

Notes

Diels–Alder Dimerization of Cyclopenta[*l*]phenanthrene (Dibenz[*e,g*]indene) with Isodibenzindene: A Computational, NMR Spectroscopic, and X-ray Crystallographic Study

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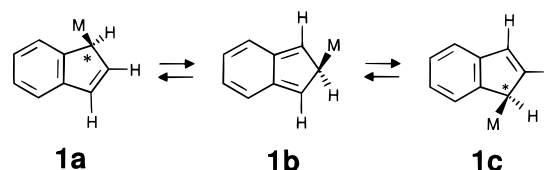
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Introduction

The ability of σ -bonded elements or molecular fragments to migrate over polyenyl organic moieties has been recognized for over two decades.¹ In the case of stereochemically nonrigid indenyl systems, the migratory pathway can be rationalized in terms of two successive [1,5]-sigmatropic shifts, which interconvert molecules **1a** and **1c**, according to the orbital symmetry rules defined by Woodward and Hoffmann (Scheme 1).² The observed increase in activation energies for such a fluxional process, on going from cyclopentadienyl to the corresponding indenyl system, is consistent with the intermediacy of the energetically less favorable isoidene structure, **1b**.³

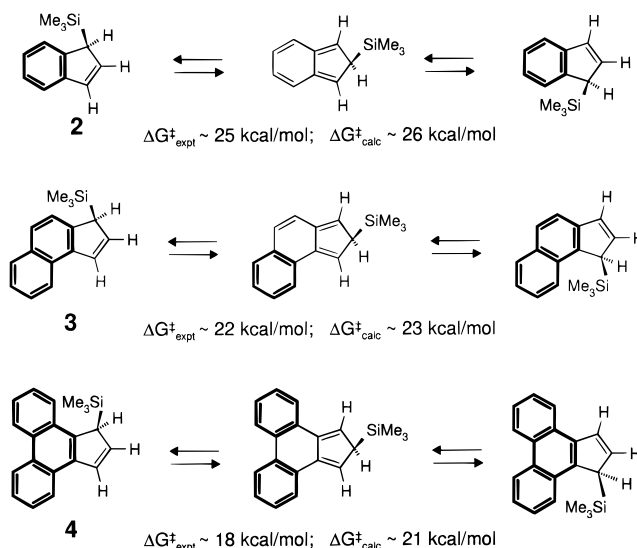
Notwithstanding the variety of *o*-xylylene complexes that have been generated, trapped, and characterized spectroscopically,⁴ transient isoidenes have proven much more difficult to isolate and characterize. The very limited reports of “free” isoidenes describe species which are usually generated photochemically, and which invariably incorporate tetrasubstitution designed to suppress any potential [1,5]-sigmatropic migrations.⁵ In fact, the

Scheme 1. [1,5]-Sigmatropic Shifts in Substituted Indenes



M = migrating fragment

Scheme 2. Barriers to Silatropic Shifts in a Series of Benzindenes



chemistry associated with these highly reactive molecules is dominated by the propensity of isoidenes to isomerize to their indene analogues, a process that is promoted by the tremendous gain in stability that results from the rearomatization of the six-membered ring. Inasmuch as isoidenes are synthetically attractive species, such isomerizations present a formidable obstacle to their use as reagents under standard experimental conditions. Moreover, the photochemical generation of isoidenes is often not feasible if other photochemically sensitive species are present. As a result, the formation of stable isoidenes under thermal, as opposed to photochemical, conditions remains an important synthetic goal.

