Face-to-Face Cyclopentadienes. Reaction Path for the Conversion of 1,8-Bis(cyclopentadienyl)naphthalene to Its Diels–Alder Adduct

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The reaction of cyclopentadienylcopper dimethyl sulfide with 1,8-diiodonaphthalene provides a method for coupling cyclopentadienyl groups to the naphthalene nucleus. The product formed by coupling of two such groups in *peri* positions on the naphthalene ring is the Diels–Alder adduct 3. Deuterium labeling experiments have been carried out which show that this product is formed through conversion of the initial 1-iodo-8-(5-cyclopentadienyl)naphthalene (9) to 1,8-di(5-cyclopentadienyl)-naphthalene (10). This, in turn, undergoes a single sigmatropic [1.5] hydrogen shift to give 1-(1-cyclopentadienyl)-8-(5-cyclopentadienyl)naphthalene (11), which collapses to the Diels–Alder adduct 3.

Some years ago we undertook the synthesis of systems in which two cyclopentadiene rings would be constrained to a face-to-face orientation as shown in **A**. Our interest

A   **B**
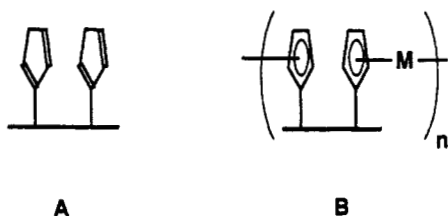
in such systems derived in large measure from their potential use as precursors to metallocene polymers with the structure depicted in **B**.[1] π-Interactions of the form inherent in **A** and **B** play a central role in defining the physical and chemical properties of cyclophanes[2] and are an important element in the design of chiral recognition in chiral solid-phase liquid chromatography[3] as well as in the complexation of neutral molecules in cyclophane hosts.[4] To the best of our knowledge, the chemistry of cyclopentadienes constrained as in **A** had not been examined, and while a number of polymers incorporating metallocenes are known,[5] none of the type exemplified by **B** had been prepared. The present paper provides an account of the preparation of 1,8-dicyclopentadienylnaphthalene and of its reactions.[6]

Several synthetic routes to this substance were initially examined, among them palladium-mediated coupling[7] of cyclopentadienyltrimethyltin[8] and cyclopentadienylzinc[9] with 1,8-diiodonaphthalene. These reactions failed to give any of the desired product but led instead to the homocoupled products, among them perylene. An attempt

Scheme I
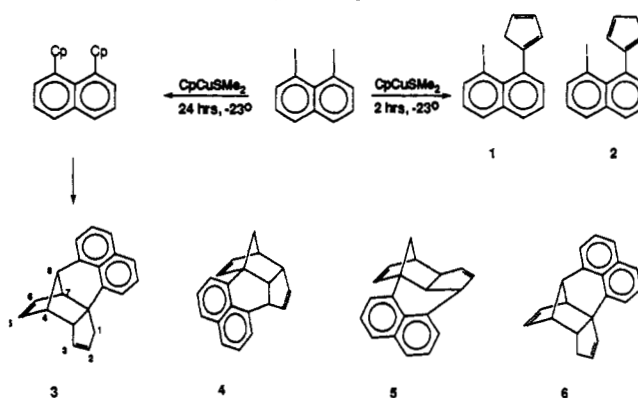
to effect the coupling of the bis-halozinc reagent derived from 1,8-diiodonaphthalene with 1-acetoxydicyclopentadiene, based upon earlier reactions of this type,[10] also failed to yield any cross-coupling product. We turned next to an examination of copper-mediated coupling reactions, especially since Nilsson, Wahren, and Wennerstrom[11] have reported the preparation of several arylcyclopentadienes by coupling of cyclopentadienylcopper tris(tri-*n*-butyl-phosphine) with aryl iodides. We found that reaction of this complex with diiodonaphthalene gave a mixture of 1-iodo-8-(1-cyclopentadienyl)naphthalene (1) and 1-iodo-8-(2-cyclopentadienyl)naphthalene (2) in low yield. In none of the several attempts to force the reaction beyond this stage by prolonged reaction and use of excess copper reagent was any of the desired dicyclopentadienylnaph-thalene formed. However, the more easily prepared and more reactive cyclopentadienylcopper–dimethyl sulfide complex prepared from cyclopentadienyllithium and copper bromide–dimethyl sulfide complex gave a mixture of 1 and 2 after brief reaction at −22 °C, while overnight reaction gave the Diels–Alder adduct 3 of the desired dicyclopentadienylnaphthalene in 39% yield. The assignment of structure to this product rests on proton homonuclear decoupling, COSY, and HETCOR experiments together with a careful comparison of its proton NMR spectrum with the spectra of *exo-* and *endo-*

(1) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, 3, 539.

