

Photochemistry | Hot Paper |

A Terminal, Fluxional η^4 -Benzene Complex with a Thermally Accessible Triplet State is the Primary Photoproduct in the Intercyclobutadiene Haptotropism of (CpCo)phenylenesThomas A. Albright,^[b] Rima Drissi,^[a] Vincent Gandon,^[c] Sander Oldenhof,^[a] Oluwakemi A. Oloba-Whenu,^[d] Robin Padilla,^[a] Hao Shen,^[a] K. Peter C. Vollhardt,^{*[a]} and Vincent Vreeken^[a]

Abstract: Low-temperature irradiation of linear [3]- and [4]phenylene cyclopentadienylcobalt complexes generates labile, fluxional η^4 -arene complexes, in which the metal resides on the terminal ring. Warming induces a haptotropic shift to the neighboring cyclobutadiene rings, followed by the previously reported intercyclobutadiene migration. NMR scrutiny of the primary photoproduct reveals a thermally accessible 16-electron cobalt η^2 -triplet species, which, according to DFT computations, is responsible for the rapid symmetrization of the molecules along their long axes. Calculations indicate that the entire haptotropic manifold along the phenylene frame is governed by dual-state reactivity of alternating 18-electron singlets and 16-electron triplets.

Unique among unsaturated polycyclic hydrocarbons, the electronically activated platform of the linear [N]phenylenes (N = number of benzene rings)^[1] enables photothermal metallohap-totropism of an attached CpCo (Cp = η^5 -cyclopentadienyl) fragment between the cyclobutadiene moieties.^[2] In the cases of linear [4]-^[2a] and [5]phenylene,^[2b] irradiation moves the metal unit from the thermodynamically preferred "inside" position (e.g., **A**) to the outer four-membered ring (**B**), a process that is

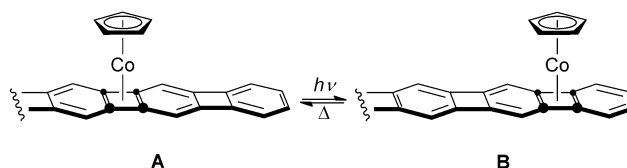
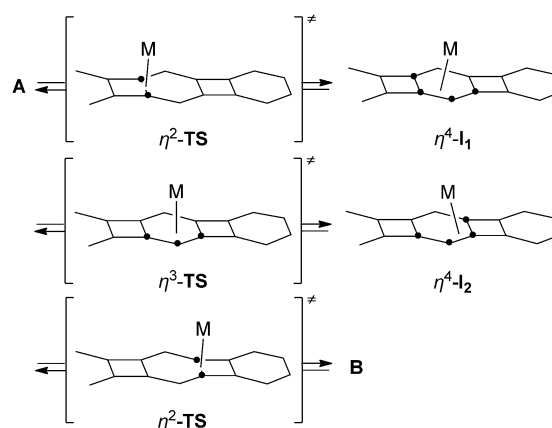


Figure 1. Generic photothermal intercyclobutadiene haptotropism in linear [N]phenylenes.

reversed on warming (Figure 1). For the linear [3] frame, de-symmetrization was provided by 2,3-bis(trimethylsilyl) substitution.^[2b] As such, these systems constitute conceptually simplest photochromic organometallics, with potential applications in photostorage^[3] and photoswitching devices.^[4]

The thermal trajectory of the CpCo sliding across the intervening benzene ring had been scrutinized initially on the singlet surface at a moderate level of theory (DFT B3LYP/3-21G; Co LANLDZ) to establish the peripheral pathway depicted in Scheme 1.^[2] Thus, the metal traverses an η^2 -cyclobutadiene transition state (TS) to reach either one of two local-symmetry-equivalent η^4 -arene intermediates **I**, which equilibrate through an η^3 -TS. A noticeable energetic feature of this manifold was the relative kinetic protection of **I** by barriers to **A** or **B** that are sizeable (≈ 16 – 18 kcal mol⁻¹). The equilibration $I_1 \rightleftharpoons I_2$ appeared



Scheme 1. Mechanism of thermal intercyclobutadiene haptotropism in linear [N]phenylenes (M = CpCo; = ligated carbon atom, TS = transition state, I = intermediate).