Recent investigations concerning the barriers to silicon (Me_3Si) shifts about the periphery of indenyl rings have demonstrated that such migrations are facilitated by the strategic incorporation of fused aromatic rings in the system. Thus, as indicated in Scheme 2, the experimentally determined barriers for [1,5]-shifts decrease from ~ 25 kcal mol⁻¹ in (trimethylsilyl)indene, **2**,³ to ~ 22 kcal mol⁻¹ in the angular benzindene, **3**, and to ~ 18 kcal mol⁻¹ in the corresponding cyclopenta[*l*]phenanthrene (dibenzindene), **4**.⁶ In all cases, the intermediacy of transient isoidenes has been established by Diels–Alder trapping as the tetracyanoethylene adduct, as depicted in Scheme

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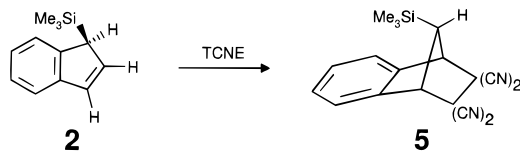
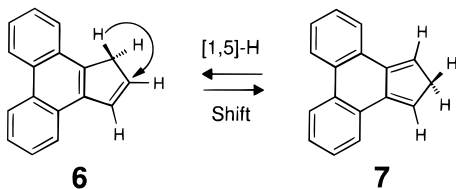
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Scheme 3. Diels–Alder Trapping of an Isoindene**Scheme 4. [1,5]-Hydrogen Shift in 6 To Give 7**

3; the TMS-indene/TCNE adduct, **5**, has been characterized by X-ray crystallography.⁷

The incremental reduction in the barrier to silatropic shifts observed in these systems has been rationalized in terms of the heightened aromatic character of the transition state in such benzannulated indenyl systems. Indeed, preliminary calculations at the semiempirical level indicated that the presence of two additional aromatic rings in the cyclopenta[1]phenanthrene derivative leads to a marked stabilization of the silylated high-energy isoindene.⁶

While cyclopenta[1]phenanthrene, **6**, has attracted recent interest as a ligand in the preparation of *ansa*-bridged metallocenes for the stereospecific polymerization of alkenes,⁸ investigations relating to its organometallic chemistry have been lacking. Given the versatility of the bonding modes available to **6**, and in continuation of our studies on the migration of organometallic fragments across polycyclic frameworks,⁹ we opted to explore the synthesis of various organometallic complexes of cyclopenta[1]phenanthrene. It was during our pursuit of such organometallic derivatives that we isolated and characterized **10**, a rare example of a thermally generated isoindene, **7**, trapped in situ by its precursor, **6**.

Results and Discussion

In an attempt to generate a tricarbonylchromium complex of cyclopenta[1]phenanthrene, **6**, the aforementioned compound was treated with $\text{Cr}(\text{CO})_6$ in dibutyl ether at 130 °C, yielding the partially hydrogenated complex **8** (see Scheme 5), which was characterized by X-ray crystallography,¹⁰ and whose formation is perhaps attributable to the presence of traces of moisture. Use of very carefully dried solvents did not lead to **8**, **9**, or any other organometallic complexes, but instead gave a 9% yield of an organic product, **10**, that was shown by mass spectrometry to be a dimer of **6**. Moreover, when

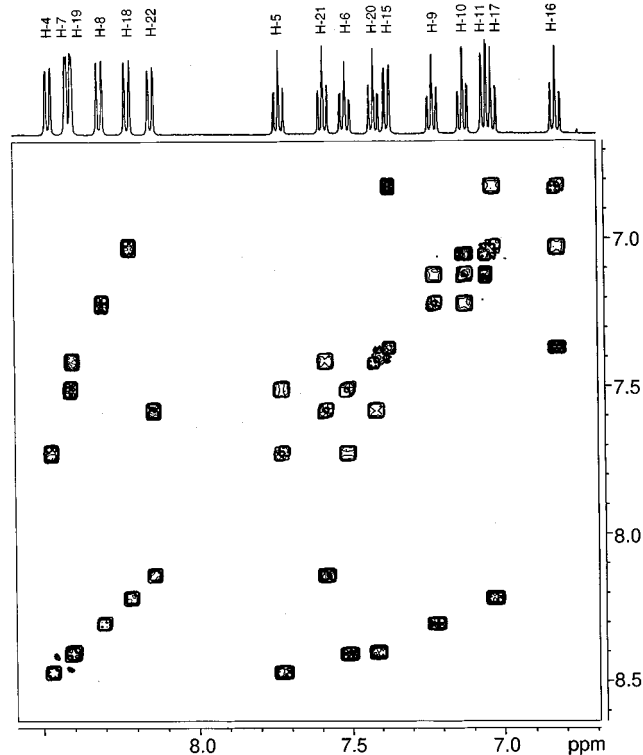
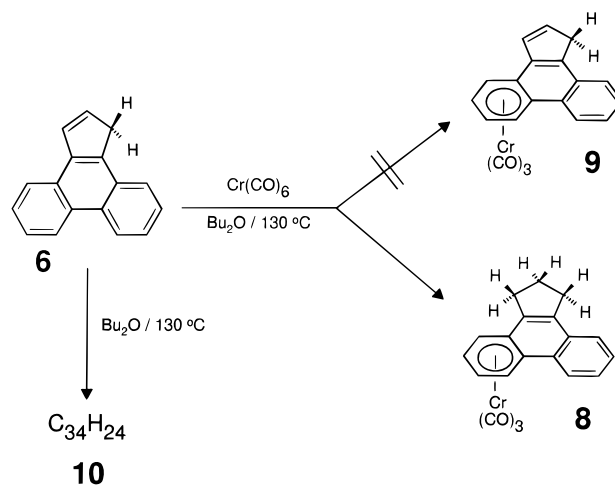