(2) *Cyclophanes*; Keehn, P. M.; Rosenfield, S. M., Ed.; Academic Press: New York, 1983; Vols. 1 and 2.

(3) Pirkle, W. H.; Hyun, M. H.; Bank, B. *J. Chromatogr.* **1984**, 316, 585.

(4) Diederich, F. *Angew. Chem.* **1988**, 100, 362.

(5) Neuse, E. W.; Rosenberg, H. *Metallocene Polymers*; Dekker: New York, 1970.

(6) A brief account of part of this work has been given earlier. Gronbeck, D. A.; Matchett, S. A.; Rosenblum, M. *Tetrahedron Lett.* **1989**, 30, 2881–2884.

(7) Negishi, E. I.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, 42, 1821. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 508.

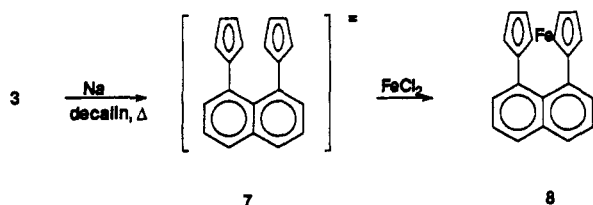(8) Lyle, M. A.; Stobart, S. R. *Inorg. Syntheses* **1977**, 17, 178.

(9) Fischer, E. O.; Hofmann, H. P.; Treiber, A. *Z. Naturforschg.* **1959**, 14b, 599.

(10) Fiaud, J.-C.; Aribi-Zouioueche, L. *J. Organomet. Chem.* **1985**, 295, 383. Yokoyama, Y.; Ito, S.; Takahashi, Y.; Murakami, Y. *Tetrahedron Lett.* **1985**, 26, 6457.

(11) Nilsson, M.; Wahren, R.; Wennerstrom, O. *Tetrahedron Lett.* **1970**, 4583.

dicyclopentadiene and derivatives of these.[12] Of the alternative Diels–Alder adducts, the more highly strained structure 4 and its *exo* analog 5[13] may be excluded since the product shows only one proton (δ 3.25) at C-8 coupled to bridgehead protons at C-4 and C-7. Furthermore, the presence of two resonances at δ 2.12 and δ 3.17 ($J_{gem} = 18$ Hz), which can readily be assigned to C-1 *endo*- and *exo*-methylene protons, respectively, in the dicyclopentadiene nucleus, also serves to exclude structures 4 and 5. Finally, the methylene protons at C-1 also exhibit typical long-range coupling to the ring juncture methylene proton at C-3a, thus excluding structure 6 for the adduct.

Several attempts were made to promote a retro-Diels–Alder reaction in 3 through proton abstraction. Cyclo-reversion reactions in norbornadiene and in several dicyclopentadiene derivatives have been observed to be greatly accelerated in the presence of strong base, owing to the formation of the cyclopentadienyl anion in the reversion process.[14] We anticipated that similar reaction of 3 would provide a route to the mono- or dianion of 1,8-dicyclopentadienylnaphthalene. However, attempts to effect this reaction by treatment of 3 with LDA, lithium tetramethylpiperidide, or potassium hydride were unsuccessful.[15] Nevertheless, when 3 was heated in refluxing decalin containing an excess of sodium hydride, the dianion 7 was formed, as evidenced by the isolation of the naphthylidene-bridged ferrocene 8 and small amounts of oligomeric product when these solutions were treated with ferrous chloride.

Figure 1. Molecular structure of 8: (a) view normal to naphthalene plane and (b) "edge-on" view showing splay of Cp rings.

