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Toward an Organometallic Molecular Brake with a Metal Foot Pedal: Synthesis, Dynamic Behavior, and X-ray Crystal Structure of [(9-Indenyl)triptycene]chromium Tricarbonyl

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The potential use of haptotropic shifts to control rotational barriers has been initiated by the synthesis of (9-indenyl)triptycene (**12**) and its chromium tricarbonyl derivative (**13**). Both complexes have been characterized by X-ray crystallography and variable-temperature NMR spectroscopy, revealing barriers to rotation of 12 and 13 kcal mol^{-1}, respectively. In the metal complex, the chromium carbonyl moiety coordinates to one of the blades of the triptycene unit rather than to the more crowded indenyl group.

Introduction

Molecular gears are of considerable current interest, as a result of their close resemblance to their macroscopic namesakes. Other microscopic analogues of common machinery[1,2] include molecular propellers,[3] motors,[4] and ratchets;[5] each functions as a result of the controlled interaction of different fragments of the molecule.

The development of gearing systems has focused on the triptycene fragment (**1**; Chart 1), since it offers three "teeth" and is readily functionalizable at the C-9 and C-10 positions. Kelly and co-workers[5] have described a molecular ratchet, **2**, in which a triptycenyl moiety serves as the ratchet wheel and a helicene acts as the pawl and spring; the barrier to rotation of the ratchet was determined to be ∼25 kcal mol^{-1}. Kelly viewed the helicene as merely a friction brake that disrupted but did not prevent the rotation of the triptycene moiety. He has subsequently succeeded in synthesizing the first chemically powered molecular motor[5a] and has recently described attempts to investigate the potential of triptycene-based motors mounted on Si surfaces.[6] More recent work by Feringa[7] has elegantly extended the range of molecular motors now available.

The use of triptycyl groups as bulky substituents with the potential for high barriers to rotation has been widely explored in the literature. In particular, the triptycenyl fragment has appeared in several reports of molecular gearing,[8−14] and barriers as high as 41.0 kcal mol^{-1} have been determined for some methylene- and oxygen-linked triptycenes (**3** and **4**).[10] Moreover, barriers for bis(9-triptycyl)ethynes (**5**) range from 11.6 (Y = fluorine) to 17.3 kcal mol^{-1} (Y = iodine)[1,11] and replacing the halogen by phenyl or mesityl groups increases this barrier to 15.8−18.8 kcal mol^{-1}.[12]

Several benzyl-,[13,14] mesityl-,[13,15] or phenoxy-substituted[14,16] triptycene derivatives have also been investigated. Peri-unsubstituted benzylic triptycenes (**6**) favor isolated rotation (gear slippage, ∼10 kcal mol^{-1}) over correlated rotation, whereas the barriers for the two processes are comparable in singly peri-substituted derivatives (>13 kcal mol^{-1}).[13,17] Substitution both on

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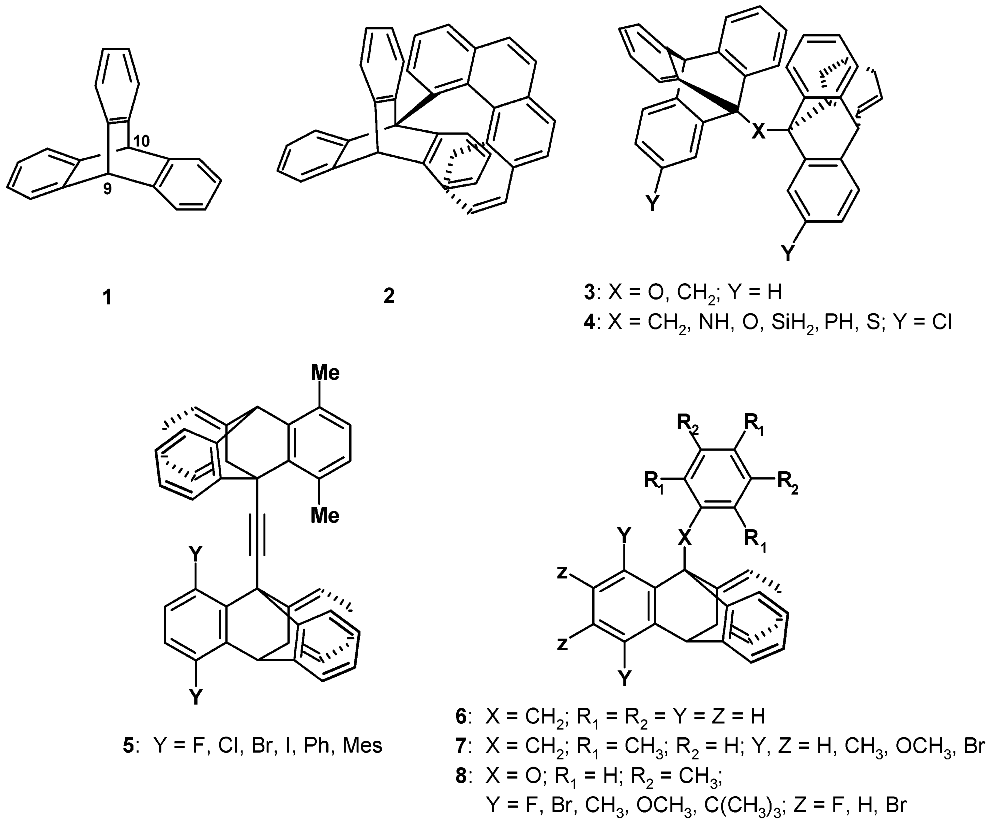
Chart 1. Triptycene-Based Molecular Gears