Figure 1. 500 MHz ^1H – ^1H COSY NMR spectrum of **10**, showing the aromatic proton region.

Scheme 5. Reaction of 6 with $\text{Cr}(\text{CO})_6$ 

6 was simply heated in dibutyl ether at 130 °C for 3 days, 85% conversion to **10** was realized, based on monomer consumed.

The identity of **10** was established by a combination of 1-D and 2-D NMR experiments. The 500 MHz ^1H NMR of **10** revealed the presence of four nonequivalent aromatic ring environments, as depicted in the ^1H – ^1H COSY spectrum shown in Figure 1. These data, together with the ^1H – ^{13}C shift-correlated spectrum, indicated that **10** was the Diels–Alder adduct of **6** with its own isoindene, **7**. Furthermore, NOE measurements within the central bicyclo[2.2.1] moiety paralleled those previously reported for dicyclopentadiene,¹¹ and suggested that

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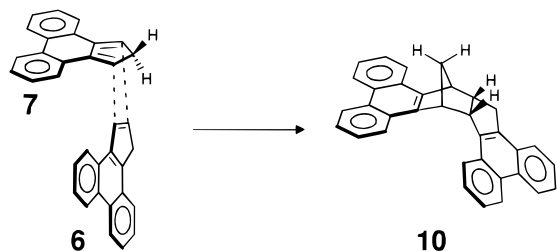
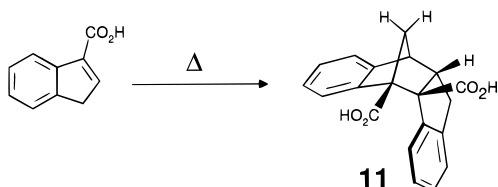
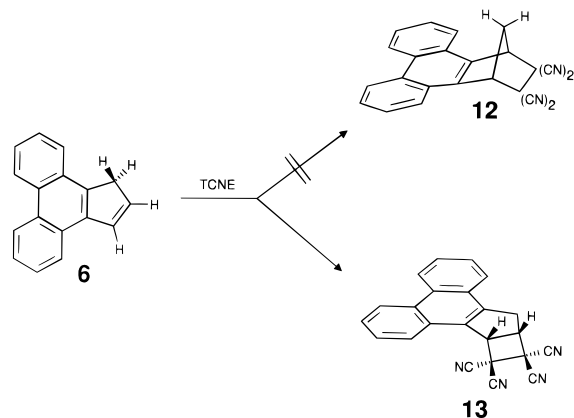
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Scheme 6. Diels–Alder Reaction of **6** with **7**Scheme 7. Dimerization Reaction of 1*H*-Indene-3-carboxylic Acid, Yielding **11**Scheme 8. Reaction of **6** with Tetracyanoethylene, Giving the [2 + 2] Cycloadduct, **13**

10 adopted the *endo* configuration, as depicted in Scheme 6. The complete ^1H and ^{13}C NMR assignments are summarized in Figure 2.