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similarly sluggish ($\approx 14\text{--}17\text{ kcal mol}^{-1}$; however, vide infra). This finding suggested that low-temperature irradiation might allow the observation of **I**, provided that it constituted a primary product of the photoexcitation of **A**. A suitable example of **A** with which to test this notion was linear 2,3,7,8-tetrakis-(trimethylsilyl)[3]phenylene **1** (Figure 2),^[2b] endowed with the favorable characteristics of ease of access, relative stability, solubility, simplicity of its NMR signature, and inherent symmetry that renders $I_1 = I_2$. If **I** from **1** were to be formed, the comparatively simple ^1H NMR spectrum of **1**—6 singlets (3 phenylene, 2 SiMe_3 , 1 Cp)—should complicate to 11 lines.

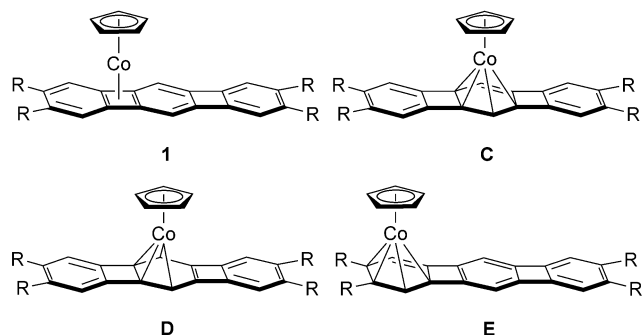


Figure 2. Possible structures **C–E** for the low-temperature species observed on irradiation of **1** ($R = \text{SiMe}_3$).

A solution of **1** in $[\text{D}_8]$ toluene was irradiated at -65°C and its ^1H NMR spectrum recorded at -30°C , revealing a dramatic change (see Supporting Information). The sample turned deep green ($\lambda = 654\text{ nm}$; see Supporting Information), and the signals for **1** had almost entirely vanished. A set of new peaks appeared, comprised of two sharp singlets at $\delta = 7.08$ and 6.44 ppm and a broad singlet at $\delta = 5.56\text{ ppm}$, all of which integrated for 2 H each. The former two are assigned to the protons of dissimilar uncomplexed arene segments, the latter to their complexed counterpart. Another broad singlet at $\delta = 3.98\text{ ppm}$ (5 H) was attributed to a new Cp group, and two new SiMe_3 peaks (9 H each) were also present. The Cp absorption displayed peculiar behavior, gradually moving to higher field ($\Delta\delta \approx 0.8\text{ ppm}$) on warming from -30°C to 10°C , during which all new peaks disappeared, and the

original spectrum of **1** had been restored. The signal at $\delta = 5.56\text{ ppm}$ showed similar, albeit much attenuated behavior. Lowering the probe temperature to -80°C had no effect (apart from some slight further broadening of the signals). To ascertain that the solvent resonances were not obscuring part of the spectrum, the experiment was repeated in $[\text{D}_6]$ acetone, producing the same species (Figure 3). Attempts to isolate the latter and obtain crystals suitable for X ray analysis failed.

While the observation of what appeared to be a new haptomer was gratifying, the NMR data posed a puzzle, as they were clearly incompatible with (a static) structure **C**. Instead, they pointed to a molecule exhibiting mirror (or “top-down”) symmetry along the long molecular axis, as in **1**, either per se or enabled by a rapid fluxional process, albeit puzzlingly restricted to only one side of the molecule, keeping the molecule unsymmetrical with respect to mirror (or “left-right”) symmetry perpendicular to the long molecular axis. The two most obvious static candidates, $\eta^2\text{-TS}$ (Scheme 1) and **D** (Figure 2), were ruled out, as the first constitutes the transition state for the thermal reversal to **A** ($=\text{B}$), and the second, featuring an inherently unfavorable benzocyclobutadiene array, collapses to **C** on attempted DFT computation (BPW91). Moreover the ^1H NMR chemical shift of $\delta = 5.56\text{ ppm}$ ($\delta = 5.57\text{ ppm}$ in $[\text{D}_6]$ acetone) is incommensurate with that expected for terminal $\eta^4\text{-CpCo}(\text{arene})$ hydrogens ($\delta \approx 2\text{--}3\text{ ppm}$).^[5] It would, however, be consistent with a fluxional structure exhibiting the averaged δ value for an uncomplexed^[5c] and an internal complexed arene hydro-