1

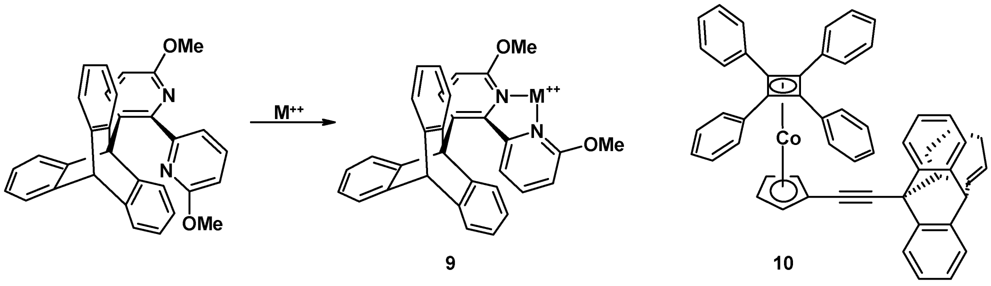
2

3: X = O, CH_2; Y = H
4: X = CH_2, NH, O, SiH_2, PH, S; Y = Cl

5: Y = F, Cl, Br, I, Ph, Mes

6: X = CH_2; R_1 = R_2 = Y = Z = H
7: X = CH_2; R_1 = CH_3; R_2 = H; Y, Z = H, CH_3, OCH_3, Br
8: X = O; R_1 = H; R_2 = CH_3;
Y = F, Br, CH_3, OCH_3, $C(CH_3)_3$; Z = F, H, Br

Scheme 1. Metal-Containing Molecular Brakes 9 and 10



9

10

the benzylic group and in the peri position (**7**) increases the barrier to gear slippage, resulting exclusively in correlated disrotation (12−17 kcal mol^{-1}).[13,15] In phenoxy derivatives (**8**), however, the lowest barrier process depends on the size of the peri substituent. When Y is fluoro or methoxy, molecules of the type **8** exhibit gear rotation (10−12 kcal mol^{-1}); in contrast, when Y is methyl, bromine, or *tert*-butyl, isolated aryl rotation is favored (15−17 kcal mol^{-1}).[16,18] Moreover, in several cases, atropisomers have been isolated and identified for peri-substituted derivatives, with barriers to rotation of ~26 kcal mol^{-1}.[17,19]

The use of metal atom coordination as a means of developing a triptycyl molecular brake was first introduced by Kelly et al., who used the attachment of a metal atom at a remote site to stop the rotation of the gear, as in **9** (Scheme 1).[20] Another application of organometallic fragments toward the development of these systems has been suggested by Richards, who reported the synthesis of the metallocene molecular gear **10**.[21] However, variable-temperature NMR studies revealed the rapid rotation of the triptycene and phenyl substituents even at 203 K; thus, the possibility of correlated rotation of the fragments could not be addressed.

A different approach to the development of this chemistry would involve the use of migrating metal fragments to control the barrier to rotation of the triptycene moiety. It is well established that the deprotonation of (η^6-indene)ML_n complexes results in an η^6-to-η^5 haptotropic shift whereby the metal migrates onto the five-membered ring;[22] the process is reversed upon protonation. The current work extends our continued interest in correlated rotation and molecular machin-

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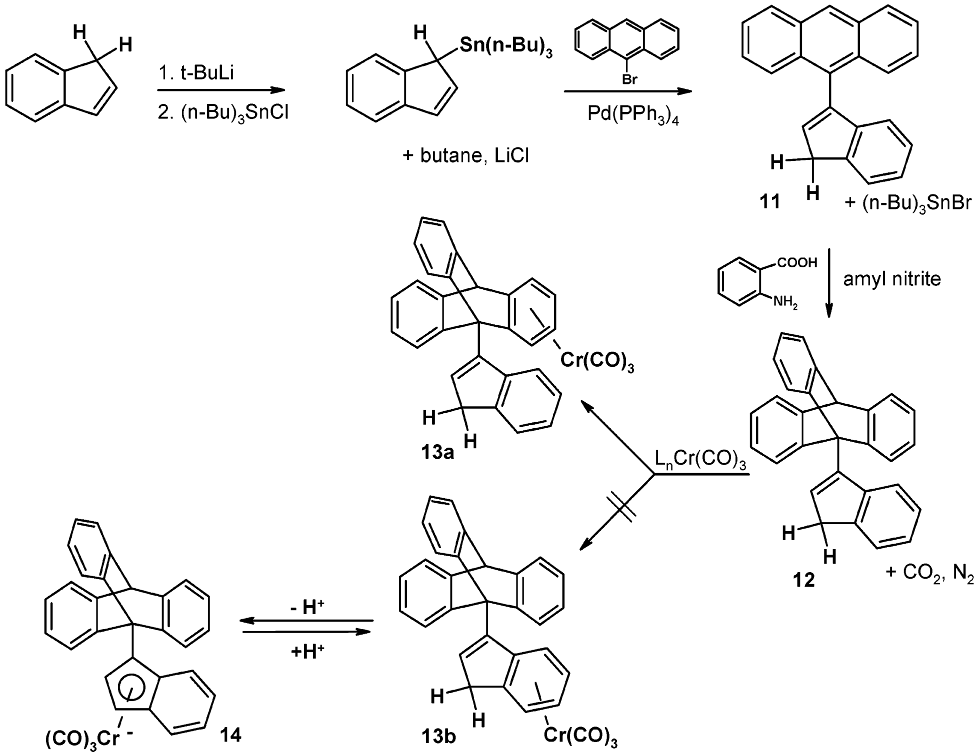
Scheme 2. Proposed Synthetic Route to the Triptycene−Metal Complex



ery,[23] and we now describe our preliminary investigations on the syntheses, structures, and dynamic behavior of (9-indenyl)triptycene complexes.

Results and Discussion

Syntheses and X-ray Crystal Structures. The synthetic route to the target molecules involves the Stille coupling of indenyltributyltin with 9-bromoanthracene, with subsequent addition of benzyne to generate the triptycene skeleton. The final stage requires coordination of the organometallic moiety onto the indenyl substituent (**13b**), with the ultimate goal of using protonation or deprotonation to induce migration (Scheme 2).

The product of the initial Stille coupling, **11**, has been characterized by NMR spectroscopy and X-ray crystallography, and its structure is displayed in Figure 1. The indenyl−anthracene C(9)−C(11) bond length is 1.492(2) Å, and the indenyl substituent is twisted at an angle of 74.1° from the plane of the anthracene, presumably so as to avoid unfavorable steric interactions between ortho hydrogens. Moreover, an indenyl hydrogen atom has migrated so that the anthracene is bonded to the less crowded sp^2 carbon.