The solid-state structure of **10** was unequivocally determined by X-ray crystallography,¹² and views of the molecule appear in Figure 3; the *endo* nature of the dimer is evident. The molecular structure of **10** possesses no exceptional geometric features and parallels several other crystallographically characterized systems that contain the dicyclopentadiene core. These include the Diels–Alder complexes arising from the 2:1 adduct of dimethyl acetylenedicarboxylate with 4-azaazulene,¹³ the 1:1 adduct of 1-(diethylamino)propyne with azulene,¹⁴ and also the dimers of dimethylfulvene,¹⁵ and of (pentafluorophen-

(12) Crystal data: colorless, $0.1 \times 0.2 \times 0.2$ mm, triclinic, $P\bar{1}$; $a = 10.958(5)$ Å, $b = 13.537(5)$ Å, $c = 16.064(4)$ Å, $\alpha = 79.11(2)^\circ$, $\beta = 74.10(2)^\circ$, $\gamma = 81.35(1)^\circ$, $Z = 4$ with two independent molecules in the asymmetric unit. Data collection: Mo-K α , 12606 reflections collected, 5739 independent reflections, $R(\text{int}) = 0.0431$. Results of solution and refinement: data-to-parameter ratio = 9.3, residual electron density max/min 0.153/–0.151 e/Å³, goodness-of-fit on $F^2 = 0.995$, final R indices ($I > 2\sigma(I)$) $R1 = 0.0494$, $wR2 = 0.1056$. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. Further details of the crystal structure investigation, including the atomic coordinates, can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U. K.

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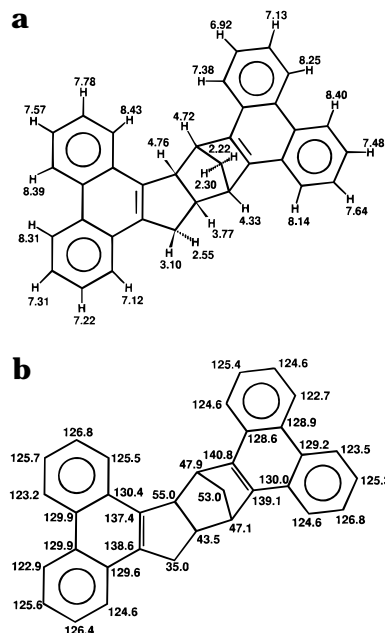


Figure 2. (a) ^1H NMR chemical shifts for **10**. (b) ^{13}C NMR chemical shifts for **10**.

yl)cyclopentadiene.¹⁶ It should be emphasized that none of these dimers resulted from the in situ trapping of an isoindene. However, we are cognizant of one report in which 1*H*-indene-3-carboxylic acid yields a Diels–Alder dimer, **11**, with its corresponding isoindene, under thermal conditions. Although **11** has apparently been characterized by X-ray crystallography,¹⁷ we are unaware of any published structural data on this molecule. Moreover, there is also a report of the Diels–Alder self-dimerization of 1,3-dimethylcyclopenta[*l*]phenanthren-2-one; again, no structural data are available.¹⁸

With the ever-increasing motivation to establish a link between the molecular basis of organic chemistry and the developments in crystal structure analysis,¹⁹ we chose to investigate the packing motif of the aromatic hydrocarbon, **10**, presented in Figure 4. When considered separately, each of the two molecules in the asymmetric unit packs such that the L-shaped molecular units interlock, giving rise to corrugated sheets. The two independent molecules are oriented relative to each other in such a fashion that the layers defined by the “dienophilic phenanthrene unit” of one molecule and the “isoindene phenanthrene unit” of the other are nearly orthogonal (93.7°).

