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Cyclobutadiene Hopping

Photo–Thermal Haptotropism in Cyclopentadienylcobalt Complexes of Linear Phenylenes: Intercyclobutadiene Metal Migration**

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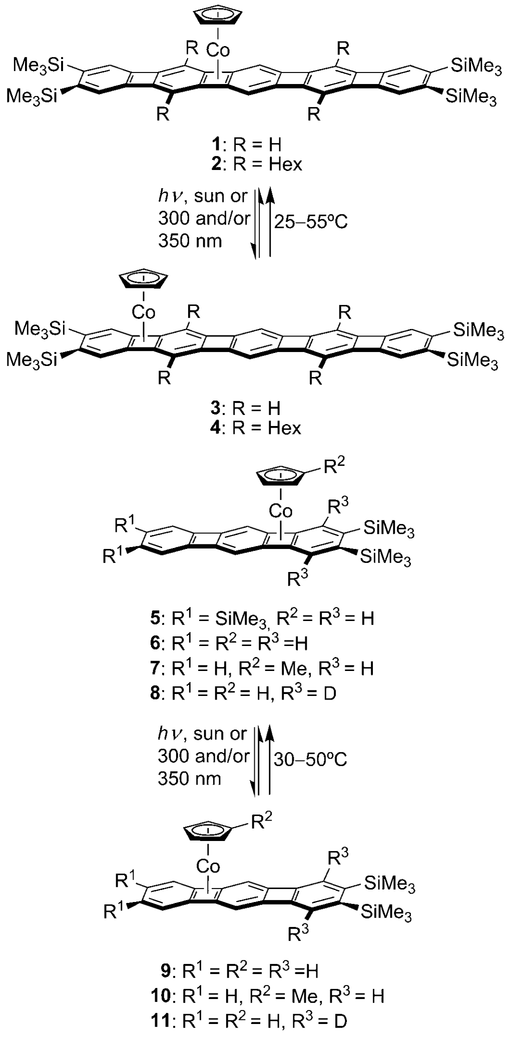
An attractive strategy for achieving solar–thermal energy conversion is to harvest sunlight in the form of activated chemical bonds through photoisomerization of a suitable molecule that can release, on demand, such stored and transportable energy by thermal reversal to its original form.[1] When such reversible isomerizations entail significant topological alterations, they provide blueprints for eliciting further functions, for example in switches, machines, data-storage, sensors, and other devices.[1,2] Because of their expanded tunability and generally favourable electronic absorption regimes, organometallic complexes are advantageous in this respect, yet have remained relatively unexplored.[3] Among them, topologically simplest are metallohaptotropic arrays in which a single metal moiety photomigrates, thermally reversibly, to a higher-energy position along a fused π framework, without the assistance of additives.[4] Only two such systems are known, $[Mo(PMe_3)_3]$ complexes of indole and quinazoline, discovered as part of a study focusing on catalytic hydrogenations of heterocycles.[5] We report 1) the photothermal reversibility of {CpCo} complexes of linear phenylenes[6] by a novel mode of haptotropism, namely, η^4:η^4 from one cyclobutadiene ring to another (Scheme 1); 2) the first X-ray structures of metalated linear phenylenes, illustrating the aromatization of the ligand on complexation; 3) mechanistic aspects of the isomerization cycles; and 4) a DFT study providing a detailed picture of how the {CpCo} unit moves across the arene separating the two cyclobutadiene rings.



Scheme 1. Photo–thermal cycles of CpCo–phenylene complexes.

The new complexes, **2**, **5**, and **6–8**, were made from the respective 2,3,6,9-tetraethynyl linear [3]phenylene, 1,2,4,5-tetraethynylbenzene, and 2,3-diethynylbiphenylene ($[D_2]$ for **8**) synthons and their cocyclization with bis(trimethylsilyl)-acetylene (BTMSA) in the presence of stoichiometric $[CpCo(CO)_2]$ (MeCp for **7**), a strategy employed previously

