Synthesis, Structure, and Dynamics of *endo*-(Starphenylene)chromium Tricarbonyl Derivatives: Observation of Metal–Arene Migration and Hindered Metal-Tripod Rotation

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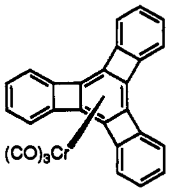
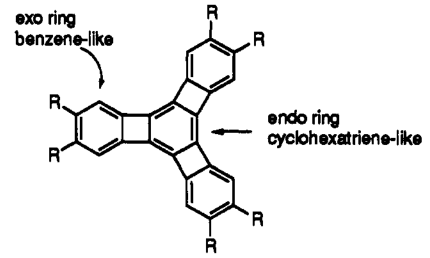
Abstract: The dynamic stereochemistry of *endo*-(starphenylene)chromium tricarbonyl, *endo*-**1**-Cr, is elucidated through NMR spectroscopic methods. Intramolecular metal–arene migration and hindered metal-tripod rotation are observed in closely related derivatives of *endo*-**1**-Cr. The stereochemistry of these systems is modeled well by *ab initio* local density functional theory methods.

Chromium tricarbonyl complexes of arenes typically display two dynamic processes with disparate energy requirements,[2] metal-tripod rotation (<3 kcal/mol)[3] and metal–arene exchange (>30 kcal/mol).[4] Complexes of specially designed arenes exhibit either relatively hindered tripod rotation[5] or facile metal–arene exchange.[6] Derivatives of *endo*-(starphenylene)chromium tricarbonyl (*endo*-**1**-Cr)[7-10] are the first molecules to demonstrate both. This report covers the syntheses of several derivatives of *endo*-**1**-Cr and the elucidation of their molecular structures. NMR experimental and *ab initio* computational evidence is presented for hindered rotation about the metal–arene bond and intramolecular metal–arene migration chemistry.



***endo*-1-Cr**



1: R = H
2: R = TMS

Figure 1. Structural character of the exo and endo rings of **1** and **2**.

Experimental Design

The structure of starphenylene (**1**) and its hexakis(trimethylsilyl) derivative (**2**) offer two distinct arene subunits where metals can bind. The central (endo) ring displays a strong bond alternation suggestive of cyclohexatriene, whereas the three symmetry-equivalent outer (exo) rings more closely resemble delocalized benzene (Figure 1).

Previous experimental and computational work predicted the barrier to rotation about the metal–arene bond of *endo*-**1**-Cr to be over 10 kcal/mol.[5a] No evidence existed concerning the potential regioselective binding of a metal to "cyclohexatriene" vs benzene. Derivatives of **1** allowed us to address both of these points.

The symmetry of *endo*-**1**-Cr or *endo*-**2**-Cr, C_{3v}, obscures the direct measurement of the barrier to rotation about the metal–arene bond by dynamic NMR spectroscopy. Substitution at one of the outer rings breaks the rotational symmetry and results in an appropriately desymmetrized model wherein the ^{13}C carbonyls of the endo metal tripod serve as probes of the motion (Figure 2). On the basis of synthetic accessibility, two targets surface for this study: *endo,exo*-**2**-Cr_2 and *endo*-**4**-Cr. In the former, the metal bound to the exo ring produces the desymmetrization; in the latter, the butyl ester groups play that role.

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[2] (a) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901. (b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

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[5] (a) Nambu, M.; Siegel, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 3675. (b) Kilway, K. V.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 2332. (c) Downton, P. A.; Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 27. (d) Mailvaganam, B.; Frampton, C. S.; Sayer, B. G.; Top, S.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 1177.

[6] (a) Traylor, T. G.; Goldberg, M. J.; Miksztal, A. R.; Strouse, C. E. *Organometallics* **1989**, *8*, 1101. (b) Kündig, P.; Desobry, V.; Grivet, C.; Rudolf, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173. (c) Treichel, P. M.; Kirss, R. U. *J. Am. Chem. Soc.* **1986**, *108*, 853.

[7] The term starphenylene, rigorously tetrastarphenylene(1.1.1), is an extension of the nomenclature proposed by Clar.[8] The original name, *triangular*[4]phenylene, proposed by Vollhardt[9] begs the abbreviation triangulene which has already been used for an isomer of dibenzopyrene.[10]

[8] Clar, E. *The Aromatic Sextet*; J. Wiley: New York, 1972; Chapter 8.

[9] Dierks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.

[10] Clar, E.; Stewart, D. G. *J. Am. Chem. Soc.* **1953**, *75*, 2667.