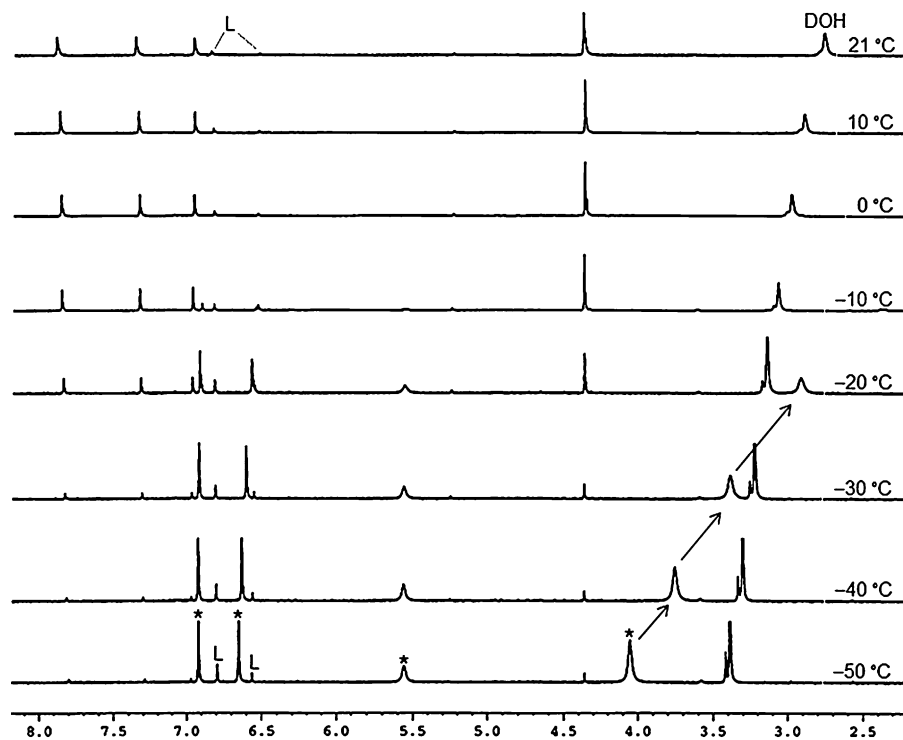


Figure 3. Stacked plot of the aromatic and Cp ^1H NMR spectral region recorded after the cold irradiation of **1** in $[\text{D}_6]$ acetone (ppm) for 5 h. New peaks are marked with * and traces of free ligand with L. The temperature dependent “drift” of the Cp signal at $\delta = 4.05\text{ ppm}$ is highlighted with arrows.

gen.^[5,6] Adding to the conundrum were the locations of the other two arene signals at $\delta = 7.08$ and 6.44 ppm ($\delta = 6.93$ and 6.66 ppm in $[D_6]$ acetone), unexpectedly high-field for a linear [3]phenylene in which the cyclic delocalization of the central ring should be largely compromised by metal complexation, resulting in relatively unperturbed 2,3-bis(trimethylsilyl)benzocyclobutene fragments (expected $\delta > 7.50$ ppm).^[7] Either the new species has an unusual electronic make-up, or the locus of the metal is elsewhere, specifically (and, if so, surprisingly) at the terminus, as in (fluxional) **E** (Figure 2).

In the hope to shed further light on the matter, low temperature ^{13}C in conjunction with 2-D NMR (HSQC, HMBC) experiments were carried out ($[D_8]$ toluene, -30°C ; see Supporting Information). Assuming the presence of top-down symmetry, as surmised by the proton spectra, one would expect to observe nine new phenylene carbon signals. The actual spectrum, however, contains only six peaks for the two uncomplexed arene rings, one set correlated to the proton signal at $\delta = 6.44$ ppm [$\delta = 112.1$ (HSQC), 146.1 and 152.1 ppm (HMBC)] and another to that at $\delta = 7.08$ ppm [$\delta = 122.6$ (HSQC), 147.6 and 150.8 ppm (HMBC)]. The Cp absorption was broadened to the point of being barely visible, and there were no cross peaks for the absorption at $\delta = 5.56$ ppm (HSQC). It thus appeared that the metal atom causes broadening of all peaks in its vicinity, those of the ligating benzene moiety to the point of being undetectable.

The combined NMR spectral data strongly indicated top-down-fluxional **E** as the framework of the low temperature entity, exhibiting a cyclobuta[*b*]biphenylene substructure with chemical shifts that are in excellent agreement with similar arrays.^[8] Notably, the paratropicity of the biphenylene part explains the relatively shielded associated ^1H NMR chemical shifts (vide supra), the similarly unusually high field ^{13}C NMR peak at $\delta = 112.1$ ppm is typical of a dicyclobuta[*a,d*]benzene,^[1,9] and the four low field absorptions between $\delta \approx 146$ and 152 ppm are readily ascribed to the three cyclobutadiene and one of the silyl-bearing carbons.^[1,7,8] The resulting assigned pattern is depicted in Figure 4.