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for the synthesis of **1** and other linear phenylenes.[6,7] Noteworthy is the use of THF as a cosolvent to BTMSA, which reduces the boiling point of the reacting mixture such as to allow the isolation of **5** and **6** without catalytic turnover of the metal.[8] These compounds are deep red, stable solids and their structural (in particular regiochemical) identity was established by complete 2D NMR assignments (supported by NICS calculations)[9] and, ultimately, X-ray crystallographic analyses of **2**, **5**, and **6**, the first such determinations of cyclobutadiene-metalated phenylenes.[7] These data highlight in unprecedented detail the profound metalloaromatization effect[10] of the metal on the entire antiaromatic,[6,11] phenylene frame, illustrated for **5** (in comparison to the free ligand) in Figure 1 (for details, see Supporting Information). Thus, {CpCo} ligation of the phenylene causes strong deshielding of the peripheral hydrogens, tapering off with increasing distance from the metal.[12] Similarly, all NICS (in particular the out-of-plane, or NICS_{zz}) values diminish, signaling increasing diatropicity (aromaticity) of the six- and decreasing paratropicity (antiaromaticity) of the four-membered rings, including the Co-bearing one. The choice of NICS(1) data in Figure 1 is for illustrative purposes only, and a more comprehensive picture, using the NICS-scan procedure and supporting the conclusions, is presented in the Supporting Information.[13] The corresponding (X-ray) structural changes reveal a significant attenuation of bond alternation in the terminal arene moieties A and E, more pronounced in the former, while the central ring C in **5** distorts from the bisallyl configuration of the free ligand[8] to the bisalkylidene frame accentuated in the resonance form depicted at the bottom of Figure 1.

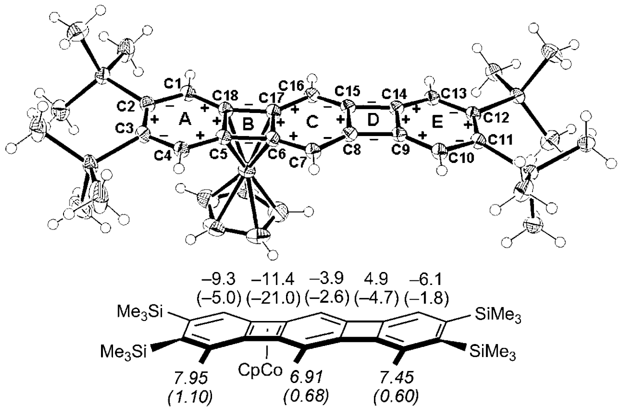

Figure 1. Top: ORTEP representation of **5**; thermal ellipsoids are set at 50% probability. Selected bond lengths (in Å; std ±0.003). The change from those in the free ligand is given in parentheses and is also indicated qualitatively by the designators "+" and "−" for the respective bonds. For example, the C1–C2 distance is 1.384 Å, decreased ("−") by 0.052 Å from that in the free ligand. C1–C2 1.384 (−0.052), C2–C3 1.474 (0.077), C3–C4 1.384 (−0.057), C4–C5 1.408 (0.052), C5–C6 1.480 (−0.032), C6–C7 1.437 (0.052), C7–C8 1.351 (−0.034), C8–C9 1.495 (−0.017), C9–C10 1.372 (0.016), C10–C11 1.423 (−0.018), C11–C12 1.427 (0.030), C12–C13 1.413 (−0.023), C13–C14 1.376 (0.017), C14–C15 1.488 (−0.025), C15–C16 1.352 (−0.033), C16–C17 1.434 (0.049), C17–C18 1.468 (−0.045), C1–C18 1.411 (0.052). Bottom: experimental (C_6D_6) and calculated [NICS (1), B3LYP/6-31+G*, for the respective parent phenylene frames] NMR chemical shift data for **5**; $\Delta\delta$ changes relative to those in the free ligand in parentheses. For example, $\delta_{\text{H10}} = 7.45$ ppm, deshielded by 0.60 ppm from the corresponding value in the free ligand. The associated benzene ring NICS(1) = −6.1 ppm, deshielded by 1.8 ppm relative to that in the free ligand.