Treatment of the indenylanthracene **11** with benzyne furnishes the required ligand **12**, which has also been characterized by NMR spectroscopy and X-ray crystallography (Figure 2). There are several interesting features of the crystal structure, notably the slight lengthening—from 1.492(2) to 1.520(4) Å—of the C(9)−C(17) bond that connects the indene and triptycene as a result of the added three-dimensional steric requirements of the triptycene unit. Moreover, this linkage is no longer coincident with the 3-fold axis of the triptycene but instead deviates from linearity by 7.3(3)°. The indenyl unit is almost perfectly staggered between two benzene components of the triptycene (dihedral angle 55.5°). Finally, we note that the interplanar angles between the blades of the triptycene have been increased to 127° for the blades bisected by the indenyl group; the other angles are decreased to 114 and 119° from the anticipated 120°.

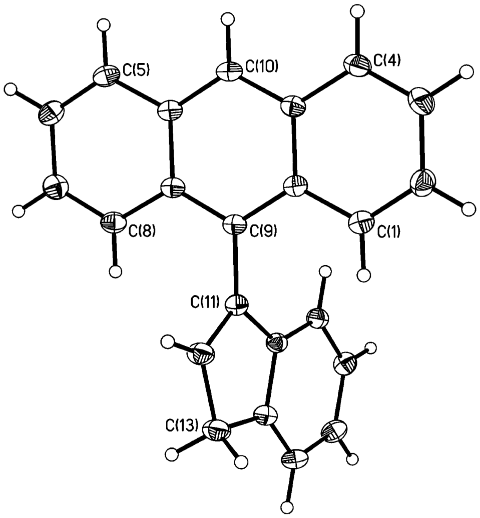


Figure 1. X-ray crystal structure of (9-indenyl)anthracene (**11**; 30% thermal ellipsoids).

We are unaware of any X-ray crystal structures of directly related derivatives in the literature for comparison. However, the C(9)−CH_2 bond lengths in **15** and **16** (Chart 2) are 1.533(4)[17] and 1.541(11) Å,[19d] respectively, and the C(9)−CMe_2 distance in **17** is 1.582(4) Å.[24] In each case, however, one of the blades of the triptycene is 1,4-dimethyl substituted, thus resulting in greater

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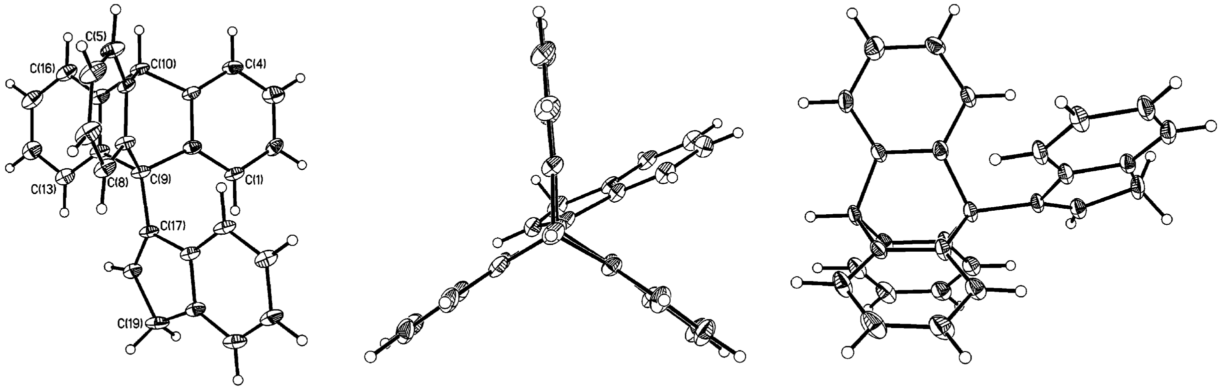


Figure 2. Views of the X-ray crystal structure of (9-indenyl)triptycene (**12**; 30% thermal ellipsoids).

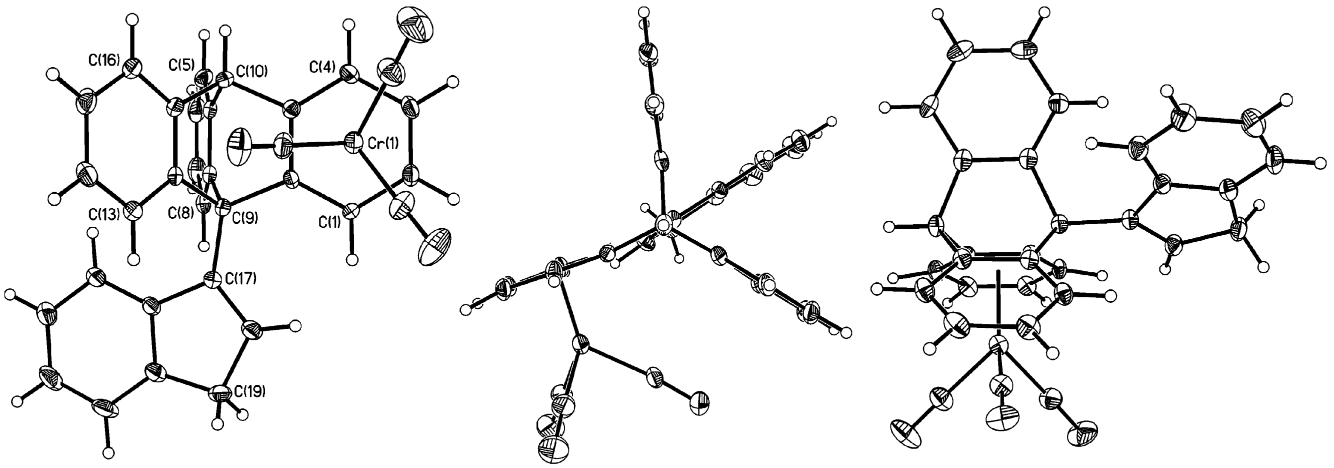
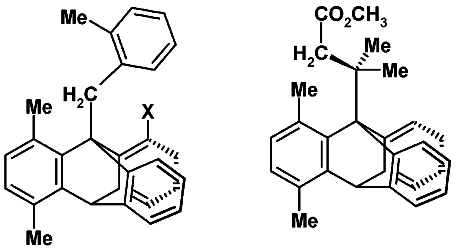


Figure 3. Views of the X-ray crystal structure of the chromium tricarbonyl complex **13a** (30% thermal ellipsoids).

Chart 2. Molecules 15−17



15: X = Br
16: X = Cl

17

interaction with the peripheral group. Nonetheless, there is clearly significant steric interaction between the indenyl substituent in **12** and the peri hydrogens of the triptycene unit.