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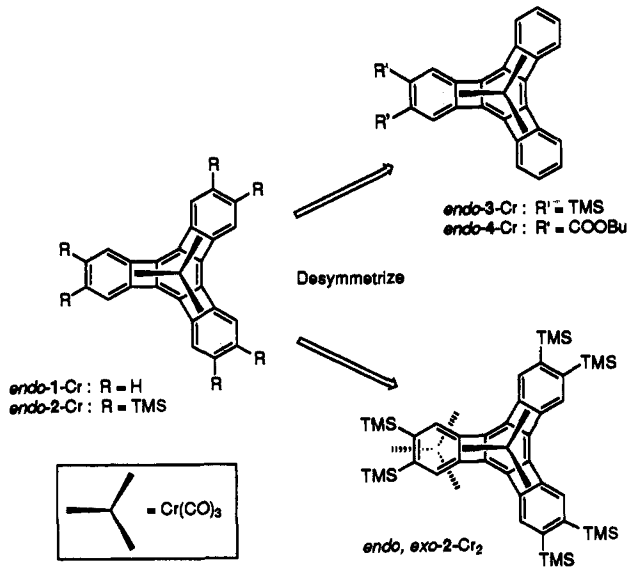
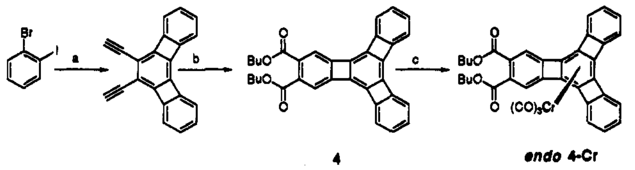


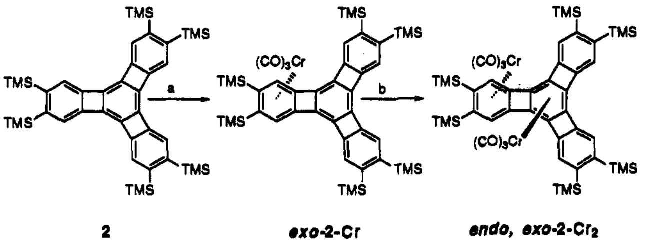
Figure 2. Desymmetrization of *endo*-1-Cr.

Scheme I[a]



[a] Key: (a) ref 9; (b) $CpCo(CO)_2$, dibutyl acetylenedicarboxylate, toluene, $h\nu$, reflux, 20 h (30% yield); (c) (naphthalene)chromium tricarbonyl-^{13}C, diethyl ether/tetrahydrofuran (99:1), 70 °C, 16 h (74% yield).

Scheme II[a]



[a] Key: (a) Triamminechromium tricarbonyl, dioxane, reflux, 14 h (57% yield); (b) (naphthalene)chromium tricarbonyl-^{13}C, diethyl ether/tetrahydrofuran (99:1), 60 °C, 14 h (43% yield).

Synthesis

Starphenylenes **1**–**3** were prepared by the procedures of Dierks and Vollhardt.[9,11] Use of butyl acetylenedicarboxylate in place of bis(trimethylsilyl)acetylene gave **4** by the same procedure used to produce **3** (Scheme I). All routes implemented $CpCo(CO)_2$ as an acetylene cyclooligomerization catalyst.[12]

Metal complexation with triamminechromium tricarbonyl in dioxane proceeded smoothly to give selectively the exo-bound isomer of each ligand. In contrast, conditions employing (naphthalene)chromium tricarbonyl in tetrahydrofuran at 50 °C resulted in selective formation of the endo metal complex. Together these two methods provided the synthetic control necessary to prepare the desired *endo,exo*-**2**-Cr_2 and *endo*-**4**-Cr (Scheme II). Samples enriched in ^{13}C were prepared from enriched (naphthalene)chromium tricarbonyl or photoinduced carbonyl exchange in the presence of ^{13}C carbon monoxide.