As depicted in Scheme 1, irradiation of **1** with 300 and/or 350 nm lamps (Rayonet), or simply sunlight for 10 h, in THF at ambient temperature caused the {CpCo} unit to shift to the outer cyclobutadiene ring to give **3** [photostationary ratios **1**:**3** = 88:12 (300 nm) and 71:29 (350 nm)], as evidenced by the appearance of 8 new singlets in the ^{1}H and 18 new peaks in the ^{13}C NMR spectra, respectively.[7] These results were unperturbed by changing the solvent (acetone, $CHCl_3$, or C_6H_6) and temperature (0 °C), or by addition of potential ligands (e.g., 1,5-cyclooctadiene, phosphines, CO). On warming, the signals for **3** disappeared to fully regenerate **1**. This photo–thermal cycle could be repeated multiple times without decomposition, allowing for the convenient measurement of concentration-independent, first-order activation parameters of the thermal reverse in C_6D_6: $\Delta H^{\neq} = 25.9(0.4)$ kcal mol^{-1}, $\Delta S^{\neq} = 1.6(1.4)$ e.u., which were essentially unchanged in [D$_8$]THF: 25.6(0.9) kcal mol^{-1}, $\Delta S^{\neq} = 0.1(3.0)$ e.u. The tetrahexyl derivative **2** exhibited similar behavior in its equilibration with **4** (THF, 10 h, 300 nm light, photostationary ratio **4**:**2** = 17:83). Thermal reversal proceeded with $\Delta H^{\neq} = 27.6(0.8)$ kcal mol^{-1}, $\Delta S^{\neq} = 7.7(0.8)$ e.u. ([D$_8$]THF) more slowly, possibly because of increased steric hindrance to migration (see below). Thus, it is clear that **1** and **2** are not only thermodynamically more stable than their respective haptomers, but also readily reached under the conditions of their preparation, providing an explanation for their exclusive formation. To probe the possibility of a similar, but now degenerate thermal haptotropism across the center ring, ^{1}H NMR spectra of **1** and **2** were recorded at elevated temperatures (up to 120 °C). However, no coalescence of the signals to the expected symmetrical pattern occurred. Similarly, spin saturation transfer was undetectable, perhaps not surprising in view of the relatively (on the NMR time scale) slow migration quantified above.

Attention was therefore focused on the linear [3]phenylene frame of **5**, in which the diminished HOMO–LUMO gap of the ligand[6,11] was anticipated to render the CpCo–phenylene bond more labile. Indeed, the homodesmotic Equation (1) is substantially exothermic by DFT. However,

$$\begin{array}{c}\text{[3]Phenylene-CpCo}\\ +\\ \text{[5]Phenylene}\end{array} \xrightarrow{-11.3\ \text{kcal mol}^{-1}} \begin{array}{c}\text{[3]Phenylene}\\ +\\ \text{[5]Phenylene-CpCo}\end{array} \tag{1}$$

NMR fluxional behavior remained elusive (^{1}H NMR, 120 °C). Consequently, and to probe the generality of the photo–thermal behavior of **1**–**4**, the desymmetrized complexes **6** and **9** were prepared by cocyclization of 2,3-diethynylbiphenylene with BTMSA and [CpCo(CO)$_2$]. Surprisingly, the ensuing inseparable mixture consisted mainly of **6** (ratio **6**:**9** = 50:1), from which it could be crystallized. An X-ray crystallographic analysis provided a speculative answer to the regiochemical preference of this haptomer: possible steric relief of the proximal *ortho*-bis(trimethylsilyl) unit (for a detailed comparison, see Supporting Information). Thus, the SiC−CSi bond in **6** is elongated by 0.05 Å compared to that in the free ligand,[14] whereas the symmetry-related $R^1C{-}CR^1$ ($R^1 = H$) bond experiences a much smaller change (+0.01 Å). This effect is also visible in the structure of **5** in comparison to that of the free phenylene: C2−C3 is expanded by 0.077 Å, C11−C12 by only 0.030 Å (Figure 1). Gratifyingly, irradiation of **6** under the same conditions as those used for **1** and **2** caused the metal to shift to provide **9** (toluene, 10 h, 310 + 365 nm lamps, photostationary ratio **6**:**9** = 50:50). Because the thermal equilibrium favors **6** strongly ($\Delta G^{\circ}_{298} = -2.3\ \text{kcal mol}^{-1}$), thermal reversal from **9** was treated by first-order kinetics with $\Delta H^{\neq} = 23.1(0.7)\ \text{kcal mol}^{-1}$, $\Delta S^{\neq} = 6.0(1.3)$ e.u. ([D$_8$]toluene), revealing it to be more rapid than that for the [5]phenylene analogues, presumably due to weaker binding of the {CpCo} unit. To confirm the intramolecularity of the photo–thermal cycle rigorously, a crossover experiment was executed involving an equimolar mixture of MeCp labeled **7** and deuterium labeled **8** and their respective haptomers **10** and **11** ($K = 50{:}1$). ^{1}H NMR and mass spectral scrutiny of the components after completion of the sequence revealed the absence of label scrambling.

