere of argon for 12 h. The reaction was monitored by TLC (20% ethyl acetate/hexanes, silica). Distillation of the solvent yielded the product mixture, which was purified by column chromatography to give a yellow solid, **6(Cr)** (0.42 g, 1.0 mmol, 56%): mp 124–125 °C; ^{1}H NMR ($CDCl_2F$, 360 MHz) δ 1.08 (12 H, t, ^3J = 7.2 Hz), 2.41 (8 H, q, ^3J = 7.2 Hz), 3.38 (6 H, s), 4.12 (6 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz) δ 17.1, 22.1, 58.8, 69.1, 103.4, 114.6, 233.9; IR (KBr) 1945, 1858 cm^{-1}; FABMS (high resolution) found 414.1498 (calcd for $C_{21}H_{30}O_5Cr$ (M^+) 414.1498).

***(tert*-Butylacetyl)benzene (13).** To a stirred solution containing dry benzene (110 g, 125 mL, 1.40 mol) and *tert*-butylacetyl chloride (19.4 g, 20 mL, 0.15 mol) in a 250-mL round-bottom flask placed in an ice bath was added aluminum chloride (21.5 g, 0.16 mol), slowly. A reflux condenser was placed on the flask and the reaction was refluxed. After 18 h, the mixture was cooled and quenched with 0.10 M HCl and ice. The organic layer was extracted with methylene chloride and dried with anhydrous sodium sulfate, which was purified via vacuum distillation, yielding **13** (16.9 g, 0.096 mol) in a 64% yield:[29] ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.07 (9 H, s), 2.87 (2 H, s), 7.45 (2 H, t, ^3J = 7.2 Hz), 7.54 (1 H, t, ^3J = 7.2 Hz, 1.5 Hz), 7.93 (2 H, dd, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 30.0, 31.2, 49.9, 128.1, 128.1, 132.5, 138.4, 200.2; MS (high resolution) found 176.1192 (calcd for $C_{12}H_{16}O$ (M^+) 176.1201).

Neohexylbenzene (14) was prepared by the Huang-Minlon modification of the Wolff–Kischner reaction.[25] Sodium hydroxide (15.4 g, 0.385 mol) and hydrazine hydrate (10 mL of 55% aqueous solution) were added to a stirred solution of **13** (16.9 g, 0.096 mol) in 150 mL of triethylene glycol, and the mixture was refluxed for 1 h. Then, the condenser was removed, and the mixture was heated to 195 °C. At that point, the condenser was replaced, and the reaction was heated at reflux for an additional 3 h. The solution was cooled, acidified with dilute HCl, and extracted with methylene chloride. The organic layer was dried with anhydrous sodium sulfate and evaporated, yielding a yellow oil. Upon cooling, a yellow oil formed in the clear oil. The solid was separated from the oil, which was the product, **14** (11.76 g, 0.072 mol, 75%)[29] (the yellow solid was identified as the dihydrazone): ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.96 (9 H, s), 1.5 (2 H, m), 2.57 (2 H, m), 7.18 (3 H, m), 7.28 (2 H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 29.4, 30.5, 31.3, 46.5, 125.5, 128.3, 143.5; MS (high resolution) found 162.1408 (calcd for $C_{12}H_{18}$ (M^+) 162.1404).

1-Neohexyl-4-(*tert*-butylacetyl)benzene (15). To a stirred solution containing **14** (12.41 g, 0.077 mol) and *tert*-butylacetyl chloride (16.0 mL, 15.5 g, 0.12 mol) in 100 mL of carbon disulfide was added aluminum chloride (20 g, 0.15 mol), slowly. The 250-mL round-bottom flask was fitted with a reflux condenser and heated. After 12 h, the solution was quenched with 0.1 M HCl/ice water. The organic layer was extracted with methylene chloride, dried with anhydrous sodium sulfate, and evaporated, yielding a light yellow liquid, **15** (10.8 g, 0.041 mol, 53%): ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.97 (9 H, s), 1.06 (9 H, s), 1.50 (2 H, m), 2.63 (2 H, m), 2.83 (2 H, s), 7.25 (2 H, d, ^3J = 8.3 Hz), 7.85 (2 H, d, ^3J = 8.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 29.3, 30.1, 30.9, 31.3, 31.4, 45.9, 49.9, 128.4, 128.4, 136.2, 149.0, 200.1; MS (high resolution) found 260.2155 (calcd for $C_{18}H_{28}O$ (M^+) 260.2140).

1,4-Dineohexylbenzene (16) was prepared by the Huang-Minlon modification of the Wolff–Kischner reaction.[25] To a stirred solution of **15** (10.8 g, 0.041 mol) in 100 mL of triethylene glycol were added sodium hydroxide (6.6 g, 0.166 mol) and hydrazine hydrate (12 mL), and the mixture was refluxed for 1 h. Then, the condenser was removed, and the mixture was heated to 195 °C. At that point, the condenser was replaced, and the reaction was heated at reflux for an additional 3 h. The solution was cooled, acidified with dilute HCl, and extracted with methylene chloride. The organic later was dried with sodium sulfate. The solvent was removed on a rotary evaporator, yielding an oil which was recrystallized with absolute ethanol to give a white crystalline solid, **16** (7.24 g, 0.030 mol, 72%): mp 86–88 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.95 (18 H, s), 1.47 (4 H, m), 2.52 (4 H, m), 7.09 (2 H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz) δ 29.3, 30.5, 30.8, 46.5, 128.1, 140.6; MS (high resolution) found 246.2345 (calcd for $C_{18}H_{30}$ (M^+) 246.2348).