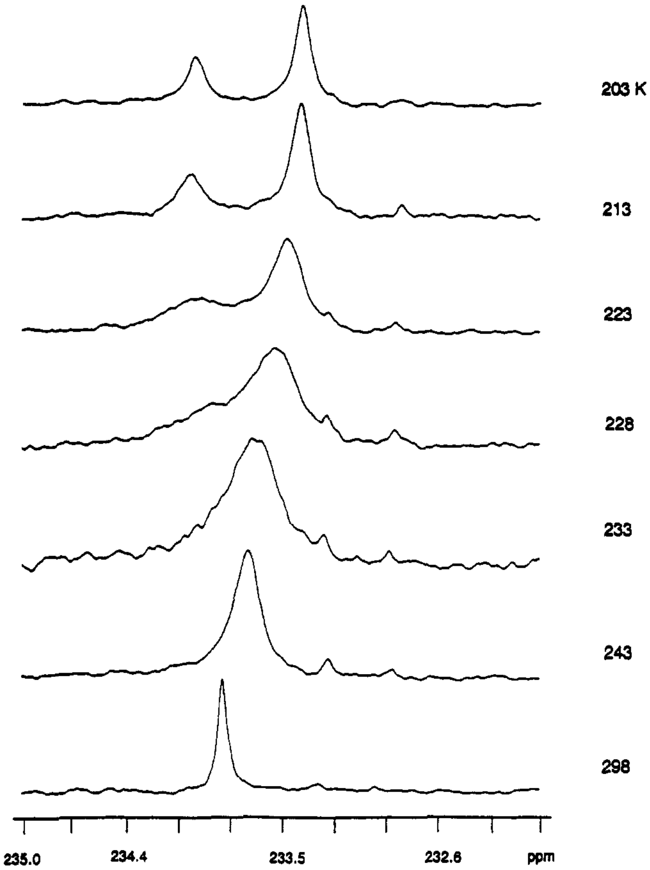


Figure 3. Variable-temperature NMR spectra of *endo*-**4**-Cr from 203 to 293 K (T_c = 233 K; $\Delta\nu$ = 80 Hz; $\Delta G^{\ddagger}$ = 11.1 ± 0.5 kcal/mol).

The regioselectivity of these conditions stems from the kinetic preference for initial attack at the more nucleophilic central "cyclohexatriene-like" ring and the thermodynamic stability of the metal complexed to the benzenoid ring. The lower temperature used with (naphthalene)chromium tricarbonyl traps the kinetic product, whereas the more vigorous triamminechromium tricarbonyl conditions drive the reaction to the thermodynamic product.

Dynamic NMR Behavior

Both *endo*-**4**-Cr and *endo,exo*-**2**-Cr_2 exhibit reversible (de)-coalescence behavior in their variable-temperature ^{13}C NMR spectra (Figure 3). At ambient temperature they display one carbonyl signal and at −100 °C (173 K) they display two signals, with intensities of ca. 2:1. Coalescence occurs at −65 °C (208 K) for *endo,exo*-**2**-Cr_2 ($\Delta\nu$ = 170 Hz) and −40 °C (233 K) for *endo*-**4**-Cr ($\Delta\nu$ = 80 Hz). Use of a weighted Gutowsky–Holm approximation to correct for the 2:1 population provides free energies of activation for rotation about the metal–arene bond at coalescence.[13] Calculated in this manner, the free energies of activation for these processes are 9.7 and 11.1 ± 0.5 kcal/mol for *endo,exo*-**2**-Cr_2 and *endo*-**4**-Cr, respectively.[14]

Metal-Arene Migration

When *endo*-**2**-Cr is heated to 90 °C, an irreversible change occurs in the carbonyl region of the ^{13}C NMR spectrum. The product, *exo*-**2**-Cr, results from an endo-to-exo metal–arene

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[11] Dierks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266.

[12] (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

[13] For unequal populations, the free energy of activation is given by

$$\Delta G^{\ddagger}_{ab} = 4.57T_c[10.62 + \log(X/2\pi(1 - \Delta P)) + \log(T_c/\Delta\nu_{ab})]$$

where X = 2.08 for a population fraction P = 0.33.

[14] (a) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 97. (b) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

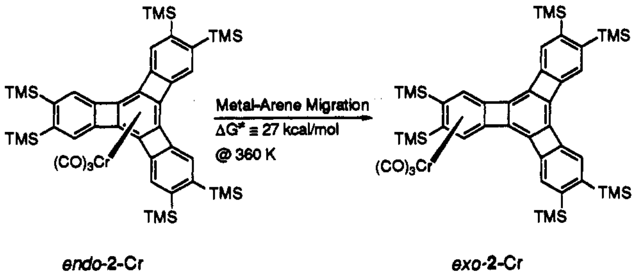

Figure 4. Metal–arene migration in *endo*-**2**-Cr.

migration (Figure 4). The kinetics show a first-order concentration dependence on *endo*-**2**-Cr with regard to migration. The barrier to this process lies in the range 27–28 kcal/mol ($k = 2.1 \times 10^{-4}$ s^{-1} at 360 K). Intramolecular migration is a considerably more facile process in *endo*-**2**-Cr than in *endo*-(dibenzobicyclooctadiene)chromium tricarbonyl (32 kcal/mol; $k = 9.4 \times 10^{-4}$ s^{-1} at 440 K)[6] or (biphenylene)chromium tricarbonyl.[15,16]

This finding supports our explanation for the difference in selectivity seen in the reaction of (naphthalene)chromium tricarbonyl vs triamminechromium tricarbonyl. The endo isomer, the kinetic product, is trapped with the former reagent, which reacts at ca. 330 K, and the exo isomer, the thermodynamic product, is produced with the latter reagent, which reacts at 360 K.