Scheme II

The structural assignment for this compound is supported by its ¹H and ¹³C NMR spectra and was confirmed by an X-ray crystal structure determination.[16] In the solid state, the molecule is highly symmetric (Figure 1), with the two cyclopentadienyl rings very nearly orthogonal to the naphthalene ring (deviations $\approx 6.5°$ from 90°). Out-of-plane distortions of the naphthalene ring are $\leq 0.040(2)$ Å. The Fe–C distances vary from 1.986 to 2.056(2) Å. The shortest distances (1.986, 1.987 Å) correspond to the Fe–C_{ipso} bonds and compare well with those reported for 1,1′-tetramethylethyleneferrocene.[17] These distances are among
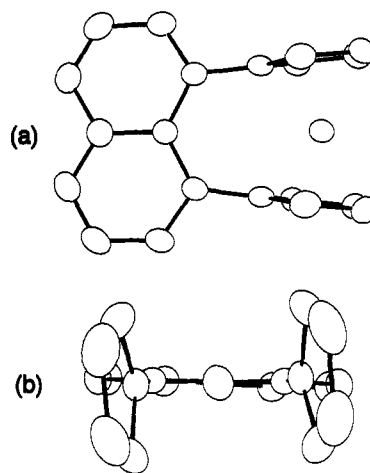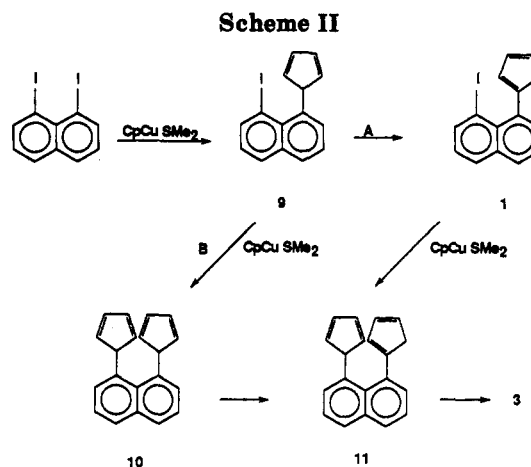
the shortest reported for bridged ferrocene systems. The C_{ipso}–C_{ipso} distances are 2.70 Å in the two-carbon-bridged 1,1′-tetramethylethyleneferrocene, 2.93 Å in 8, and 3.10 Å in α-oxo-1,1′-trimethyleneferrocene. The splaying angle of the cyclopentadienyl rings (13.8°) is somewhat larger than analogous distortions observed in three-carbon-bridged ferrocenes such as α-oxo-1,1′-trimethylenefer-rocene[18] (8.8°), α-oxo-α'-phenyl-1,1′-trimethylenefer-rocene[19] (10°), α-phenyl-α'-(2-hydroxypropyl)ferrocene[20] (10°), and 1,1′-(1″,3″-cyclopentanediyl)ferrocene[21] (11°). The angle is considerably less than that observed for 1,1′-tetramethylethyleneferrocene (28°).[17]

We consider lastly the mechanism by which 3 is formed. The formation of this compound as the sole Diels–Alder product of the coupling reactions requires in turn that its immediate precursor be the dicyclopentadienylnaphtha-lene (11). Two general paths (A, B), which provide plausible routes to 11, are depicted in Scheme II. In the first, a [1.5] sigmatropic shift in the initial coupling product 9 precedes introduction of the second cyclopentadienyl ring to yield 1 and then 11, while in the second pathway

(12) Sergeyev, N. M.; Avramenko, G. I.; Korenevsky, V. A.; Ustynyuk, Yu. A. *Org. Magn. Reson.* 1972, *4*, 1972. Foster, R. G.; McIvor, M. C. *J. Chem. Soc. B* 1969, 188.

(13) MM2 calculations (Serena Software, 489 Serena Lane, Bloomington, IN) yield values of bond angle bending strain associated with the aryl-ring bond of 69.2 and 56.8 kcal/mol, respectively, for 4 and 5.