In light of our previous success in the Diels–Alder trapping of (trimethylsilyl)isoindenes, attempts were made to intercept the isoindene, **7**, with tetracyanoethylene. However, treatment of **6** with TCNE did not yield **12**, the [4 + 2] Diels–Alder adduct of the isoindene, **7**, but instead reacted via a [2 + 2] cycloaddition to give **13**, whose identity was readily established by means of

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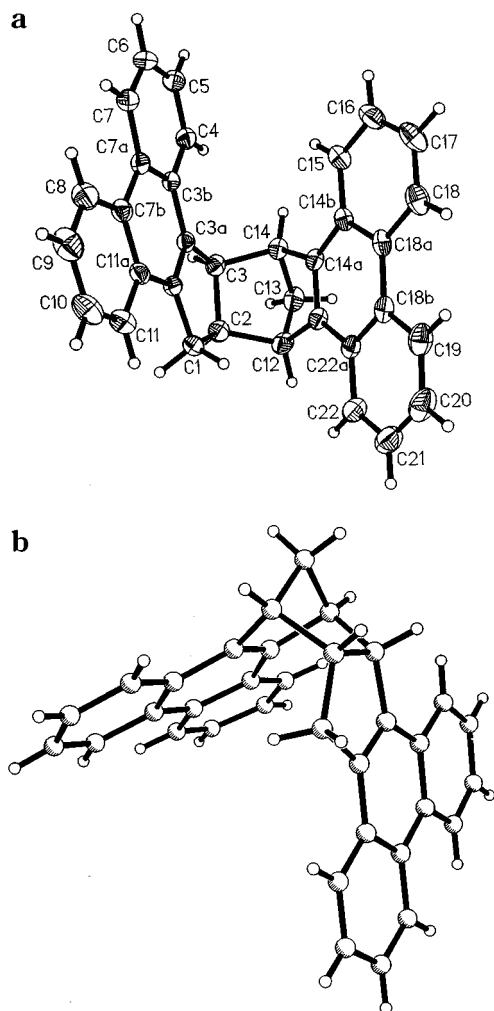


Figure 3. (a) The X-ray crystal structure of **10**, showing the atom numbering scheme. (b) Side view of **10**, emphasizing the *endo* structure.

^1H and ^{13}C NMR studies. This observation parallels the known [2 + 2] cycloaddition chemistry of indene with tetracyanoethylene.²⁰ We note that other excellent dienophiles, such as 4-phenyl-1,2,4-triazoline-3,5-dione,²¹ maleic anhydride,²² and dimethyl acetylenedicarboxylate (DMAD),²³ likewise undergo a variety of cycloaddition reactions with indene.

Encouraged by the correlation between the experimentally and computationally determined barriers to [1,5]-sigmatropic shifts, we proceeded to extend these calculations (at a higher level of theory) to encompass hydrogen migrations in the parent hydrocarbons. The results of optimizations carried out at the RHF level, using either the AM1 Hamiltonian or the 3-21G(*) basis set (semiempirical results provided in parentheses), reveal that a

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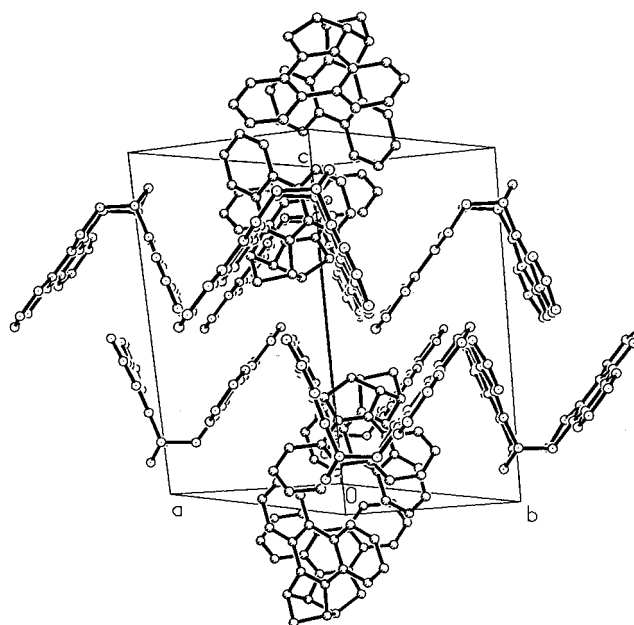


Figure 4. Crystal packing of **10** showing the layers of interlocking molecular units.