Results from Local Density Functional Theory Computations

Prior work with local density function (LDF) theory[17] points out its utility for modeling both the static and dynamic stereochemistry of organometallic compounds.[18] LDF computations on *endo*-**1**-Cr predict a static structure with the carbonyls eclipsing the annelated rings. Assuming that the electron density within the central ring is concentrated in the short bonds, this structure corresponds to pseudooctahedral coordination around the metal. X-ray crystallography of *endo*-**1**-Cr displays this same conformation.[19]

Rotation of the metal tripod by 60° staggers the carbonyls with respect to the annelated rings. This structure models a pseudo trigonal prismatic coordination of the metal and a possible transition state for the Bailar–Twist[20] mechanism for tripod rotation.[21] Figure 5 shows this mechanism, with rotation proceeding through **1**-Cr-I and **1**-Cr-II (Figure 5). A value of 8.1 kcal/mol is calculated for the difference in energy between these two tripod conformers, in reasonable agreement with the experimental barrier of 11.3 kcal/mol.

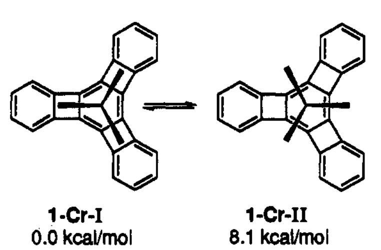

Figure 5. Relative energies (LDF) of two metal-tripod conformations of *endo*-**1**-Cr.

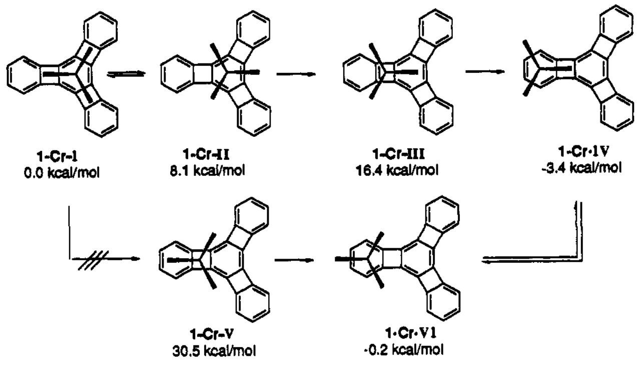

Figure 6. Relative energies (LDF) of various states along two paths to metal–arene migration.

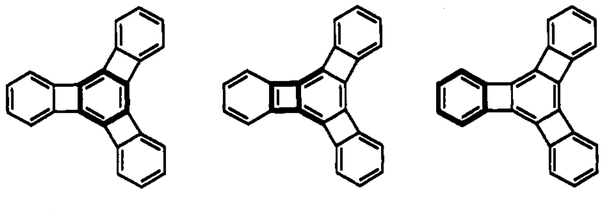

Figure 7. "Cyclohexatriene" (left), dimethylenecyclobutene (middle), and benzene (right) subgraphs within the skeleton of **1**.

Following either the path I → II → III → IV or I → V → VI → IV, one traces a possible path of intermediate structures in the metal–arene migration process (Figure 6). The highest energy intermediate lies 16.4 kcal/mol above the ground state for the former path and 30.5 kcal/mol for the latter. The former path, as calculated by LDF, is significantly lower in energy. The prediction, therefore, is that the tripod first rotates and then migrates from the rotated structure. Migration without rotation leads to a formidable energy cost.

The experimental value of 27–28 kcal/mol for the barrier is significantly higher than that of the calculated structures I–IV. This probably indicates that I–IV are intermediates and not actual transition structures.

Both of the modeled paths proceed along a direct line from the endo to the exo ring. This need not be the case. Albright has predicted,[4a,b] using EHMO calculations, that in (biphenylene)chromium tricarbonyl metal–arene migration occurs through a more circuitous route.

Within the overall structure of **1**, one can trace out "cyclohexatriene", dimethylenecyclobutene, and benzene subgraphs (Figure 7). All of these polyenes have been shown to form isolable chromium tricarbonyl adducts, which have been characterized crystallographically.[22] The path predicted by LDF has chromium η^6-bound to one of these units at all times, hence our belief that the path I–IV is a reasonable model for the intermediate states of the metal-migration process.

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[15] Oprunenko, Y. F.; Malyugina, S. G.; Babushkina, O. Y.; Ustynyuk, Y. A.; Nesterenko, P. N.; Ustynyuk, N. A.; Kravtsov, D. N.; Piven, Y. A. *Metalloorg. Khim.* **1988**, *1*, 384.

[16] Thermolysis of *endo*-angular-terphenylene also shows evidence of endo-to-exo metal–arene migration. This takes place at temperatures around 140 °C. See: Nambu, M. Ph. D. Dissertation, UCSD, 1992.