How does the {CpCo} moiety migrate from one cyclobutadiene unit to the next? Two extreme alternatives present themselves: a least-motion movement across the intervening arene unit or a more circuitous pathway along the periphery. To address the relative feasibility of these options, DFT calculations were performed for the parent CpCo–phenylene complexes.[4a,15] The potential energy surface was determined by keeping the {CpCo} unit at 1.8 Å above the π system and performing a scan calculation (incremental intervals 0.2 Å). Transition states and minima were then located and confirmed by frequency calculations and energies refined at a relatively higher basis set (for calculational and structural details, see Supporting Information). Figure 2 reveals that, after an initial displacement from the center of the four-membered ring along the long axis of the ligand, the metal deflects to walk along the edge. Specifically, from η^4-haptomer **a** (corresponding to **1** and **2**), which is predicted correctly to be the lowest-energy form, the metal moves either outward to reach η^2-cyclobutadiene transition state *b* (37.0 kcal mol^{-1}) or, slightly more readily, inward to η^2-*h* (35.7 kcal mol^{-1}). Traversal of the respective adjacent six-membered rings proceeds through η^4-benzene intermediates **c** (20.3 kcal mol^{-1}), **e** (19.6 kcal mol^{-1}), and **i** (19.0 kcal mol^{-1}), the former pair connected by transition state *d* (36.7 kcal mol^{-1}), whereas the symmetry equivalent **i**/**i** duet interconverts through *j* (35.9 kcal mol^{-1}). Forcing the metal to proceed through the least-motion path across the arene nuclei leads to an unstable 20-electron species, 36 kcal mol^{-1} above the η^4-intermediate (e.g. **c**). Finally, the "photoproduct" **g** stores 9.7 kcal mol^{-1} of thermal energy. The calculations explain why the degenerate shift across the center of the molecule is not detectable by NMR techniques. In addition, the computed barrier from **g** to **a**, 27.3 kcal mol^{-1}, is in excellent agreement with the measured values for the thermal reversals of **3** and **4**, respectively (25.6–27.6 kcal mol^{-1}), in particular considering that the terminal *o*-bis(trimethylsilyl) substitution likely activates haptomer **g** (see above).

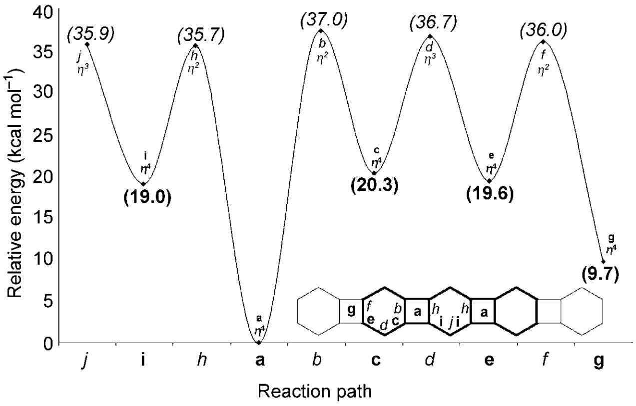

Figure 2. Potential energy diagram for the {CpCo} shift along the linear [5]phenylene frame. The position of the {CpCo} is indicated in letters. Energies (in kcal mol^{-1}) are given relative to the global ground state **a** (corresponding to **1** and **2**). Intermediates are labeled in bold, transition states in italic letters, including the nature of η-coordination.

Why is haptomer **a** more stable than **g**? Calculations show that the energies required to distort linear [5]phenylene to the geometries found in the complexed isomers are very similar (16 versus 14 kcal mol^{-1}), hence the answer rests on electronic grounds. Indeed extended Hückel calculations reveal that the overlap populations between the frontier orbitals on the {CpCo} fragment and the HOMO and the LUMO of the π system is greater for **a** (0.0793 and 0.0745, respectively) than for **g** (0.0556 and 0.0517, respectively). A didactically more instructive valence-bond view recognizes that metalloaromatization of the inside four-membered ring allows the formulation of more resonance forms that avoid antiaromatic cyclobutadiene circuits (see Supporting Information).