(14) Finnegan, R. A.; McNees, R. N. *J. Org. Chem.* 1964, *29*, 3234. Blumel, J.; Kohler, F. H. *J. Organomet. Chem.* 1988, *340*, 303. Neukam, W.; Grimme, W. *Tetrahedron Lett.* 1978, 2201.

(15) We thank Dr. L. Barinelli for carrying out these experiments.

(16) Crystals of 8 are triclinic, space group $P\bar{1}$, $a = 7.609(1)$ Å, $b = 9.759(2)$ Å, $c = 10.046(2)$ Å; $\alpha = 73.31(2)°$, $\beta = 75.19(2)°$, $\gamma = 72.72(2)°$; $Z = 2$. Data were collected to a maximum $2\theta(\lambda_{MoK\alpha}) = 55°$. Full-matrix least-squares refinement of positional and anisotropic displacement parameters for all atoms (isotropic for fixed H atoms, total parameters = 190) led to $R = 0.028$ and $R_w = 0.038$, using 2731 data for which $I > 196\sigma(I)$. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(17) Laing, M. B.; Trueblood, K. N. *Acta Crystallogr.* 1965, *19*, 373.

(18) Jones, N. D.; Marsh, R. E.; Richards, J. H. *Acta Crystallogr.* 1965, *19*, 330.

(19) Lecomke, P. C.; Dusausoy, Y.; Protas, J.; Moise, C.; Tirouflet, J. *Acta Crystallogr., Sect. B* 1973, *B29*, 488.

(20) Lecomke, P. C.; Dusausoy, Y.; Protas, J.; Moise, C. *Acta Crystallogr., Sect. B* 1973, *B29*, 1127.

(21) Batail, P.; Grandjean, D.; Astruc, D.; Dubard, R. *J. Organomet. Chem.* 1975, *102*, 79.

these events are reversed. Neither of these mechanisms can be excluded on *a priori* grounds, since the rate of replacement of the first iodo substituent in 1,8-diiodonaphthalene is observed to be significantly greater than the substitution of the second. The very great difference observed in these rates can be accounted for in mechanism B by the increased steric crowding anticipated in the conversion of 9 to the highly crowded intermediate 10. This intermediate is sterochemically incapable of undergoing a Diels–Alder reaction, since the product would be very highly strained. The alternative reaction path A presupposes that this second coupling step is preceded by conversion of 9 to 1.[22] This mechanism would also require that a further sigmatropic shift in 1 be slower than the second coupling step. Some evidence on this latter point has been provided by McLean and Haynes, who have reported that thermal conversion of 5-methylcyclopentadiene to 1-methylcyclopentadiene was considerably faster than the conversion of the latter product to 2-methylcyclopentadiene.[23]

In order to distinguish between these mechanisms, two reactions were carried out. In the first, 1,8-diiodonaphthalene was converted at −23° to 1-iodo-8-(5-cyclopentadienyl)naphthalene (9) by treatment with cyclopentadienylcopper–dimethyl sulfide. At the end of 3 h, analysis of the reaction mixture showed that 1,8-diiodonaphthalene was completely consumed. At this point, an equivalent amount of perdeuteriocyclopentadienylcopper–dimethyl sulfide, prepared from perdeuteriocyclopentadiene[24] (>90% C5D6), was added to the reaction mixture, and the reaction was continued at −23 °C for an additional 18 h. The product dicyclopentadiene 3 was then isolated.[25] In a second experiment these steps were precisely reversed. The proton distribution in the dicyclopentadiene products derived from each of these reactions was determined by measuring the ratio of integrated resonances for H-2, H-3 protons (δ 5.33; 5.63) to H-5, H-6 protons (δ 6.27; 6.33). The product from the first experiment gave a ratio of 1.7 ± 0.1 for these resonances, while that from the second yielded a value of 1.8 ± 0.1. That little if any proton or deuterium exchange has taken place between the two cyclopentadienyl rings in the intermediates 10 or 11 is seen in the integrated ratios of H-2 to H-3 and H-5 to H-6 protons in the product 3, which are both unity in each of the above experiments.