[17] For further information on LDF theory see: (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864. (b) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133. (c) Wimmer, E.; Freeman, A. J.; Fu, C.-L.; Cao, P.-L.; Chou, S.-H.; Delley, B. In *Supercomputer Research in Chemistry and Chemical Engineering*; Jensen, K. F., Truhlar, D. G., Eds.; ACS Symposium Series 353; American Chemical Society: Washington, DC, 1987; Chapter 4.

[18] Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

[19] Crystals of *endo*-**2**-Cr were poorly suited for accurate X-ray crystallographic analysis of the internal geometry such as precise bond lengths and angles. Nonetheless, data were collected using Mo Kα radiation (λ = 0.710 73 Å) at ambient temperature on a crystal grown from hexanes (0.08 × 0.08 × 0.28 mm), and the structure was solved in $P2_1/c$ with the cell parameters a = 9.190(5) Å, b = 22.665(8) Å, c = 28.385(9) Å, β = 98.70(4)°, V = 5844(8) Å^3, and Z = 4. The refinement was by least-squares methods including 1636 reflections for 256 parameters (R = 0.16, R_w = 0.18). The molecular conformation could have been deduced with good certainty, but no further analysis was warranted. The chromium tricarbonyl sits in the center of the endo ring, and the carbonyls eclipse the annelated four-membered rings. The short bonds of the aromatic nucleus lie at the sites that correspond to the octahedral coordination of chromium.

[20] (a) Bailar, J. C., Jr. *Rev. Pure Appl. Chem.* **1966**, *16*, 91. (b) Jackson, W. G. In *Stereochemistry of Inorganic and Organometallic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Chapter 4.

[21] The symmetric 60°-rotated structure is the conformation that is consistent with the transition state for rotation as calculated by Albright and Hoffmann using EHMO techniques. The symmetry restriction simplifies the calculation.

Reversing the subgraph analogy, one can speculate on the barrier to rotation in (dimethylenecyclobutene)chromium tricarbonyl (**5**-Cr) from the LDF computations on **1**-Cr-III and **1**-Cr-V. The calculations predict a barrier to metal-tripod rotation in this complex on the order of 10–15 kcal/mol, well within the range attainable by dynamic NMR spectroscopy.

5-Cr

Structures I and IV in Figure 6 represent the endo and exo ground-state conformations of **1**-Cr. The exo isomer is predicted to be 3.4 kcal/mol more stable than the endo isomer. This prediction corroborates the experimental observation of metal–arene migration from the endo to the exo site, but not the reverse, and further solidifies the explanation of the regioselectivity seen in the metal complexation reaction (see above).

(Starphenylene)chromium systems clearly offer many points of comparison between experiment and LDF theory. In terms of the prediction of static structure, kinetic activation parameters, and thermodynamic stability of isomers, one sees that LDF handles these reasonably large organometallic systems well on all fronts.

Experimental Section

General Data. Proton NMR spectra were recorded on a ^{1}H-NMR spectrometer equipped with a Nicolet 1180E computer interfaced with an Oxford magnet operating at 360 MHz, on a GE/Nicolet QE300 spectrometer, or on a Varian Unity 500-MHz spectrometer. Carbon NMR were recorded on a QE300 spectrometer operating at 75 MHz, on a Nicolet NT200 spectrometer operating at 50 MHz, or on a Varian Unity spectrometer operating at 125 MHz. Infrared spectra were recorded on a Perkin-Elmer 1420 IR spectrometer. Unless otherwise stated, commercial chemicals were used as supplied.

***endo*-(Starphenylene)chromium Tricarbonyl (*endo*-1-Cr).** Starphenylene **1** (13 mg, 0.043 mmol), (naphthalene)chromium tricarbonyl (11 mg, 0.043 mmol), tetrahydrofuran (2.5 mL), and diethyl ether (8 mL) were combined in a glass bomb, which was then degassed by three freeze/pump/thaw cycles. The bomb was placed in a 70 °C sand bath, where it was allowed to stir for 48 h. The solvents were removed by rotary evaporation, the resulting solid was dissolved in a large amount of chloroform, and the mixture was filtered through a 5-cm column of silica gel, with all but the orange band discarded. The chloroform was removed under reduced pressure to yield *endo*-**1**-Cr (10 mg, 57%) as an insoluble red–orange powder: mp 220 °C dec; UV–vis (dichloromethane) λ_{max} (log ϵ) 266 (5.01), 297 (4.63), 312 (4.53), 426 (4.22) nm; IR (KBr) 1958, 1870 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 436 (M^+, 9), 380 ($M^+ - 2CO$, 15), 352 ($M^+ - 3CO$, 85), 300 ($M^+ - Cr(CO)_3$, 48), 149 (22), 137 (13), 125 (24), 111 (42), 97 (67), 83 (65), 71 (100); HRMS calcd for $C_{27}H_{12}CrO_3$ 436.0191, found 436.0203.