The reaction of **12** with Cr(CO)$_6$ in di-*n*-butyl ether/THF results in the formation of complex **13a**, in which the chromium tricarbonyl unit is coordinated to one of the blades of the triptycene, instead of the apparently more crowded six-membered ring of the indenyl substituent, as in **13b** (Figure 3). There have been several reports of organometallic derivatives of triptycene itself in which a metal moiety is coordinated to one or more of the propeller blades;[25−27] however, we are unaware of any metal complexes in which there is also a substituent on the 9-position of the triptycene.

The complex crystallizes in space group $P\bar{1}$, and there is one benzene solvent molecule present in the structure. As anticipated, the carbonyl groups are almost perfectly staggered relative to the carbon atoms in the ring of the triptycene blade. The C(9)−C(17) bond length (1.519(5) Å) has not changed significantly from that found in **12**, and the bend of the indenyl substituent out of the plane is 8.4(2)°, only slightly larger than in the uncomplexed ligand. However, there are dramatic changes in the interplanar angles between the triptycene blades: the angle between the blades bisected by the indenyl group is 126°, as is the angle containing the metal moiety. To accommodate the bulky groups between the other blades, the angle lacking substitutents has been drastically reduced to 108°. In the structures of the mono-, bis-, and tris(chromium tricarbonyl) triptycene complexes[25,26] there are only small deviations from the expected 120° (∼2°), whereas a bulkier $Co_4(CO)_9$ moiety increases the angle to 124.1° and decreases those between the uncoordinated blades to 117.0 and 118.9°.[26] Both instances display less deviation from 120° than does complex **13a**, emphasizing that the presence of the

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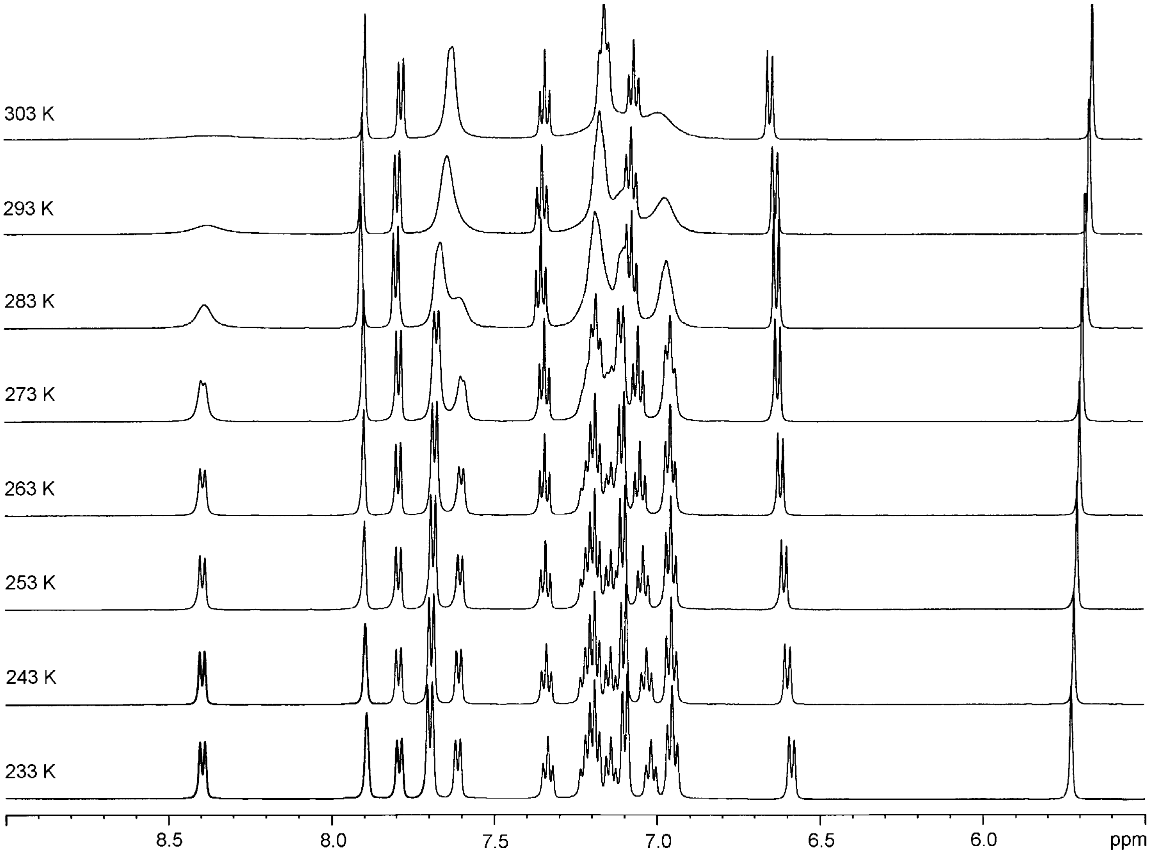

Figure 4. 500 MHz ^{1}H variable-temperature NMR spectra of **12** (CD_2Cl_2).

indenyl substituent clearly has a significant impact on the arrangement of the ligands in terms of minimizing nonbonded repulsions.

Mass spectrometric evidence for the presence of the bis(chromium carbonyl) complex was also acquired; however, sufficient quantities of a pure sample could not be obtained for satisfactory NMR characterization. As a result, the coordination site of the second metal moiety has not been determined.

NMR Spectroscopic Data. Since the room-temperature ^{1}H NMR spectrum of the indenyltriptycene species **12** exhibited significant broadening, variable-temperature data were acquired so as to characterize its fluxional behavior. It is evident from the resulting spectra that the presence of the indenyl substituent is itself sufficient to cause restricted rotation of the triptycene fragment. As the sample is cooled, the peaks begin to sharpen and decoalesce (Figure 4) and, at 233 K, the triptycene exhibits slowed rotation on the NMR time scale such that the indene is located between two of the benzene units, as in the solid-state structure.