1,4-Dineohexyl-2,3,5,6-tetraethylbenzene (7) was synthesized by exhaustive ethylation of **16**.[30] A mixture of **16** (0.290 g, 1.2 mmol), ethyl chloride (1.72 g, 27 mmol, 2 mL), and aluminum chloride (0.71 g, 5.3 mmol) was stirred in a 5-mL screwtop vial at 5 °C for 18 h. The reaction was quenched with ice water. The resulting organic layer was extracted with methylene chloride, dried with sodium sulfate, and evaporated, yielding a white solid which was a mixture of starting material and product. The product was purified by recrystallization from absolute ethanol to give **7** (0.172 g, 0.5 mmol, 40%): mp 197 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.99 (18 H, s), 1.18 (12 H, t, ^3J = 7.2 Hz), 1.42 (4 H, m), 2.52 (4 H, m), 2.59 (8 H, q, ^3J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 15.2, 21.6, 23.6, 28.5, 30.1, 44.8, 135.0, 137.4; MS (high resolution) found 358.3606 (calcd for $C_{26}H_{46}$ (M^+) 358.3600).

(1,4-Dineohexyl-2,3,5,6-tetraethylbenzene)chromium Tricarbonyl (7(Cr)). A mixture of **7** (100 mg, 0.28 mmol) and chromium hexacarbonyl (91 mg, 0.42 mmol) in 15 mL of dry dioxane was heated to reflux under an atmosphere of argon for 16 h. The reaction was monitored by TLC (20% ethyl acetate/hexanes, silica). Distillation of the solvent yielded a greenish-yellow solid, which was purified by column chromatography on silica gel to give **7(Cr)** (48 mg, 0.1 mmol) as a light yellow crystalline solid in 36% yield: mp 187–194 °C dec, ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.99 (18 H, s), 1.25 (12 H, t, ^3J = 7.2 Hz), 1.47 (4 H, m), 2.32 (4 H, m), 2.38 (8 H, q, ^3J = 7.2 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, −60 °C) δ 14.0, 19.4, 19.9, 20.9, 22.4, 24.2, 28.3, 30.5, 43.3, 49.3, 107.1, 108.7, 116.5, 117.1, 234.4; IR (KBr) 1825.6, 1852.2 cm^{-1}; FABMS (high resolution) found 494.2898 (calcd for $C_{29}H_{46}O_3Cr$ (M^+) 494.2852).

Variable-Temperature NMR Measurements. All variable-temperature experiments were run on the above-described 500-MHz instrument. The temperature was regulated by a chilled stream of nitrogen gas. Temperatures were corrected by a calibration graph. A copper–constantan thermocouple was inserted into an NMR tube with solvent at a similar height to that on a normal sample. Thermocouple readings from inside the tube were then correlated to readings from the thermocouple mounted in the probe. This calibration was repeated from time to time. Temperatures during a given experimental run were then extrapolated from the calibration curve and the reading from the probe thermocouple. Temperature readings are accurate within 5 °C.

Samples were prepared in dichlorofluoromethane-d_1,[15] transferred cold, and inserted into the probe at −35 °C. Chromium complexes were dissolved under argon.

Error Analysis. Following a standard propagation of error analysis on the equation, $k_c = \pi/2(\Delta\nu_{ab}^2 + 6J_{ab}^2)^{1/2}$, one arrives at the error in k_c. The free energy of activation is calculated from the Gutowsky–Holm approximation, $\Delta G^*_c = 4.576T_c(10.319 + \log T_c/k_c)$ cal/mol. The contribution of k to the error in ΔG^*_c comes through a small log term added to a large constant and is relatively small compared to the contribution from T_c. For simplicity, we have treated the term within the parentheses as being without error as compared to T_c and calculated the error in ΔG^*_c as directly proportional to the error in T_c.

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(30) We find this procedure to be quite sensitive to the quality of the aluminum chloride and ethyl halide as well as the reaction conditions. Under certain conditions, acid-induced rearrangements of the alkyl groups were observed.

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Registry No. 5, 137039-59-9; **5(Cr)**, 137039-65-7; **6**, 137039-60-2; **6(Cr)**, 137039-66-8; **7**, 137039-61-3; **7(Cr)**, 137039-67-9; **8**, 3450-15-5; **9**, 137039-62-4; **10**, 2715-54-0; **11**, 635-81-4; **12**, 65870-23-7; **13**, 31366-07-1; **14**, 17314-92-0; **15**, 137039-63-5; **16**, 137039-64-6; $Fe(CO)_5$, 13463-40-6; $Cr(CO)_6$, 13007-92-6; triaminechromium tricarbonyl, 14974-11-9; 3-hexyne, 928-49-4; 1,2,4-triethylbenzene, 877-44-1.