[1,5]-hydrogen shift in the nonsilylated starting material, cyclopenta[*h*]phenanthrene, **6**, proceeds via a calculated barrier of ~ 49.1 (42.1) kcal mol⁻¹ to yield the corresponding isoindene, **7**, which lies approximately 11.7 (5.6) kcal mol⁻¹ above the ground state of **6**. In comparison, the transition state for a [1,5]-hydrogen shift in indene, **1a** (M = H), lies ~ 58.3 (49.4) kcal mol⁻¹ above the energy of the starting configuration, while the isoindene intermediate, **1b**, is situated in a potential well 27.7 (18.1) kcal mol⁻¹ above the ground state. Consequently, one would expect that, under thermodynamic control, the equilibrium population of the isoindene intermediate in the dibenzindene system, **7**, would be markedly greater than in the nonsubstituted indene analogue, **1**, given the relative energies of these species. Furthermore, these data suggest that the intermediate isoindene, **7**, should be sufficiently long-lived for Diels–Alder trapping reactions to be competitive with a second [1,5]-hydrogen shift, which regenerates cyclopenta[*h*]phenanthrene, **6**. We can therefore rationalize the observed [2 + 2] cycloaddition between **6** and TCNE, rather than the [4 + 2] Diels–Alder reaction involving **7**, since the isomerization of **6** to **7** is strongly disfavored at ambient temperature.

To conclude, the ready generation and unequivocal characterization of the Diels–Alder dimer **10** is in accord with the RHF/3-21G(*) calculations, which suggest that the isoindene, **7**, is relatively stable; clearly it is sufficiently long-lived to be trapped by its progenitor. Our investigations into the synthetic utility of this stabilized isoindene and its derivatives will be the subject of future reports.

Experimental Section

General. All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware using solvents which were previously dried according to standard procedures. Tetracyanoethylene (Aldrich), *n*-butyl ether (Aldrich), and hexacarbonylchromium (Strem) were used without purification. Cyclopenta[*h*]phenanthrene, **6**, was prepared by Eliasson's

method.²⁴ Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario, Canada. Mass spectra (DEI) were obtained on a VG Analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10000. Infrared spectra were obtained by use of a Bio Rad FTS-40 FT-IR spectrometer and a SPC 3200 workstation using NaCl 0.1 mm solution cells. NMR spectra were acquired on a Bruker Avance DRX-500 spectrometer, equipped with an 11.74 T superconducting magnet. These experiments consisted of 1-D ¹H and ¹³C NMR spectra as well as 2-D ¹H–¹H COSY, 2-D ¹H–¹H NOESY, ¹H–¹³C shift-correlated and long range ¹H–¹³C shift-correlated spectra. Proton spectra were acquired at 500.13 MHz using a 5 mm broadband inverse probe with triple axis gradient capability. Carbon-13 NMR spectra were recorded at 125.76 MHz using the aforementioned probe. All NMR spectra were recorded on spinning samples (except during the acquisition of 2-D spectra), locked to a solvent signal. Peaks were referenced to a residual proton signal of the solvent, or to a ¹³C solvent signal.

X-ray crystallographic data for **10** were collected from a single-crystal sample, which was mounted in a 0.2 mm sealed glass capillary. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K Charge-Coupled Device (CCD) Area Detector (using the program SMART²⁵) and a rotating anode using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512×512 pixel mode, utilizing 2×2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 \AA resolution. Processing was carried out by use of the program SAINT,²⁶ which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS²⁷ was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct methods procedure in the Siemens SHELXTL program library,²⁸ and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the attached carbon.