Similar calculations were executed for the degenerate shift in CpCo–[3]phenylene (bold substructure in Figure 2). Adopting the notation of Figure 2 for the degenerate **a** to **a** transfer to this topology (labeled by an asterisk), the metal wanders through *h** (relative energy 26.9 kcal mol^{-1}) to **i*** (10.9 kcal mol^{-1}) and crosses the center through *j** (24.9 kcal mol^{-1}). The overall barrier is reduced by about 10 kcal mol^{-1} compared to that in CpCo–[5]phenylene (**a**→**a**), a value that is close to the weaker bond strength to the metal [11.3 kcal mol^{-1}; Equation (1)], supporting the notion that it is the ground-state energy of the complexes that controls the ease of migration. The experimental barrier for the thermal conversion of **9** to **6**, 23.1 kcal mol^{-1}, is reasonably close to the calculated value, especially when again considering the higher energy of **9**. Finally, it is instructive to compare the calculated trajectory of {CpCo} in our systems to that of other haptotropic shifts,[4a] in particular those occurring in [(arene)Cr(CO)$_3$] complexes, all of which also choose peripheral trails.[15] In these, instead of the initial $\eta^4 \rightarrow \eta^2$ displacement, the metal typically moves straight to the edge to adopt an η^4 (often described as η^1) trimethylenemethane-like transition state on the way to a neighboring ring, a consequence of the different electronic requirements of the {Cr(CO)$_3$} unit. Illustrative is the computed course of the $\eta^6{:}\eta^6$ interconversion of [(biphenylene)Cr(CO)$_3$].[16] The metal slides from the (near)center of one benzene ring to the quaternary (four-membered) ring carbon to reach a distorted trimethylenemethane maximum, and then proceeds to the edge of the bridging cyclobutadiene bond. This species represents a minimum on the potential energy curve and adopts an η^2-like complexed cyclobutadiene topology ("quasi-η^4"), from which it continues by the microscopic reverse on to the other benzene nucleus.

In summary, we have discovered a novel photochemical energy storage system that is based on an unprecedented reversible η^4:η^4 cyclobutadiene haptotropic shift of an attached {CpCo} unit. The fact that simple substitution engenders noticeable changes in ground state (i.e. **6** versus **9**) and transition state energies (i.e. for **3** versus **4**) bodes well for future efforts aimed at tailoring these molecules toward more efficient constructs. Moreover, the simplicity of the sandwich array featuring a readily functionalizable Cp ring, coupled with the property of reversible mobility, suggests applications in molecular mechanical switching devices. Such will be the subject of future efforts.

Experimental Section

5: KF·2H$_2$O (700 mg, 7.44 mmol), [18]crown-6 (100 mg, 0.38 mmol) and 1,2,4,5-tetrakis[(trimethylsilyl)ethynyl]benzene (370 mg, 0.80 mmol)[8] in degassed THF (25 mL) were stirred for 70 min at room temperature. The orange liquid was filtered through a plug of silica gel (1 × 3 cm) that was rinsed with degassed THF (15 mL) to furnish a light-yellow solution. After addition of [CpCo(CO)$_2$] (260 mg, 1.44 mmol), the mixture was shielded from light and added through a syringe pump over a period of 6 h to boiling, degassed BTMSA (50 mL) and THF (200 mL) under N$_2$, while irradiating with a slide projector lamp (GE ELH, 300 W). Boiling and irradiation were continued for 15 h. After the solvents had been removed by vacuum transfer, the black residue was filtered through a plug of neutral alumina (activity III), eluting with hexanes/THF (50:1), and the solvent evaporated. The dark brown residue was crystallized from degassed acetone, yielding **5** (330 mg, 0.52 mmol, 65 %), black needles; m.p. 192–195 °C (decomp); ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta =$ 7.94 (s, 2H), 7.44 (s, 2H), 6.90 (s, 2H), 4.41 (s, 5H), 0.35 (s, 18H), 0.31 ppm (s, 18H); ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 149.4$, 148.4, 143.3, 139.4, 136.0, 125.6, 115.5, 80.2, 78.1, 73.9, 2.69, 2.61 ppm; IR (neat): $\tilde{\nu} = 2951$, 2898, 1259, 1248, 1073, 830 (s), 799 (s), 752 cm^{-1} (s); UV/Vis (ethanol): λ_{max} (lg ε) 288 (4.86), 299 (5.00), 352 (4.45), 410 (4.39), 4.38 (4.49), end absorption to 550 nm; MS (70 eV): m/z (%): 638 (9) [M^+], 514 (100), 499 (3), 387 (2), 73 (24); HR-MS (FAB): calcd for $C_{37}H_{72}Si_3Co$: 638.2087; found: 638.2095. Elemental analysis calcd for $C_{35}H_{47}CoSi_4$: C 65.78, H 7.41; found: C 65.82, H 7.21.