Use of Prochiral Phosphaalkene Complexes in the Synthesis of Optically Active Phosphines

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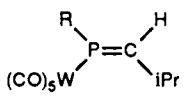
Abstract: Prochiral L-menthyl phosphaalkene complexes were prepared from "phospha-Wittig" reagents, $[MenP(H)-P(O)(OR)_2]M(CO)_5$ (M = Mo, W), and several aldehydes. Their catalytic hydrogenation using RhL_2^+ catalysts and their [2 + 4] cycloaddition with cyclopentadiene proceeded with full diastereoselectivity. A molecular model of such a phosphaalkene complex showed that a preferred conformation exists that minimizes the combined interactions of the isopropyl substituent of the L-menthyl group with the complexing group and the phosphavinylic C–H bond. In this conformation, only the *si* face of the phosphaalkene is free for the incoming reagents. Both hydrogenation and [2 + 4] cycloaddition with cyclopentadiene selectively take place on this face as demonstrated by the X-ray crystal structure analysis of two of the resulting complexes. A two-step procedure was devised for the conversion of $[MenPH_2]Mo(CO)_5$ into optically pure phosphines. In the first step, the primary phosphine complex was phosphorylated, the resulting phospha-Wittig reagent was allowed to react with an aldehyde, and the phosphaalkene complex thus formed was trapped by cyclopentadiene. The decomplexation of the resulting molybdenum complex was carried out by heating with diphos. An optically pure 2-L-menthyl-2-phospha-5-norbornene was thus prepared.

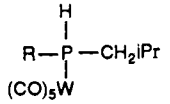
Prochiral phosphaalkenes or phosphaalkene complexes are a potential source of optically active P^{III} species provided that face selectivity can be achieved during the additions or cycloadditions onto the P=C double bond. We have recently devised a versatile route to phosphaalkene complexes via the so-called phospha-Wittig reaction.[1,2] Prochiral P=C double bonds thus became easily accessible, and we were naturally led to investigate the synthesis of optically active P^{III} ligands from these P^{II} complexes.

Results and Discussion

In a previous work,[3] we have described the catalytic hydrogenation of phosphaalkene P–$W(CO)_5$ complexes using Rh(diphos)X (X = Cl, PF_6) as the catalyst. Using prochiral phosphaalkene complexes **1** and $[RhL_2^*]^+PF_6^-$ (L_2^* = chiraphos, dipamp, diop) as the catalyst, we first carried out a series of hydrogenation experiments under the standard conditions.[3b] We never observed a significant ee in the resulting P^{III} complexes **2**.



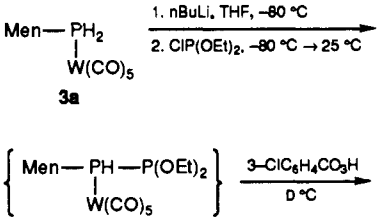
1a: R = Ph
b: R = cyclohexyl



2

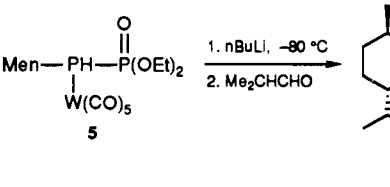
Since the synthesis of carbonyl C-substituted phosphaalkene complexes was hampered by their instability,[4] it was impossible to create a second coordination site in the phosphaalkene complex in order to increase the face selectivity as in the case of dehydroaminoacids.[5] We thus decided to change our approach and to incorporate the optically active group into the structure of the phosphaalkene complex. During our preliminary study of the catalytic hydrogenation of the P=C double bond,[3] we noted that the speed of the reaction was much more sensitive to the steric bulk of the substituents at phosphorus than to the steric bulk of the substituents at carbon. It was thus logical to introduce the optically active group as a substituent at phosphorus where it could better influence the catalytic process.

In a first step, the L-menthyl phospha-Wittig reagent **5** was prepared as follows (eq 1):



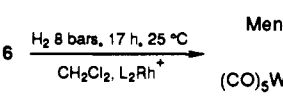
(1)

This route to phospha-Wittig reagents is described more in depth elsewhere.[1c] It gives better yields of **5** than the other possible routes.[1a,b] This reagent was then used to prepare the *P*-menthyl phosphaalkene complex **6** (eq 2):



(2)

The hydrogenation experiments were carried out under the standard experimental conditions[3] (eq 3):



(3)

(1) (a) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382. (b) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793. (c) Bauer, S.; Marinetti, A.; Mathey, F. *Heteroatom. Chem.* **1991**, *2*, 277.
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(3) (a) de Vaumas, R.; Marinetti, A.; Mathey, F. *J. Organomet. Chem.* **1991**, *413*, 411. (b) de Vaumas, R. Ph.D. Thesis, Ecole Polytechnique, 1991.
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