The sequence of doublet, triplet, triplet, and doublet resonances at 6.51, 6.98, 7.29, and 7.75 ppm is attributable to H(23), H(22), H(21), and H(20), respectively: i.e., the protons in the six-membered ring of the indenyl fragment that are essentially temperature independent. In contrast, the doublet, triplet, triplet, doublet peak patterns attributable to the aromatic blades of the triptycene are each split in a 2:1 ratio at the low-temperature limit. The "inner" ortho protons were assigned on the basis of their large chemical shift difference—doublets at 8.40 ppm (1H) and 7.10 ppm (2H)—while their "outer" counterparts give rise to doublets at 7.70 ppm (2H) and 7.61 ppm (1H). Assuming that the structure in solution closely matches that found in the solid state, the two "inner" ortho protons should lie within the shielding cone of the indenyl aromatic ring, and the observed doublet at 7.10 ppm supports this assertion. Likewise, the ^{13}C NMR spectra exhibited analogous 2:1 splitting patterns at low temperature.

Line shape analysis of the proton spectra yielded a barrier of 11.9 ± 0.5 kcal mol^{-1} for rotation of the indenyl group relative to the triptycene fragment. This barrier lies within the range of singly peri-substituted benzylic derivatives ($\sim$12−17 kcal mol^{-1})[13,17] but is less than those highly substituted in the peri position of the triptycene and on the benzylic group ($\sim$26 kcal mol^{-1}).[17,19] Moreover, as far as we are aware, this is the largest barrier for a system that is *not* substituted on the blades of the triptycene unit.

Variable-temperature NMR spectra were also acquired for the chromium derivative **13a**. In this case, the extremely complicated low-temperature ^{1}H spectra (Figure 5) were collected in CD_2Cl_2 and reveal the presence of two rotamers in an approximate 2:1 ratio, as determined by peak integration and assigned by standard two-dimensional NMR techniques. For instance, it is clear that the well-resolved doublets at 5.74 ppm (2H) and at 6.02 ppm (1H) are coalescing at 303 K; these protons have been assigned to the triptycene blade coordinated to the metal. Line shape analysis gave a barrier to rotation of 12.8 ± 0.5 kcal mol^{-1}, which is not significantly different from that observed for the uncoordinated organic ligand.

The spectra are also complicated in the region of the indenyl methylene protons. Their diastereotopic char-

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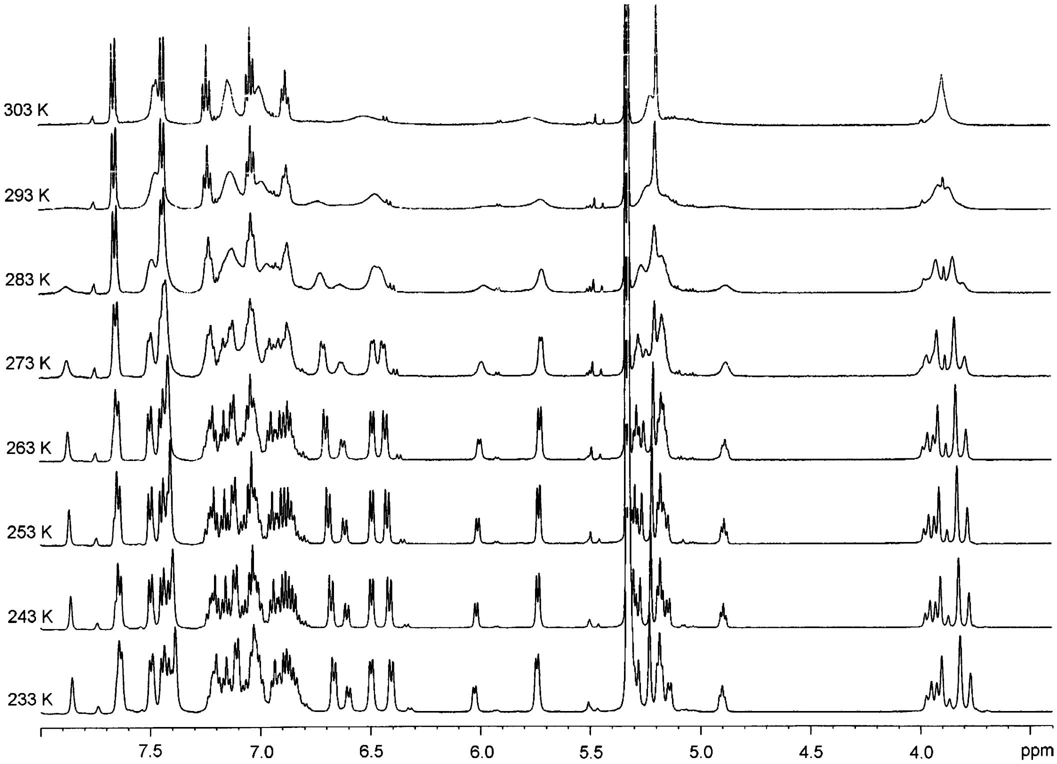
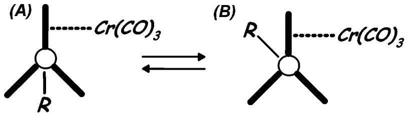


Figure 5. 500 MHz ^{1}H NMR spectra of the chromium complex **13a**, revealing the presence of two isomers in a 2:1 ratio at low temperature (CD_2Cl_2).

Scheme 3. Two Possible Rotamers of the Chromium Complex 13a



acter, combined with the presence of two rotamers in a 2:1 ratio, gives rise to a complex multiplet at low temperature. Moreover, the singlet peak at ~5.2 ppm attributable to the bridgehead proton, H(10), also splits into two singlets as the temperature is reduced.

The ^{13}C NMR spectra confirm the presence of two rotamers by displaying two peaks for the indenyl methylene carbon, as well as two environments for the metal carbonyls at low temperature. We suggest that the two isomers arise because of restricted rotation of the indenyl substituent about the triptycene unit such that the indene is located in one of two staggered positions, A and B, neither of which eclipses the chromium tricarbonyl (Scheme 3). Thus, there are two possible sites for the indene and, according to the crystal structure, rotamer A appears to be the more sterically favored.

Warming the sample to room temperature results in extreme broadening of the peaks, and so the spectra were re-collected over a higher temperature range in DMSO. At 343 K (see Figure 6), only one species is apparent, implying that rotation of the indenyl substituent relative to the 3-fold axis of the triptycene is now fast on the ^{1}H NMR time scale; likewise, the ^{13}C spectra are assignable in terms of a single species.