These results clearly exclude mechanism A but are consistent with path B, since they require a reaction path in which, at some point, both labeled and unlabeled cyclopentadienyl groups become structurally equivalent. Additionally, the experimental results provide a value of 1.75 ± 0.1 for the ratio of k_h/k_d in the rearrangement of

half-labeled 10 to 11. This value is significantly smaller than the kinetic isotope ratio of 5.75 (27°) found for the sigmatropic shift in 5-methylcyclopentadiene,[26] but it is difficult to directly compare these figures since the rearrangement of 10 to 11 must take place over a temperature range of −23 °C to room temperature. Moreover, a lower value for the deuterium isotope effect in the rearrangement of 10 is to be expected, owing to the greater difference in partial bond strengths of the C⋯H⋯C′ bonds in the transition state for this reaction, compared with that in the conversion of 5-methylcyclopentadiene to 1-methylcyclopentadiene.[27]

The fact that 10 is formed in the coupling of cyclopentadienylcopper with 1,8-diiodonaphthalene exposes the possibility of trapping this intermediate as either the mono- or biscyclopentadienide. Consequently, it may be possible to use these salts as starting materials for the preparation of organometallic polymers. Experiments, designed to test this prospect, are currently in progress.

Experimental Section

General. Reactions were carried out using standard Schlenk techniques under an argon atmosphere. ^{1}H and ^{13}C NMR spectra, as well as COSY and HETCOR 2-D NMR spectra, were recorded on a Varian XL-300 FT NMR spectrometer and were referenced to internal tetramethylsilane. UV–vis spectra were recorded on a Perkin-Elmer PE 323 UV–vis spectrophotometer.

HPLC analyses were done using a system incorporating a Waters Model 410 automated gradient controller, two Model 510 pumps, a Model U6-K injector, and either a Model 440 UV detector with a Hewlett-Packard Model 3390A integrator or a Waters Model 401 refractive index detector with a 10-mV chart recorder. The column used was a Waters μ-Porasil column.

Low-resolution mass spectra were obtained on a Hewlett-Packard HP Model 5985 B GC-MS. Elemental analyses were performed by Desert Analytics Inc. in Tucson, AZ.

1,8-Diiodonaphthalene was prepared by the method of House et al.[28] from commercially available 1,8-diaminonaphthalene,[29] after purification by distillation from zinc powder. The product was obtained in 21% yield as light brown crystals, mp 108–109.5 °C (lit.[28] mp 110 °C).

Iodocopper tri-*n*-butylphosphine tetramer was prepared by the method described by Kauffman and Teter.[30] The crude product was recrystallized twice from a 1.5:1 mixture of ethanol and 2-propanol to give the desired product in 77% yield as a white crystalline solid, mp 74–75 °C (lit.[31] mp 75 °C).

1-Cyclopentadienyl-8-iodonaphthalene (1 and 2). Use of CpCu·P(C$_4$H$_9$)$_3$.[32] A 100-mL round-bottom flask, equipped with a fritted glass filter sidearm terminating in a male ground glass joint, was fitted with a 100-mL Schlenk sidearm Kjeldahl flask. The apparatus was flame dried *in vacuo*, purged with argon, and charged with cyclopentadienylthallium (937 mg, 3.48 mmol). After being purged with argon, the CpTl was slurried in 10 mL of dry ether, while a solution of [ICuP(C$_4$H$_9$)$_3$]$_4$ (1.364 g, 0.869 mmol) in 10 mL of ether was added by cannula. Immediately, an orange precipitate was observed to form. After being stirred for 30 min the milky greenish-white solution was filtered from the solid orange TlI into the Kjeldahl flask by slowly inverting the glassware. The filter sidearm flask was then removed, and the Kjeldahl flask and its contents were cooled to −23 °C. A solution of diiodonaphthalene (422 mg, 1.11 mmol) in 10 mL of ether was added to the solution of the copper complex by cannula. Within

(22) The rates of sigmatropic shift in cyclopentadiene (Roth, W. R. *Tetrahedron Lett.* **1964**, 1009) and in 5-methylcyclopentadiene[23] would appear to preclude a sufficiently rapid sigmatropic shift in 9 at −23 °C for the reaction to be complete within 24 h, but the effect of steric compression in 9 in accelerating its rate of conversion to the less sterically compressed intermediate 1 cannot be excluded. For some references to steric compression effects on reactivity, see: *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956. Hart, H.; Oku, A. *J. Org. Chem.* **1972**, *37*, 4269, 4274. Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977** 3143. DeTar, D. F. *J. Am. Chem. Soc.* **1974**, *96*, 1255.