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[1] For selected general reviews, see: a) V. Balzani, A. Credi, M. Venturi, *Chem. Soc. Rev.* **2009**, *38*, 1542; b) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72; *Angew. Chem. Int. Ed.* **2007**, *46*, 72; c) S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77; d) D. Gust, T. A. Moore, A. L. Moore, *Chem. Commun.* **2006**, 1169; e) G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* **2005**, *105*, 1281; f) C. Dugave, L. Demange, *Chem. Rev.* **2003**, *103*, 2475; g) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; h) *Photochromism, Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, Amsterdam, **2003**.

[2] For selected recent illustrative studies, see a) Y. Kishimoto, J. Abe, *J. Am. Chem. Soc.* **2009**, *131*, 4227; b) R. S. Stoll, M. V. Peters, A. Kuhn, S. Heiles, R. Goddard, M. Bühl, C. M. Thiele, S. Hecht, *J. Am. Chem. Soc.* **2009**, *131*, 357; c) K. Guo, Y. Chen, *J. Mater. Chem.* **2009**, *19*, 5790; d) M. Müri, K. C. Schuermann, L. De Cola, M. Mayor, *Eur. J. Org. Chem.* **2009**, 2562; e) S. Silvi, E. C. Constable, C. E. Housecroft, J. E. Beves, E. L. Dunphy, M. Tomasulo, F. M. Raymo, A. Credi, *Chem. Commun.* **2009**, 1484; f) A. Ben-Asuly, A. Aharoni, C. E. Diesendruck, Y. Vidavsky, I. Goldberg, B. F. Straub, N. G. Lemcoff, *Organometallics* **2009**, *28*, 4652.

[3] For selected reviews, see: a) *Photofunctional Transition Metal Complexes* (Ed.: V. W. W. Yam), Springer, Berlin, **2007**; b) P. Coppens, I. Novozhilova, A. Kovalevsky, *Chem. Rev.* **2002**, *102*, 861; c) P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, *219–221*, 839.

[4] For a recent review of metallohaptotropism, see: a) I. D. Gridnev, *Coord. Chem. Rev.* **2008**, *252*, 1798; for the only examples of dimetallo photo–thermal haptotropism, see: b) K. Tsuchiya, K. Ideta, K. Mogi, Y. Sunada, H. Nagashima, *Dalton Trans.* **2008**, 2708, and references therein; for examples of additive-mediated mononuclear systems, see: c) H. C. Jahr, M. Nieger, K. H. Dötz, *Chem. Eur. J.* **2005**, *11*, 5333; d) D. E. Herbert, M. Tanabe, S. C. Bourke, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2008**, *130*, 4166; e) N. S. Ieong, I. Manners, *J. Organomet. Chem.* **2008**, *693*, 802, and references therein.

[5] a) G. Zhu, K. Pang, G. Parkin, *J. Am. Chem. Soc.* **2008**, *130*, 1564; b) G. Zhu, J. M. Tanski, D. G. Churchill, K. E. Janak, G. Parkin, *J. Am. Chem. Soc.* **2002**, *124*, 13658.

[6] For a review of the phenylenes, see: O. Š. Miljanić, K. P. C. Vollhardt in *Carbon-Rich Compounds: From Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, pp. 140–197.