Preparation of the Dimer of Cyclopenta[*l*]phenanthrene, **10.** This compound was first isolated in an attempt to synthesize (*n*⁶-cyclopenta[*l*]phenanthrene)Cr(CO)₃. A solution of carefully dried cyclopenta[*l*]phenanthrene (0.23 g, 1.07 mmol) and Cr(CO)₆ (0.24 g, 1.08 mmol) in 18 mL of *n*-Bu₂O and 2 mL of THF was heated under reflux for 3 days. The green solid was filtered off using Schlenk procedures. The solvent was removed in vacuo, leaving a green residue. Flash chromatography on silica using hexane/methylene chloride (2:1) gave starting ligand and **10** as a white solid (0.020 g, 0.046 mmol; 9%), mp 239–240 °C. Mass spectrum (DEI)⁺, *m/z* (%): 432 (10) ([M]⁺), 216 (100) ([M – 216]⁺). Anal. Calcd for C₃₄H₂₄: C, 94.40; H, 5.60. Found: C, 94.31; H, 5.76. ¹H NMR (CD₂Cl₂): δ 8.43 (d, 8.0 Hz, 1H) H-4, 8.40 (d, 8.3 Hz, 1H) H-19, 8.39 (d, 8.2 Hz, 1H) H-7, 8.31 (d, 8.3 Hz, 1H) H-8, 8.25 (d, 8.3 Hz, 1H) H-18, 8.14 (d, 8.0 Hz, 1H) H-22, 7.78 (tr, 7.6 Hz, 1H) H-5, 7.64 (tr, 7.3 Hz, 1H) H-21, 7.57 (tr, 7.3 Hz, 1H) H-6, 7.48 (tr, 7.2 Hz, 1H) H-20, 7.38 (d, 8.0 Hz, 1H) H-15, 7.31 (tr, 7.1 Hz, 1H) H-9, 7.22 (tr, 7.4 Hz, 1H) H-10, 7.13 (tr, 7.1 Hz, 1H) H-17, 7.12 (d, 7.4 Hz, 1H) H-11,

6.92 (tr, 7.5 Hz, 1H) H-16, 4.76 (d, 8.7 Hz, 1H) H-3, 4.72 (s, 1H) H-14, 4.33 (d, 3.5 Hz, 1H) H-12, 3.77 (m, 1H) H-2, 3.10 (d, 16.9 Hz of d, 10.1 Hz, 1H) H-1a, 2.55 (d, 16.6 Hz, 1H) H-1b, 2.30 (d, 8.1 Hz, 1H) H-13a, 2.22 (d, 8.1 Hz of d, 1.6 Hz, 1H) H-13b. ¹³C NMR (CD₂Cl₂): δ 140.8 C-14a, 139.1 C-22b, 138.6 C-11b, 137.4 C-3a, 130.4 C-3b, 130.0 C-22a, 129.9 C-7b, 129.6 C-11a, 129.2 C-18b, 128.9 C-18a, 128.6 C-14b, 126.8 C-21, C-5, 126.4 C-10, 125.7 C-6, 125.6 C-9, 125.5 C-4, 125.4 C-16, 125.3 C-20, 124.8 C-17, 124.6 C-15, C-22, C-11, 123.5 C-19, 123.2 C-7, 122.9 C-8, 122.7 C-18a, 55.0 C-3, 53.0 C-13, 47.9 C-14, 47.1 C-12, 43.5 C-2, 35.0 C-1. The dimer, **10**, was also prepared by refluxing a solution of cyclopenta[*l*]phenanthrene (0.100 g, 0.463 mmol) in 30 mL of *n*-Bu₂O for 3 days. After removal of the solvent, ¹H NMR of the crude product revealed it to be about 1:1 ligand to dimer. The dimer was separated from the ligand using a chromatotron, with hexane as eluent, yielding unreacted **6** (0.051 g, 0.236 mmol) and **10** (0.042 g, 0.097 mmol; 42%). The product, **10**, was recrystallized from acetone/heptane to give clear colorless prismatic crystals, suitable for single-crystal X-ray diffraction studies.