Numerous attempts to coordinate a potentially η^5 organometallic moiety, such as $Mn(CO)_3$ or $Fe(C_5H_5)$, to the five-membered ring of the indenyl substituent have thus far proven unsuccessful. It may be that this position is too crowded to allow direct incorporation of a metal carbonyl substituent. Current investigations are directed toward linking the six-membered ring of an indenyl group to the C(9) position of the triptycene framework so that addition of an organometallic unit to the five-membered ring may become more facile, thereby leading to controlled modification of rotation barriers by means of haptotropic shifts.

To conclude, the attachment of an indenyl substituent to the C(9) position of triptycene engenders a sizable barrier to rotation about the 3-fold axis of the molecule. Addition of a chromium tricarbonyl moiety results in coordination to one of the aromatic blades rather than to the six-membered ring of the indenyl group. The chromium complex **13a**, which has been characterized by X-ray crystallography and variable-temperature NMR spectroscopy, exists as a 2:1 mixture of two rotamers at low temperature. Variable-temperature NMR studies yield rotation barriers of approximately 12 and 13 kcal mol^{-1}, respectively, for the indenyltriptycene **12** and its chromium tricarbonyl complex **13a**.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Silica gel (particle size 20−45 μm) was employed for flash column chromatography. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DRX 500 spectrometer operating at 500.13 and 125.76 MHz, respectively, and were referenced to the residual proton or ^{13}C signal of the solvent. Assignments were based on standard ^{1}H−^{1}H and ^{1}H−^{13}C two-dimensional techniques. NMR simulations were carried out by using the multisite EXCHANGE program generously provided by Professor R. E. D. McClung (University of Alberta at Edmonton). High-resolution electron impact (HRMS)

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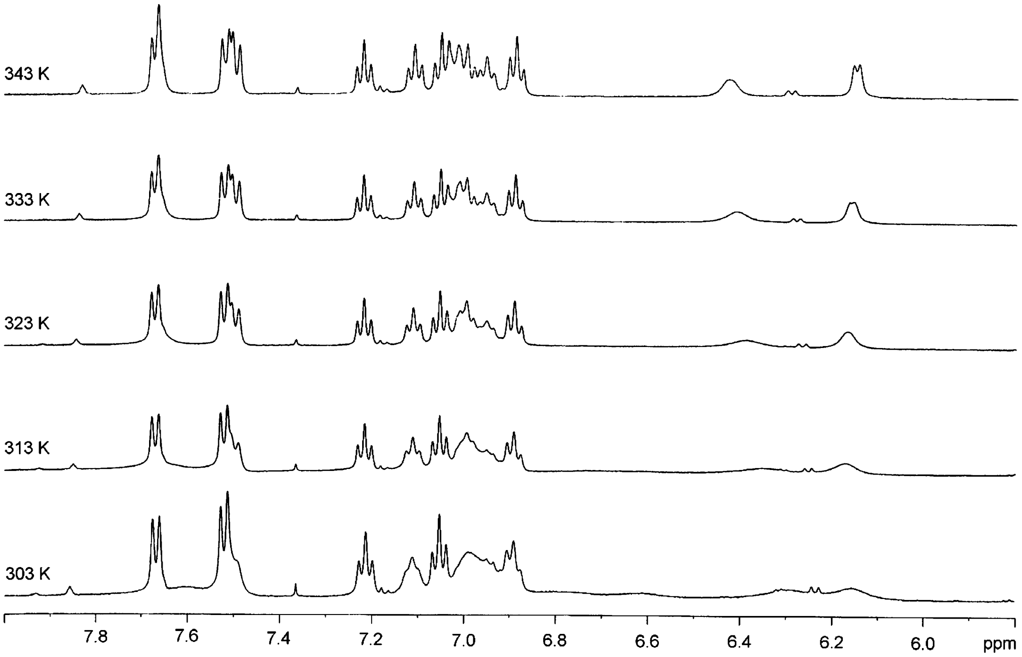

Figure 6. 500 MHz high-temperature ^{1}H NMR spectra of **13a** (DMSO).

mass spectra were obtained on a Micromass GCT TOF spectrometer, and infrared spectra were recorded on a Bruker Tensor 27 FT-IR. Melting points (uncorrected) were determined on a Fisher-Johns melting point apparatus.

Tributyltin chloride, 9-bromoanthracene, palladium dichloride, anthranilic acid, isoamyl nitrite, and chromium hexacarbonyl were obtained from commercial sources and used as received. Indene was distilled prior to use.

Crystallographic Data. X-ray crystallographic data were collected from suitable samples mounted with epoxy on the end of thin glass fibers. Data were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector (employing the program SMART)[28a] and a rotating anode utilizing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Data processing was carried out by use of the program SAINT,[28b] while the program SADABS[28c] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct-methods procedure in the Bruker SHELXL[28d] program library and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. Crystal data and structural refinement parameters are given in Table 1.

Table 1. Crystal Data and Structural Refinement Parameters for 11, 12, and 13a

	11	**12**	**13a**
empirical formula	$C_{23}H_{16}$	$C_{29}H_{20}$	$C_{38}H_{26}CrO_3$
formula wt	292.36	368.45	582.59
temp (K)	143(2)	173(2)	173(2)
wavelength (Å)	1.541 78	1.541 78	0.710 73
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
unit cell dimens			
a, Å	8.1708(3)	9.4874(14)	9.242(3)
b, Å	7.4691(2)	16.312(2)	11.356(3)
c, Å	25.9547(8)	25.114(5)	14.531(4)
α, deg	90	90	107.468(6)
β, deg	97.517(2)	100.711(8)	95.565(7)
γ, deg	90	90	93.490(6)
V (Å^3)	1570.36(9)	3818.9(10)	1441.2(7)
Z	4	8	2
F(000)	616	1552	604
θ range for data collecn (deg)	3.44−68.38	3.25−68.29	1.48−27.54
index ranges	$-9 \le h \le 9$ $-8 \le k \le 8$ $-27 \le l \le 31$	$-6 \le h \le 11$ $-17 \le k \le 19$ $-16 \le l \le 20$	$-11 \le h \le 9$ $-11 \le k \le 14$ $-18 \le l \le 12$
no. of rflns collected	7588	6688	7724
no. of indep rflns	2724 (*R*(int) = 0.0423)	4381 (*R*(int) = 0.0476)	5980 (*R*(int) = 0.0434)
no. of data/restraints/params	2724/0/209	4381/0/523	5980/0/380
goodness of fit on F^2	1.094	1.049	1.007
final *R* indices ($I > 2\sigma(I)$)			
R1	0.0502	0.0760	0.0766
wR2	0.1427	0.1820	0.1515
R indices (all data)			
R1	0.0563	0.1001	0.1542
wR2	0.1474	0.2048	0.1794