(23) McLean, S.; Haynes, P. *Tetrahedron Lett.* **1964**, 2385. In addition, the steric compression present in 9 is reduced in 1 and would be expected to further increase the difference in rates of sigmatropic shift for these compounds. Greenberg, A.; Lieberman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

(24) Lambert, Y. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 1954.

(25) The only other characterized products of the reaction sequence were perylene and 1-iodonaphthalene.

(26) McClean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.

(27) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

(28) House, H. O.; Koepsel, D. G.; Campbell, W. *J. Org. Chem.* **1972**, *37*, 1003.

(29) Aldrich Chemical Company, Milwaukee, WI.

(30) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

(31) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 135.

(32) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 5114.

30 min the solution had become maroon-red in color. The reaction temperature was maintained at –23 °C for 24 h and then at –15 °C for an additional 24 h. The reaction mixture was worked up by filtering through a Sep-pak silica cartridge (to remove residue TlI), followed by removal of the solvent in vacuo. The crude residue was extracted with hexane, and the extracts were concentrated and purified by preparative TLC (silica/hexane). Three major bands were isolated: The first with R_f = 0.49 was found to be 1-iodonaphthalene; that with R_f = 0.21 was found to be perylene. The band with R_f = 0.34 proved to contain the desired product 1 and 2 (50 mg, 14%), isolated as a light yellow oil: ^{1}H NMR (CDCl$_3$) δ 3.10–3.17 (m, 2H, Cp methylene), 6.30–6.70 (m, 3H, Cp olefinic H's), 7.06–7.13 (dd, 1H, ^3J = 8.1 Hz, ^3J = 7.3 Hz, H$_6$), 7.40–7.44 (d, 1H, ^3J = 5.5 Hz, H$_4$), 7.42–7.44 (d, 1H, ^3J = 4.1 Hz, H$_2$), 7.76–7.82 (dd, 1H, ^3J = 5.5 Hz, ^3J = 4.1 Hz, H$_3$), 7.85–7.96 (dd, 1H, ^3J = 8.1 Hz, ^4J = 1.3 Hz, H$_5$), 8.19–8.22 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.3 Hz, H$_7$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 48.83 (Cp methylene), 92.23 (C$_8$), 125.07 (C$_2$), 126.35 (C$_6$), 128.75 (C$_3$), 129.59 (C$_5$), 129.72 (C$_4$), 132.09 (ipso), 132.40 (ipso), 132.67 (ipso), 133.39 (two degenerate olefinic Cp), 134.34 (olefinic Cp), 135.34 (ipso Cp), 141.70 (C$_7$); mass spectrum m/e 318 (C$_{15}$H$_{11}$I, M$^+$), 241 (C$_9$H$_6$I), 228 (C$_8$H$_5$I), 215 (C$_7$H$_4$I), 191 (C$_{15}$H$_{11}$, base peak), 165 (C$_{13}$H$_9$), 152 (C$_{12}$H$_8$).

1-Cyclopentadienyl-8-iodonaphthalene (1 and 2). Use of CpCu·SMe$_2$. To a flame-dried 50-mL Schlenk sidearm Kjeldahl flask was added freshly cracked cyclopentadiene (0.46 mL, 5.59 mmol), followed by 10 mL of dry THF. The solution was cooled to 0 °C, and a 2.5 M solution of n-butyllithium in hexanes (1.49 mL, 3.73 mmol) was added dropwise under argon and stirred for 1 h. Meanwhile, a flame-dried 100-mL Schlenk sidearm Kjeldahl flask was charged with copper(I) bromide–dimethyl sulfide complex (766 mg, 3.73 mmol) and purged with argon. The complex was then suspended in 10 mL of dry THF and stirred for 30 min. The resulting milky white suspension was subsequently cooled to –23 °C, and the solution of cyclopentadienyllithium, precooled to –78 °C, was added by cannula. The resulting solution was stirred for 1 h at –23 °C. A solution of diiodonaphthalene (1.042 g, 2.74 mmol) in 6 mL of dry THF was cooled to –78 °C and added to the solution of the copper complex by cannula. The reaction was allowed to continue for 2 h and was then quenched by pouring into saturated aqueous ammonium chloride. The solution was extracted with ether, and the ether was removed. The residue was then extracted with hexane. The hexane extracts were concentrated to a volume of approximately 20 mL and were flash chromatographed on silica (hexane eluent) to give 339 mg (39%) of a mixture of 1 and 2 as a light yellow oil. This product was contaminated with small amounts of diiodonaphthalene and 3.