[7] All new isolated compounds gave satisfactory analytical and spectral data (see Experimental Section and Supporting Information). Complexes **2**, **5**, and **6** were subjected to X-ray crystallographic analysis. **2** gave poor crystals and a qualitative structural rendition (synchrotron radiation, SRS Daresbury), confirming connectivity, is included in the Supporting Information. **5**: $C_{35}H_{47}CoSi_4$, crystal size $0.25 \times 0.20 \times 0.05$ mm^3, space group $P\bar{1}$, scan range $2.45 < 2\theta < 30.24°$, $T = 100.0(2)$ K, $a = 9.497(3)$, $b = 12.321(4)$, $c = 16.469(5)$ Å, $\alpha = 74.058(5)$, $\beta = 82.154(5)$, $\gamma = 72.276(5)°$, $V = 1762.0(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.204$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.71073$ cm^{-1}, 9209 unique reflections, of which 6958 were taken as observed [$I > 2\sigma(I)$], $R = 0.0503$, $R_w = 0.1272$. **6**: $C_{29}H_{31}CoSi_2$, crystal size $0.30 \times 0.20 \times 0.05$ mm^3, space group $C2/c$, scan range $2.42 < 2\theta < 25.03°$, $T = 120(2)$ K, $a = 43.91(3)$, $b = 7.472(4)$, $c = 16.869(11)$ Å, $\alpha = 90.00$, $\beta = 111.522(11)$, $\gamma = 90.00°$, $V = 5149(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.276$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.71073$ cm^{-1}, 4266 unique reflections, of which 2981 were taken as observed [$I > 2\sigma(I)$], $R = 0.0892$, $R_w = 0.2042$. CCDC 746176 (**5**) and 746177 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] B. C. Berris, G. H. Hovakeemian, Y.-H. Lai, H. Mestdagh, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1985**, *107*, 5670.

[9] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[10] a) A. Datta, S. K. Pati, *J. Am. Chem. Soc.* **2005**, *127*, 3496; b) J. W. Chinn, Jr., M. B. Hall, *Inorg. Chem.* **1983**, *22*, 2759;

c) B. E. Bursten, R. F. Fenske, *Inorg. Chem.* **1979**, *18*, 1760; for this effect in [(benzocyclobutadiene)CpCo], see: d) R. I. Duclos, Jr., K. P. C. Vollhardt, L. S. Yee, *J. Organomet. Chem.* **1979**, *174*, 109.

[11] J. M. Schulman, R. L. Disch, *J. Phys. Chem. A* **2003**, *107*, 5223.

[12] The observed relatively large chemical shifts of the arene hydrogens are minimal values, since the magnetic anisotropy of {CpCo} in this area of space is (if anything) shielding. For selected references, see ref. [10d] and: a) A. G. Myers, M. Sogi, M. A. Lewis, S. P. Arvedson, *J. Org. Chem.* **2004**, *69*, 2516; b) V. Wolfart, M Ramming, R. Gleiter, B. Nuber, H. Pritzkow, F. Rominger, *Eur. J. Inorg. Chem.* **1999**, 499; c) R. H. Mitchell, Y. Chen, N. Khalifa, P. Zhou, *J. Am. Chem. Soc.* **1998**, *120*, 1785; d) M. J. McGlinchey, R. C. Burns, R. Hofer, S. Top, G. Jaouen, *Organometallics* **1986**, *5*, 104.

[13] For a caveat regarding the use of single-point NICS values in assessing the aromaticity of $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3]$, see a) F. Feixas, J. O. C. Jiménez-Halla, E. Matito, J. Poater, M. Solà, *Pol. J. Chem.* **2007**, *81*, 783; for the NICS-scan methodology, see: b) A. Stanger, *J. Org. Chem.* **2006**, *71*, 883; c) A. Stanger, *Chem. Eur. J.* **2006**, *12*, 2745; d) A. C. Tsipis, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8244; for a recent appraisal of the concept of aromaticity, see: e) A. Stanger, *Chem. Commun.* **2009**, 1939.

[14] D. Holmes, S. Kumaraswamy, A. J. Matzger, K. P. C. Vollhardt, *Chem. Eur. J.* **1999**, *5*, 3399.

[15] For very recent literature compilations of theoretical (and experimental) treatments of haptotropism in arene–metal complexes, see: a) O. Joistgen, A. Pfletschinger, J. Ciupka, M. Dolg, M. Nieger, G. Schnakenburg, R. Fröhlich, O. Kataeva, K. H. Dötz, *Organometallics* **2009**, *28*, 3473; b) A. Pfletschinger, M. Dolg, *J. Organomet. Chem.* **2009**, *694*, 3338; c) J. O. C. Jiménez-Halla, J. Robles, M. Solà, *Organometallics* **2008**, *27*, 5230; d) E. Kirillov, S. Kahlal, T. Roisnel, T. Georgelin, J.-Y. Saillard, J.-F. Carpentier, *Organometallics* **2008**, *27*, 387, and references therein.

[16] Y. Oprunenko, I. Gloriozov, K. Lyssenko, S. Malyugina, D. Mityuk, V. Mstislavsky, H. Günther, G. von Firks, M. Ebener, *J. Organomet. Chem.* **2002**, *656*, 27.