Preparation of (9-Indenyl)anthracene (11). In a 100 mL round-bottom flask, 9-bromoanthracene (6.19 g, 24.1 mmol) and freshly prepared Pd(PPh_3)$_4$[29] (0.88 g, 0.76 mmol) were stirred in DMF (35 mL). (Tributylstannyl)indene[30] (7.50 g, 18.5 mmol) was added with a syringe, and the orange solution was stirred at 110 °C for 2 h. The mixture was cooled to room temperature, and water (20 mL) was added, followed by extraction with diethyl ether. The combined organic extracts were washed with saturated NaCl solution and water, dried over $MgSO_4$, and filtered and the solvent removed under vacuum. The crude beige solid was purified by using flash column chromatography (100% hexanes to 50/50 hexanes/CH_2Cl_2) to give **11** as a pale yellow solid (2.19 g, 7.48 mmol; 42%). Mp: 142−145 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 303 K; numbering is in accord with the crystal structure): δ 8.57 (s, H_{10}, 1H), 8.10 (d, $J = 8.5$ Hz, $H_{1,8}$, 2H), 7.96 (dd, $J = 8.8$ Hz, 0.7 Hz, $H_{4,5}$, 2H), 7.70 (d, $J = 7.5$ Hz, H_{17}, 1H), 7.51 (ddd, $J = 7.6$ Hz, 7.5 Hz, 1.0 Hz, $H_{2,7}$, 2H), 7.38 (ddd, $J = 7.8$ Hz, 7.7 Hz, 1.1 Hz, $H_{3,6}$, 2H), 7.30 (dd, $J = 8.0$ Hz, 7.7 Hz, H_{16}, 1H), 7.15 (dd,

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J = 7.4 Hz, 7.4 Hz, H$_{15}$, 1H), 6.77 (t, *J* = 1.9 Hz, H$_{12}$, 1H), 6.71 (d, *J* = 7.6 Hz, H$_{14}$, 1H), 3.88 (d, *J* = 1.8 Hz, H$_{13}$, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 147.3 (C$_{17a}$), 144.6 (C$_{13a}$), 142.5 (C$_{11}$), 135.8 (C$_{12}$), 132.2 (C$_{8a,9a}$), 131.6 (C$_9$), 130.9 (C$_{4a,10a}$), 129.1 (C$_{1,8}$), 127.3 (C$_{10}$), 127.2 (C$_{4,5}$), 126.9 (C$_{15}$), 126.0 (C$_{3,6}$), 125.9 (C$_{2,7}$), 125.6 (C$_{16}$), 124.5 (C$_{17}$), 121.2 (C$_{14}$), 39.6 (C$_{13}$). HRMS (EI): calcd for $C_{23}H_{16}$, 292.1252; found, 292.1233.

Preparation of (9-Indenyl)triptycene (12). In a 100 mL three-neck round-bottom flask with a reflux condenser, **11** (2.51 g, 8.59 mmol) was dissolved in DME (20 mL) and heated to 100 °C. Anthranilic acid (5.50 g, 40.1 mmol) and isoamyl nitrite (8.7 mL, 64.0 mmol) were added cautiously dropwise from separate syringes over 3−4 h. The mixture was heated overnight and then cooled to room temperature, and the solvent was removed under vacuum. The residue was subjected to flash column chromatography (100% hexanes to 50/50 hexanes/CH_2Cl_2), to give **12** as a white solid (0.91 g, 2.47 mmol; 29%). Mp: 247−249 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K; numbering is in accord with the crystal structure): δ 8.39 (d, *J* = 7.7 Hz, H$_{13}$, 1H), 7.90 (s, H$_{18}$, 1H), 7.79 (d, *J* = 7.4 Hz, H$_{20}$, 1H), 7.69 (d, *J* = 7.3 Hz, H$_{4,5}$, 2H), 7.61 (d, *J* = 7.1 Hz, H$_{16}$, 1H), 7.34 (dd, *J*(HH) = 7.3 Hz, 7.3 Hz, H$_{21}$, 1H), 7.25 (m, H$_{14}$, 1H), 7.20 (m, H$_{3,6}$, 2H), 7.15 (dd, *J*(HH) = 7.3 Hz, 7.3 Hz, H$_{15}$, 1H), 7.10 (d, *J*(HH) = 7.6 Hz, H$_{1,8}$, 2H), 7.01 (dd, *J*(HH) = 7.5 Hz, 7.5 Hz, H$_{22}$, 1H), 6.95 (dd, *J*(HH) = 7.5 Hz, 7.5 Hz, H$_{2,7}$, 2H), 6.59 (d, *J*(HH) = 7.8 Hz, H$_{23}$, 1H), 5.71 (s, H$_{10}$, 1H), 3.97 (s, H$_{19}$, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 148.4 (C$_{11}$), 146.7 (C$_{12}$), 145.4 (C$_{8a,9a,19a}$), 144.5 (C$_{4a,10a}$), 143.8 (C$_{23a}$), 140.1 (C$_{17}$), 134.8 (C$_{18}$), 125.9 (C$_{1,8}$), 125.5 (C$_{3,6,23}$), 124.9 (C$_{14,22}$), 124.8 (C$_{15}$), 124.5 (C$_{21}$), 124.4 (C$_{2,7}$), 124.1 (C$_{16}$), 123.8 (C$_{20}$), 123.5 (C$_{4,5}$), 123.3 (C$_{13}$), 56.4 (C$_9$), 54.3 (C$_{10}$), 39.4 (C$_{19}$). HRMS (EI): calcd for $C_{29}H_{20}$, 368.1565; found, 368.1531.