Confirmation of the topology of **E** was acquired through an experiment featuring $^{13}\text{C}_6\text{-1}$, bearing an isotopically labelled central benzene ring ($[D_6]$ acetone; see Supporting information). Indeed, enhancement of the appropriate ^{13}C signals assigned to **E**, at $\delta = 112.8$, 146.2 , and 152.0 ppm (see Figure 4) was seen, and, in the corresponding ^1H spectrum, the peak at

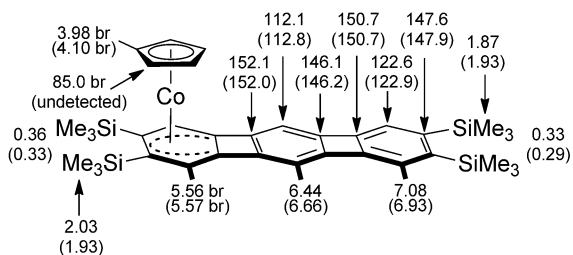
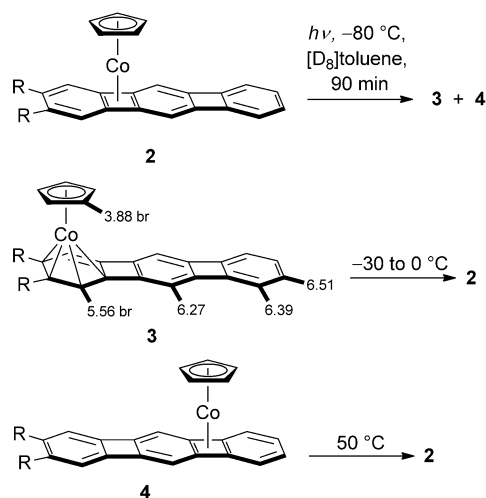


Figure 4. ^1H and ^{13}C NMR assignments of (top-down fluxional) **E** in $[D_8]$ toluene and (parentheses) $[D_6]$ acetone (ppm). The signals for the two trimethylsilyl groups are assigned tentatively.

$\delta = 6.66$ ppm (Figure 3 and 4) now appears as a broad doublet ($J_{\text{C-H}} = 166$ Hz), the remaining absorptions left unchanged. In addition, time-dependent density functional theory (TDDFT) computations rendered electronic spectra for **C** and **E**, of which only that for the latter was in reasonable agreement with that obtained experimentally (vide supra and Supporting Information).

To gain further information about the photodynamics of the CpCo[3]phenylene frame, we turned to the left-right desymmetrized 2,3-bis(trimethylsilyl) derivative **2**, originally employed to detect the photothermal equilibration with **4** at room temperature (Scheme 2).^[2b] Unlike **1**, this molecule might form two different terminal ring haptotropisomers, at the silyl substituted and the unsubstituted end, respectively.

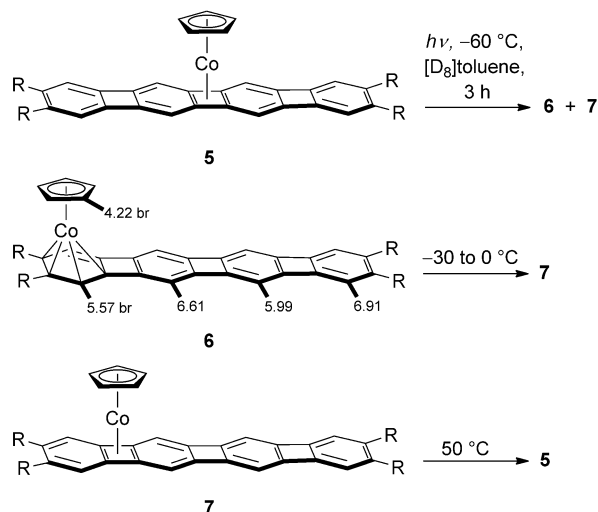


Scheme 2. Low temperature irradiation of **2** generates (top-down fluxional) **3** (chemical shifts in ppm, $[D_8]$ toluene, -30°C) and **4** ($\text{R} = \text{SiMe}_3$).