Preparation of Cyclopenta[*l*]phenanthrene–TCNE adduct, **13.** To a stirred solution of cyclopenta[*l*]phenanthrene (0.033 g, 0.153 mmol) in 25 mL of dry tetrahydrofuran was added tetracyanoethylene (0.078 g, 0.609 mmol). The solution immediately turned very deep purple. Stirring was continued for 1 week. Removal of the solvent under vacuum, followed by flash chromatography, using methylene chloride as eluent, yielded **13** as a light pink solid (0.045 g, 0.131 mmol; 86%), mp (with decomposition) 197–198 °C. Mass spectrum (DEI)⁺, *m/z* (%): 344 (30) ([M]⁺), 216 (100) ([C₁₇H₁₂]⁺). Mass spectrum (high resolution, DEI): calculated for mass ¹²C₂₁H₁₂N₄ ([M]⁺), 334.1062 amu; observed 344.1059 amu. ¹H NMR (THF-*d*₆): δ 8.87–8.84 (m, 2H) H-8, H-7, 8.01 (d, 1.0 Hz of d, 7.9 Hz, 1H) H-4, 7.83–7.80 (m, 1H) H-11, 7.78–7.75 (m, 1H) H-6, 7.74–7.69 (m, 3H) H-5, H-9, H-10, 5.42 (d, 1.6 Hz of d, 8.2 Hz, 1H) H-3, 4.46 (d, 2.3 Hz of tr, 8.5 Hz, 1H) H-2, 4.02 (d, –18.2 Hz of d, 2.3 Hz of d, 1.6 Hz, 1H) H-1, 3.92 (d, –18.2 Hz of d, 8.8 Hz, 1H) H-1'. ¹³C NMR (THF-*d*₆): δ 140.9 C-3a, C-11b, 133.0 C-7a, 132.2 C-7b, 131.5 C-11a, 129.5 C-3b (C-11a and C-3b may be interchanged), 128.9 C-6, 128.3 C-5, 128.2 C-10 (C-5 and C-10 may be interchanged), 128.0 C-9, 126.7 C-4, 125.7 C-11, 124.6 C-7, 124.5 C-8 (C-7 and C-8 may be interchanged), 113.0, 113.1, 110.6, 110.3, CN's, 54.7 C-3, 45.4 C-2, 41.3 C-12, C-13, 37.5 C-1.

Computational Details. The geometry optimization (without constraints) of all systems was conducted at the restricted Hartree–Fock level, utilizing both the AM1 Hamiltonian²⁹ and the 3-21G(*) basis set available in the Spartan computational package (AM1 results provided in parentheses).³⁰ All transition states connecting the indene analogues to their respective isoindene structures exhibited one imaginary frequency corresponding to the anticipated molecular motion along the particular reaction coordinate ($\nu = -1577.41$ (–1756.15) and –1588.26 (–1766.31) cm^{–1} for **6** to **7** and **1a** to **1b**, respectively). The calculated H–C(1) and H–C(2) bond distances for the transition state relating to a [1,5]-hydrogen shift in **6** to give **7** were 1.367 (1.411) and 1.306 (1.380) \AA , respectively, significantly longer than the value of 1.086 \AA determined for **6**; the C(1)–C(2) bond length in the transition state was 1.491 (1.490) \AA , and the H–C(2)–C(1) bond angle was 58.1 (58.7)°. In the transition state for the rearrangement of **1a** to **1b** (where M = H), the calculated distances and angles were found to be: H–C(1) 1.411 (1.448) \AA , H–C(2) 1.275 (1.347) \AA , C(1)–C(2) 1.494 (1.490) \AA and H–C(2)–C(1) 60.7 (61.1)°.

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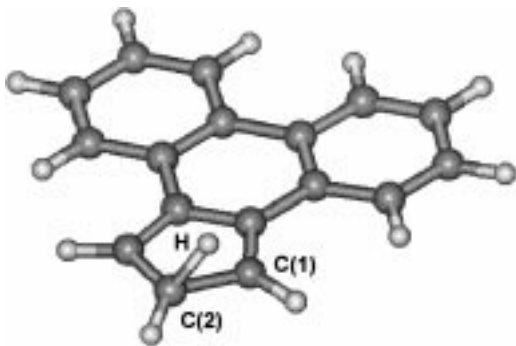
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Supporting Information Available: Optimized geometrical structures in Cartesian coordinates for all stationary points, calculated at the HF/3-21G(*) level for **10** (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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