***endo*-(2,3,6,7,10,11-Hexakis(trimethylsilyl)starphenylene)chromium Tricarbonyl (*endo*-2-Cr).** Hexakis(trimethylsilyl)starphenylene **2** (209 mg, 0.286 mmol), (naphthalene)chromium tricarbonyl (140 mg, 0.530 mmol), tetrahydrofuran (10 mL), and diethyl ether (10 mL) were placed in a glass bomb, which was then degassed by three freeze/pump/thaw cycles. The bomb was then heated in a 65 °C sand bath for 24 h. After cooling, the solvents were removed by rotary evaporation, and the resulting solid was subjected to chromatography on silica gel with pentane. A yellow band was collected, and after the solvent was removed, 21 mg of the starting phenylene was recovered. Next, a red band was collected, and removal of solvent yielded *endo*-**2**-Cr (201 mg, 89%) as a red solid: mp 235–237 °C dec; UV–vis (dichloromethane) λ_{max} (log ϵ) 230 (4.64), 284 (4.89), 315 (4.44), 434 (3.96) nm; IR (KBr) 1960, 1885, 1252, 1059, 841, 655 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 868 (M^+, 9), 853 (5), 838 (4), 812 (10), 784 (100), 732 (92); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 6H), 0.37 (s, 54H); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.39 (s, 6H), 0.40 (s, 54H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 233.90, 149.88, 147.27, 125.78, 103.97, 2.28. Anal. Calcd for $C_{45}H_{60}CrO_3Si_6$: C, 62.25; H, 6.96. Found: C, 62.60; H, 7.18.

***endo,exo*-(2,3,6,7,10,11-Hexakis(trimethylsilyl)starphenylene)dichromium Hexacarbonyl (*endo,exo*-2-Cr$_2$).** *exo*-2,3,6,7,10,11-(Hexakis(trimethylsilyl)starphenylene)chromium tricarbonyl *exo*-**2**-Cr (30 mg, 0.034 mmol), (naphthalene)chromium tricarbonyl (48 mg, 0.182 mmol), tetrahydrofuran (100 μL), and diethyl ether (2 mL) were added to a pressure sealable Schlenk flask. The mixture was degassed with five freeze/pump/thaw cycles and then heated in an oil bath to 65 °C for 14 h. The solvents were removed in vacuo, leaving a red solid. Chromatography on silica gel with 5% dichloromethane/hexanes yields *endo,exo*-**2**-Cr_2 (15 mg, 43%) and a mixture of other chromium adducts (8 mg). *endo,exo*-**2**-Cr_2 was further purified by HPLC using an Absorbosphere HS 5-μm silica gel column with 7% dichloromethane/hexanes to give mp >200 °C dec; UV–vis (hexane) λ_{max} 221, 251, 281, 313, 427; IR (KBr) 1955, 1905 cm^{-1}; ^{1}H NMR (360 MHz, CD_2Cl_2) δ 7.37 (s, 2H), 7.36 (s, 2H), 5.71 (s, 2H), 0.47 (s, 18H), 0.39 (br s, 36H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 233.71, 233.56, 150.54, 150.51, 146.94, 146.53, 126.08, 126.04, 113.33, 105.01, 103.75, 100.38, 93.08, 2.34, 2.23.

***endo*-(2,3-Bis(trimethylsilyl)starphenylene)chromium Tricarbonyl (*endo*-3-Cr).** A solution of bis(trimethylsilyl)starphenylene **3** (16 mg, 0.039 mmol), (naphthalene)chromium tricarbonyl (16 mg, 0.059 mmol), and tetrahydrofuran (5 mL) in diethyl ether (8 mL) in a glass bomb was degassed by three freeze/pump/thaw cycles. The reaction mixture was heated in a 65 °C sand bath for 40 h, after which the solvents were removed by rotary evaporation. The resulting solid was purified by chromatography on silica gel with 15% dichloromethane/hexanes, followed by the removal of solvents under reduced pressure. Recrystallization by diffusion of hexanes into a dichloromethane solution of the residue at room temperature gave 14 mg (68%) of *endo*-**3**-Cr as red needles: mp >200 °C; UV–vis (dichloromethane) λ_{max} (log ϵ) 247 (4.65), 273 (4.78), 316 (4.26), 428 (3.98) nm; IR (KBr) 1954, 1895, 1257, 843, 743, 660 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 580 (M^+, 3), 524 (5), 496 (55), 444 (100); ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 2H), 7.06 (ABCDm, 8H), 0.37 (s, 18H); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.35 (s, 2H), 7.11 (ABCDm, 8H), 0.39 (s, 18H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 233.24, 149.31, 147.67, 147.61, 146.77, 129.36, 125.21, 125.18, 120.09, 119.92, 103.70, 102.35, 101.93, 2.17; HRMS calcd for $C_{33}H_{28}CrO_3$ 580.0981, found 580.0975.