Remarkably, irradiation at low temperature generated, in addition to the cyclobutadiene haptomer **4**,^[2b] one new species, assigned (top-down fluxional) structure **3** (ratio **2:3:4** = **1:6:4**) on the basis of ^1H NMR data (Scheme 2 and Supporting Information), with chemical shifts that are exactly as expected in comparison to those of **E**, after correcting for the shielding effect of removing the SiMe_3 groups ($\approx 0.4\text{--}0.7$ ppm).^[1,2,7,8] Warming the sample and NMR monitoring revealed that **3** reverted to **2** smoothly over the temperature range -30 to 0°C , leaving **4** unchanged until intercyclobutadiene hopping to **4** occurred at $> 40^\circ\text{C}$, as recorded previously.^[2b] As in the case of **E**, the proton signals of the Co-ligated fragments in **3** were broadened and shifted to higher field with increasing temperature (see Supporting information). Thus, the (observable) primary photoproduct of **2** is only the terminal bis(trimethylsilyl)-arene complex. Among the two simplest explanations for this outcome, the first, namely a relatively greater instability of haptomer bearing the CpCo moiety at the unsubstituted terminus with respect to the formation of **4** than that of **3** on the way to **2**, appears unlikely in view of a DFT estimate of the corresponding activation barriers (BPW91; see Supporting Infor-

mation), which, while similar, arrive at a value that is slightly higher for the former (14.8 kcal mol⁻¹) than the latter (14.6 kcal mol⁻¹). We therefore believe that the unobserved arene complex is either not formed under the conditions employed or (more likely) is sufficiently photolabile to be undetectable in the photostationary state distribution of products.

Is the terminal ring the initial target of the CpCo-migration even in extended systems that require the traversal of several rings? To answer this question, the same experiments were executed with [4]phenylene derivative **5**,^[2a] displaying behavior identical to those of **1** and **2** (Scheme 3 and Supporting Infor-



Scheme 3. Low temperature irradiation of **5** generates (top-down fluxional) **6** (chemical shifts in ppm, [D₈]toluene, -30 °C) and **7** (R = SiMe₃).

mation). Indeed, irradiation for 3 h at -60 °C produced a mixture of **5**, (top-down fluxional) **6**, and **7** (1:2:1). Notably, four new phenylene singlets appeared for species **6**, with chemical shifts in agreement with one (end)complexed ring and a linear [3]phenylene substructure.^[1] Gradual warming converted **6** exclusively to **7**, which then reverted to **5** as described previously.^[2a]

What is the origin of the peculiar NMR characteristics of **E**, **3**, and **6** in the vicinity of the metal, that is, the broadening of signals to the point of rendering the ¹³C peaks for the complexed benzene ring unobservable, and the temperature dependent drifting of (particularly) the CpH absorptions, and could these phenomena be related to the mechanism of top-down fluxionality? A quantitative measure of the respective line widening was provided by a determination of the relaxation times of the H-signals in **E** ([D₈]toluene): Those of the CpH, δ = 3.98 ppm, 0.108 s, and arene signals, δ = 5.56 ppm, 0.05 s, are much shorter than those of the remainder (δ = 6.44 and 7.08 ppm, 0.997 and 2.309 s, respectively). That trace paramagnetic impurities were the cause of line broadening was made unlikely by executing the cold irradiation experiment of **1** in the presence of the radical trap 1,3-cyclohexadiene, which produced spectra identical to those recorded in its absence. The combined experimental data suggested the intervention

of a triplet state cobalt species, either per se, or accessed by thermal equilibration.^[10] A distinction can be made by Curie-like plots, in which chemical shifts are plotted as a function of temperature. A linear relationship pinpoints the presence of a triplet ground state, while curved behavior is indicative of a singlet-triplet equilibrium.^[10d,e,11] Indeed, for the three cases investigated, the latter was recorded (see Supporting Information). Not surprisingly,^[10c] ESR analysis failed to detect a signal. Similarly, in view of the small concentration of triplet (vide infra), magnetization of the solution was not detectable by the Evans method.