Preparation of [(9-Indenyl)triptycene]chromium Carbonyl (13a). Chromium hexacarbonyl (128 mg, 0.58 mmol) and **12** (202 mg, 0.55 mmol) were dissolved in dry THF (5 mL) and *n*-Bu$_2$O (30 mL) in a 100 mL round-bottom flask, under an atmosphere of dry nitrogen and with protection from light. The mixture was stirred at reflux for 4 days, during which time the solution changed from colorless to deep yellow. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum; the residue was then subjected to flash column chromatography (100% hexanes to 50/50 hexanes/CH_2Cl_2), to give **13a** as a yellow solid (124 mg, 0.25 mmol; 45%). Mp: 129−131 °C. IR (solid): 1978, 1907 cm^{-1} (CO's); lit.[26] IR for triptycene chromium carbonyl 1975, 1910 cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 243 K; numbering is in accord with the crystal structure and peaks for the minor rotamer are marked with an asterisk): δ 8.14, 7.40, 7.11, 6.85 (H$_{5,6,7,8}$*, 4H), 7.86 (s, H$_{18}$*, 1H), 7.64 (d, *J* = 6.8 Hz, H$_8$, 2H), 7.50 (d, *J* = 7.2 Hz, H$_{13}$, 2H), 7.49, 7.45−7.40, 7.23−7.11, 7.07−7.01, 6.95−6.83 (H$_{23}$, H$_{23}$*, H$_{22}$, H$_{22}$*, H$_{21}$, H$_{21}$*, H$_{20}$, H$_{20}$*, 12H), 7.40 (s, H$_{18}$, 2H), 7.40, 7.11, 6.85 (H$_{5,6,7}$*, 3H), 7.40, 7.01, 6.93, 6.60 (H$_{13,14,15,16}$*, 4H), 7.19 (m, H$_7$, 2H), 7.14, 6.93 (H$_{14,15}$, 4H), 6.94 (m, H$_6$, 2H), 6.68 (d, *J* = 7.7 Hz, H$_{16}$, 2H), 6.49 (d, *J* = 6.6 Hz, H$_4$, 2H), 6.41 (d, *J* = 7.0 Hz, H$_5$, 2H), 6.02 (d, *J* = 6.2 Hz, H$_4$*, 1H), 5.74 (d, *J* = 6.14 Hz, H$_1$, 2H), 5.30 (m, H$_2$, 2H), 5.27 (s, H$_{10}$*, 1H), 5.22 (s, H$_{10}$, 2H), 5.18 (dd, *J* = 6.2 Hz, 6.2 Hz, H$_3$* and H$_3$, 3H), 5.14 (d, *J* = 6.5 Hz, H$_1$*, 1H), 4.90 (dd, *J* = 6.1 Hz, 6.1 Hz, H$_2$*, 1H), 3.78−3.99 (m, H$_{19}$ and H$_{19}$*, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2, 243 K): δ 233.2 (CO*), 233.0 (CO), 147.0, 146.4, 145.1, 144.6, 144.0, 142.5 (C$_{8a,10a,11,12,19a,23a}$, C$_{8a,10a,11,12,19a,23a}$*), 138.7, 138.5 (C$_{17}$, C$_{17}$*), 137.5 (C$_{18}$*), 135.1 (C$_{18}$), 135.1, 126.1, 125.1, 124.9 (C$_{20,21,22,23}$), 126.7, 125.8, 124.0, 122.4 (C$_{20,21,22,23}$*), 126.6 (C$_5$*), 126.4, 125.5, 123.5 (C$_{13,14,15}$*), 125.4, 125.1 (C$_{14,15}$), 125.2 (C$_5$, C$_{16}$), 125.1 (C$_{16}$*), 124.9 (C$_{6,7}$, C$_{6,7}$*), 123.9 (C$_8$), 123.1 (C$_{13}$), 122.2 (C$_8$*), 119.5, 117.9, 117.5 (C$_{4a,9a}$, C$_{4a,9a}$*), 93.3 (C$_1$*), 92.1 (C$_4$*), 91.9 ($C_1 + C_4$), 90.9 (C$_3$), 90.0 (C$_3$*), 89.7 ($C_2 + C_2$*), 55.5 (C$_9$), 55.1 (C$_9$*), 51.9 (C$_{10}$, C$_{10}$*), 39.6 (C$_{19}$*), 39.4 (C$_{19}$). ^{1}H NMR (500 MHz, CD_2Cl_2, 343 K): δ 7.67 (d, *J* = 7.3 Hz, 1H), 7.66 (br s, H$_{18}$, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.22 (dd, *J* = 7.5 Hz, 7.4 Hz, 1H), 7.11 (dd, *J* = 7.5 Hz, 7.4 Hz, 1H), 7.07−6.98 (m, 5H), 6.95 (dd, *J* = 7.7 Hz, 7.5 Hz, 1H), 6.89 (dd, *J* = 7.5 Hz, 7.4 Hz, 1H), 6.43 (br s, 1H), 6.15 (d, *J* = 6.0 Hz, 1H), 5.51 (dd, *J* = 6.2 Hz, 6.2 Hz, 1H), 5.55 (s, H$_{10}$, 1H), 5.33 (dd, *J* = 6.3 Hz, 6.0 Hz, 1H), 3.92 (br s, H$_{19}$, 2H).^{13}C NMR (125 MHz, CD_2Cl_2, 343 K): δ 212.8 (CO), 143.9, 143.7, 143.2, 137.4, 135.2, 134.2, 123.3, 122.6 (C$_{4a,8a,9a,10a,11,12,19a,23a}$), 128.8, 125.5, 124.6, 124.4, 124.2, 123.6, 123.5, 123.1 (C$_{5,6,7,8,13,14,15,16,18,20,21,22,23}$), 92.4, 92.2, 90.8, 90.2 (C$_{1,2,3,4}$), 53.3 (C$_9$), 50.7 (C$_{10}$), 38.6 (C$_{19}$). HRMS (EI): calcd for $C_{32}H_{20}O_3Cr$, 504.0818; found, 504.1776. Also isolated from the reaction mixture as a yellow solid was the bis(chromium carbonyl) complex (crude yield: 30 mg, 0.05 mmol, 9%); however, satisfactory NMR data were not obtained. HRMS (EI): calcd for $C_{35}H_{20}O_6Cr_2$, 640.0070; found, 640.0079.

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Supporting Information Available: Tables giving X-ray crystallographic data and tables, as well as fully labeled thermal ellipsoid plots; data are also available as CIF files. This information is available free of charge at http://pubs.acs.org.

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