***endo,exo*-(2,3-Bis(trimethylsilyl)starphenylene)dichromium Hexacarbonyl (*endo,exo*-3-Cr$_2$).** *exo*-(Bis(trimethylsilyl)starphenylene)chromium tricarbonyl *exo*-**3-Cr** (22.8 mg, 0.393 mmol), (naphthalene)chromium tricarbonyl (73.2 mg, 0.28 mmol), tetrahydrofuran (2.5 mL), and diethyl ether (15 mL) were placed in a glass bomb, which was then degassed by three freeze/pump/thaw cycles. This was placed in a 70 °C sand bath for 4 d. After cooling, the solvents were removed by rotary evaporation. The residue was subjected to chromatography on silica gel with 2% ethyl acetate/petroleum ether to yield *endo,exo*-**3**-Cr_2 (12.1 mg, 42%) as a red solid: mp 216 °C dec; UV–vis (dichloromethane) λ_{max} (log ϵ) 231 (4.80), 247 (4.77), 269 (4.79), 303 (4.63), 329 sh (4.29), 340 sh (4.20), 354 sh (4.11), 424 (4.13) nm; IR (KBr) 1963, 1953, 1895, 1883, 1254, 847, 833 cm^{-1}; MS (70 eV) *m/z* (relative intensity) 717 (M^+, 2), 716 (3), 660 (3), 633 (4), 632 (6), 605 (5), 604 (7), 580 (5), 578 (7), 577 (11), 576 (18), 550 (5), 549 (9), 548 (13), 525 (4), 523 (12), 499 (8), 498 (25), 497 (55), 496 (100), 495 (5), 494 (8), 445 (7), 444 (16); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.12 (ABCDm, 8H), 5.67 (s, 2H), 0.46 (s, 18H); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (ABCDm, 8H), 5.56 (s, 2H), 0.44 (s, 18H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 236.13, 234.32, 149.32, 147.77, 129.77, 124.60, 120.49, 120.25, 114.20, 112.34, 103.03, 102.01, 101.57, 92.08, 2.26; HRMS calcd for $C_{36}H_{28}Cr_2O_6Si_2$ 716.023 42, found 716.023 00.

2,3-Dicarbobutoxystarphenylene (4). A solution of diethynylangular-[3]phenylene (132 mg, 0.48 mmol) in toluene (55 mL) was flushed with argon, and $CpCo(CO)_2$ (80 mL, 0.64 mmol) was added via syringe. This solution was then injected over a 12-h period into dibutyl acetylenedicarboxylate (8.0 mL) in boiling toluene (200 mL). During the addition, the reaction mixture was irradiated with a slide projector lamp, and heat and irradiation were maintained for 8 h after the addition was complete. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was subjected to chromatography on silica gel with 25% dichloromethane/hexanes. Recrystallization from hexanes yielded **4** (72.6 mg, 30%) as yellow needles: mp 114 °C; UV–vis (hexanes) λ_{max} (log ϵ) 236 (4.61), 244 (4.69), 274 sh (4.59), 286 (4.75), 302 (4.91), 328 (4.32), 340 (4.31), 358 (4.08), 393 (3.84) nm; IR (chloroform) 3058, 2959, 2872, 1721, 1580, 1465, 1409, 1388, 1360, 1277, 1102, 1074, 936, 802 cm^{-1}; MS (70 eV) *m/z* (relative intensity)

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501 (37), 500 (M^+, 100), 444 (10), 427 (2), 388 (9), 371 (12), 371 (35), 299 (13), 298 (29); ^1H NMR (200 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.19 (br s, 8H), 4.30 (t, $J = 7$ Hz, 4H), 1.72 (m, 4H), 1.42 (m, 4H), 0.96 (t, $J = 7$ Hz, 6H); ^1H NMR (200 MHz, CD_2Cl_2) δ 7.44 (s, 2H), 7.22 (br s, 8H), 4.29 (t, $J = 7$ Hz, 4H), 1.74 (m, 4H), 1.47 (m, 4H), 0.99 (t, $J = 7$ Hz, 6H); $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2) δ 167.78, 150.59, 148.96, 148.13, 133.24, 133.00, 131.09, 129.77, 129.44, 128.37, 120.62, 120.42, 119.70, 66.00, 30.94, 19.58, 13.90. Anal. Calcd for $C_{34}H_{28}O_4$: C, 81.58; H, 5.64. Found: C, 81.91; H, 5.52.