1,8-(3a,4,7,7a-Tetrahydro-4,7-methanoindene-7a,8a-diyl)-naphthalene (3). To a flame-dried 50-mL Schlenk flask was added 10 mL of dry, degassed THF and freshly cracked cyclopentadiene (0.19 mL, 2.3 mmol) under argon atmosphere. The solution was cooled to 0 °C and n-butyllithium (0.92 mL, 2.3 mmol of a 2.5 M solution in hexanes) was added by syringe. The resulting solution of cyclopentadienyllithium was stirred for 1 h at 0 °C. A flame-dried 100-mL Schlenk flask was charged with copper(I) bromide–dimethyl sulfide complex (473 mg, 2.30 mmol), and to this was added 10 mL of dry, degassed THF. The suspension was cooled to –78 °C, and the solution of CpLi, cooled to –78 °C, was added to it by cannula. The resulting mixture was allowed to warm to –23 °C and was stirred for 1 h. A solution of diiodonaphthalene (219 mg, 0.575 mmol) in THF was cooled to –78 °C and then added by cannula to the solution of CpCu·SMe$_2$ to give a reddish-orange colored solution, which was stirred overnight at –23 °C. At the end of this time the reaction mixture was poured into 100 mL of saturated aqueous NH$_4$Cl solution. The phases were separated, the organic phase was dried over MgSO$_4$, the solution was filtered, and solvent was removed under reduced pressure. The residue was extracted with hot hexane, and the solvent was removed under reduced pressure to give 128 mg of the crude product as a yellow oil. TLC analysis showed the presence of iodonaphthalene and perylene as well as 3. Preparative silica plate separation gave 3 (38%) as a colorless, crystalline solid: mp 129–130 °C; ^{1}H NMR (CDCl$_3$) δ 2.07–2.17 (dd, 1H, $J_{1x,1y}$ = 18.0 Hz, $J_{1x,3a}$ = 3.6 Hz, H$_{1x}$), 2.87–2.91 (m, 1H, H$_7$), 2.92–2.98 (m, 1H, H$_{3a}$), 3.11–3.17 (m, 1H, H$_4$), 3.11–3.23 (dd,

1H, $J_{1y,1x}$ = 18.0 Hz, $J_{1y,3a}$ = 2.4 Hz, H$_{1y}$), 3.23–3.26 (m, 1H, H$_{8a}$), 5.52–5.58 (dd, 1H, $J_{2,3}$ = 6.0 Hz, ^3J = 2.1 Hz, H$_2$), 5.62–5.68 (dd, 1H, $J_{3,2}$ = 6.0 Hz, ^3J = 2.1 Hz, H$_3$), 6.25–6.30 (ddd, 1H, $J_{5,6}$ = 6.0 Hz, $J_{5,4}$ = 3.3 Hz, $J_{5,7}$ = 0.9 Hz, H5), 6.33–6.38 (ddd, 1H, $J_{6,5}$ = 6.0 Hz, $J_{6,7}$ = 3.3 Hz, $J_{6,4}$ = 0.9 Hz, H$_6$), 7.19–7.23 (m, 1H, ArH), 7.35–7.41 (m, 3H, ArH), 7.59–7.65 (m, 1H, ArH), 7.67–7.71 (m, 1H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$) δ 34.21 (C$_{7a}$), 34.99 (C$_1$), 52.24 (C$_4$), 54.61 (C$_7$), 64.17 (C$_8$), 66.19 (C$_{3a}$), 117.51 (Ar), 124.17 (Ar), 125.33 (Ar), 125.50 (Ar), 125.62 (Ar), 126.52 (Ar), 129.53 (C$_2$), 131.77 (C$_3$), 133.67 (Ar-quat), 133.85 (C$_6$), 135.74 (Ar-quat), 138.48 (Ar-quat), 138.95 (C$_5$), 145.35 (Ar-quat). Anal. Calcd for C$_{20}$H$_{16}$: C, 93.71; H, 6.29. Found: C, 93.44; H, 6.01.