To aid in the formulation of a mechanism that reflects the preceding observations, DFT calculations were performed for the parent system (and **2**) at the BPW91 level of theory (Figure 5; for a complete appraisal, see Supporting Information), significantly augmenting and amending earlier computations.^[2] Thus, inspection of both the singlet and triplet path of haptotropism (Figure 5a) suggests that η^4 -species **b** (corresponding to **E**, **3**, or **6**; relative energy 11.3 kcal mol⁻¹), generated from ground state **d** (corresponding to **1**, **2**, or **5**; relative energy 0 kcal mol⁻¹) during low temperature irradiation, can be top-down fluxional via an η^2 -triplet intermediate (relative energy 15.6 kcal mol⁻¹) that is reached through minimum energy crossing point **CP1** (18.8 kcal mol⁻¹). The resulting barrier-

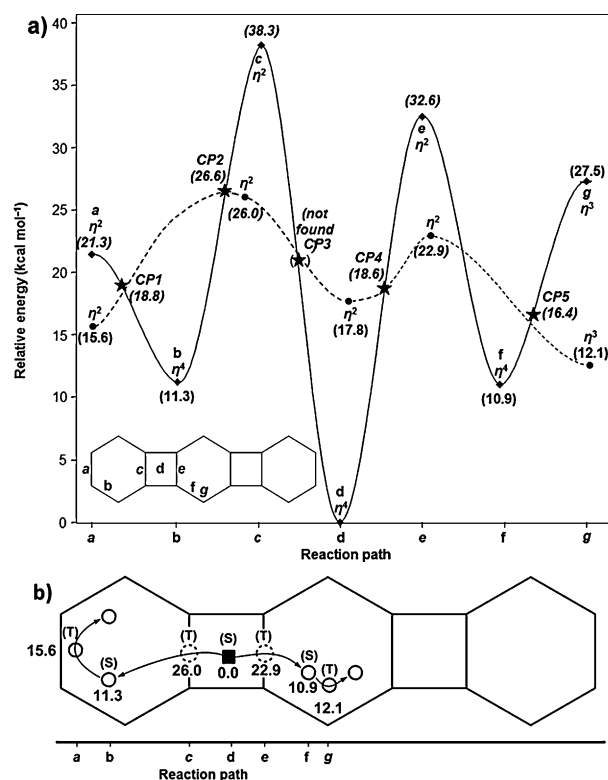


Figure 5. a) Singlet (straight line) and triplet trajectory (dashed line) of the CpCo moiety along the linear [3]phenylene scaffold. Energies (kcal mol⁻¹) are given relative to the ground state **d** = 0; minimum energy crossing points (CP) are indicated by stars; singlet transition state descriptors are in italics; (approximate) hapticity is described by η^n . b) Suggested lowest energy trajectory for the system exhibiting two-state reactivity [kcal mol⁻¹]; (S) = singlet, (T) = triplet; ○ = local minimum, dashed circle = transition state, ■ = ground state].

er of only 7.5 kcal mol⁻¹ is reflected in the absence of decoalescence of the NMR signals (attempted for **E**) at -80 °C. The symmetry-equivalent alternative, singlet transition state **a**, lies higher in energy. The intervention of triplet 16-electron CpCo species alternating with their singlet 16-electron counterparts, dubbed two-state reactivity,^[12] is also indicated computationally, and indeed mandated experimentally, for the remainder of the potential energy trajectory. Accordingly, the relatively facile shift of CpCo in **E**, **3**, and **6** to the neighboring cyclobutadiene at -30 to 0 °C is not compatible with the traversal over singlet transition state **c** (38.3 kcal mol⁻¹), but nicely accommodated by its triplet analogue (26.0 kcal mol⁻¹), preceded by **CP2** (26.6 kcal mol⁻¹), with a computed barrier of 15.3 kcal mol⁻¹. Similarly, a triplet transition state (22.9 kcal mol⁻¹), accessed via MECP **CP4** (18.6 kcal mol⁻¹), and a triplet species (12.1 kcal mol⁻¹) reached via **CP5** (16.4 kcal mol⁻¹) for intercyclobutadiene haptotropism are in good agreement with the measured barrier of 23.1 kcal mol⁻¹ for the **4** to **2** migration,^[2b] whereas singlet **e** (32.6 kcal mol⁻¹) and **g** (27.5 kcal mol⁻¹) are not. Figure 5b summarizes the suggested lowest energy trajectory.

In summary, irradiation causes the metal in linear phenylene CpCo complexes to “jump” to the terminal arene ring, from where it returns thermally in steps to its CpCo-cyclobutadiene ground state. This unprecedented behavior is not only intriguing fundamentally, but also provides stimulus for the design of organometallic functional materials exhibiting staged response cascades.^[4]

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Keywords: ab initio calculations · arene ligands · haptotropism · isomerization · photochemistry

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