***endo*-(Dicarbobutoxystarphenylene)chromium Tricarbonyl (*endo*-4-Cr).** A solution of dicarbobutoxystarphenylene **4** (30.0 mg, 0.0600 mmol), (naphthalene)chromium tricarbonyl (33 mg, 0.12 mmol), and tetrahydrofuran (5 mL) in diethyl ether (10 mL) was placed in a glass bomb and degassed by three freeze/pump/thaw cycles. The reaction mixture was heated for 16 h in a 70 °C sand bath. After cooling, the solvents were removed by rotary evaporation. The residue was subjected to chromatography on silica gel with 25% dichloromethane/hexanes to yield *endo*-**4**-Cr (28.1 mg, 74%) as a red solid: mp 183 °C; UV–vis (dichloromethane) λ_{max} (log ϵ) 236 (4.77), 246 (4.78), 274 sh (4.76), 284 (4.77), 304 (4.77) 340 sh (4.28), 357 sh (4.15), 424 (3.83) nm; IR (chloroform) 2960, 2928, 1970, 1906, 1714, 1254, 1103, 1073, 649, 607 cm^{-1}; MS (FAB^+) m/z (relative intensity) 637 (13), 636 (M^+, 12), 580 (12), 553 (23), 552 (42), 525 (10), 501 (32), 500 (39), 372 (35), 371 (100); ^1H NMR (200 MHz, $CDCl_3$) δ 7.19 (s, 2H), 7.04 (ABCDm, 8H), 4.27 (t, $J = 7$ Hz, 4H), 1.70 (m, 4H), 1.43 (m, 4H), 0.96 (t, $J = 7$ Hz, 6H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 233.87, 166.86, 150.35, 150.14, 147.21, 129.74, 129.64, 129.27, 120.26, 120.21, 119.43, 101.90, 98.99, 98.47, 65.91, 30.53, 19.21, 13.88. Anal. Calcd for $C_{37}H_{28}CrO_7$: C, 69.81; H, 4.43. Found: C, 69.93; H, 4.71.

^{13}C Enrichment of the Carbonyls in (Naphthalene)chromium Tricarbonyl. (Naphthalene)chromium tricarbonyl (91 mg, 0.34 mmol), tetrahydrofuran (5 mL), and diethyl ether (20 mL) were placed in a quartz Schlenk flask. The flask was degassed by three freeze/pump/thaw cycles, and ^{13}C-labeled carbon monoxide (approximately 50 mL) was admitted. This solution was irradiated at 300 nm in a Rayonet photoreactor for 30 min. The flask was reevacuated by three freeze/pump/thaw cycles, and more ^{13}C-labeled carbon monoxide (~50 mL) was added. Irradiation was resumed and continued for 1 h. The solvents were removed by rotary evaporation, and the residue was purified by chromatography on silica gel with 5% diethyl ether/hexanes to yield orange (naphthalene)chromium tricarbonyl (50 mg, 55%): mp 137 °C dec; IR (chloroform) 1968, 1898, 1888 cm^{-1}; MS (70 eV) m/z (relative intensity) 269 (3), 268 (5), 267 (9), 266 (15), 265 (16), 264 (7) (this corresponds to 47% ^{13}C-labeling in the carbonyls); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.65 (m, 4H), 6.15 (AA′m, 2H), 5.55 (BB′m, 2H). [Literature data for unlabeled compound: mp 138 °C dec; IR 1974, 1910, 1898 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.34–7.61 (m, 4H), 6.12 (dd, 2H), 5.52 (dd, 2H).][23]

Theoretical Methods

The molecular structures of all stationary points were determined with the local density functional (LDF) approach using the software DMOL.[24] The atomic basis functions are given numerically on an atom-centered, spherical–polar mesh. The integrals arising from the expression for the energy are evaluated over a grid which is generated in terms of radial functions and spherical harmonics. The Coulomb potential, corresponding to the electron repulsion term, is determined directly from the electron density by solving the Poissons equation. The form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin.[25]

All calculations were done with a double-numerical basis set augmented by polarization functions. This basis set is comparable in terms of size to a polarized double-ζ basis set in traditional Hartree–Fock molecular orbital calculations. Geometry optimizations were performed with the aid of analytically determined gradients and the search algorithms contained in DMol. All bond lengths are reported to three decimal places only. Full structural information on all molecules is available as supplementary material.

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Supplementary Material Available: Tables of atomic coordinates for structures **1-Cr-I**–**1-Cr-VI** as computed from local density functional theory. (coordinates for **1-Cr-I**, **1-Cr-II**, **1-Cr-IV**, and **1-CrV** in angstroms; coordinates for **1-Cr-III** and **1-Cr-VI** in bohrs) (6 pages). Ordering information is given on any current masthead page.

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