1,1′-(1,8-Naphthalenediyl)ferrocene (8). A 50-mL two-necked round-bottom flask, equipped with condenser and gas inlet tube, was charge with NaH (0.91 g, 23 mmol of a 60% dispersion in mineral oil), washed with hexanes (3 × 5 mL), and dried *in vacuo*. Compound 3 (56.4 mg, 0.220 mmol), dissolved in 5 mL of dry, degassed decalin under argon, was transferred by cannula to the dried NaH. The resulting suspension was heated to reflux (190 °C) with stirring for 20 h and was then cooled to room temperature. Anhydrous ferrous chloride (450 mg, 3.55 mmol) was added to this mixture, followed by 10 mL of dry, degassed THF. The reddish-gray suspension was stirred at room temperature for 20 h and subsequently quenched by dropwise addition of EtOH until gas evolution had ceased. The mixture was then diluted with ether and filtered. The filtrate was concentrated under reduced pressure. TLC analysis of the crude product on silica showed the presence of starting material, perylene, and the ferrocene compound 8. These were separated by flash chromatography on silica, eluting with 10% (v/v) in hexane to give 8 (11%) as a bright yellow solid: mp 264–265 °C; ^{1}H NMR (CDCl$_3$) δ 4.23–4.26 (t, 4H, J = 1.8 Hz, H$_b$), 4.29–4.32 (t, 4H, J = 1.8 Hz, H$_a$), 7.42–7.48 (dd, 2H, ^3J = 8.1 Hz, ^3J = 6.3 Hz, H$_3$), 7.61–7.66 (dd, 2H, ^3J = 6.3 Hz, ^3J = 1.5 Hz, H$_2$), 7.88–7.93 (dd, 2H, ^3J = 8.1 Hz, ^4J = 1.5 Hz, H$_4$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 70.02 (Cp), 71.38 (Cp), 86.94 (Cp-quat); 116.46 (Ar-quat), 124.17 (Ar), 124.21 (Ar-quat), 128.82 (Ar), 130.90 (Ar), 131.39 (Ar-quat); UV (MeCN) λ_{max} (e) 432 nm (331), 349 nm (501), 300 nm (2399), 389 nm (2818), 278 nm (2344), 226 nm (11,749). Anal. Calcd for C$_{20}$H$_{10}$Fe: C, 77.45; H, 4.55. Found: C, 75.55; H, 4.65.

Crystal Structure Determination of 8. X-ray quality crystals of 8 were grown by vapor diffusion from CH$_2$Cl$_2$/hexanes at –20 °C. A pale yellow specimen, measuring 0.48 × 0.20 × 0.16 mm, was mounted and used for the subsequent data collection. Laué photographs indicated the crystal to be of excellent quality; the crystal was transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[33] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[34] All computational work was carried out on a VAX 8650 computer using the Enraf-Nonius SDP package.[35]

Deuterium Labeling Experiments. Perdeuteriocyclopentadiene was prepared following the procedure of Lambert and Finzel[36] employing NaOD in D$_2$O/DMSO solution. Exchange was repeated through four cycles starting from 8 mL of freshly prepared cyclopentadiene and yielded 3 mL of material which was shown to be >90% deuterated (NMR). This was stored at 0 °C.

A solution of CpCu·SMe$_2$ was prepared as previously described from 0.4 mL (4.8 mmol) of cyclopentadiene, 2.15 mmol of n-butyllithium, and 0.44 g (2.14 mmol) of CuBr·SMe$_2$ in 10 mL of THF. This was then added to a solution of 0.6 g (1.58 mmol) of 1,8-diiodonaphthalene in 5 mL of THF cooled at –23 °C. The reaction was continued at –23 °C for 3 h, at the end of which time no starting diiodonaphthalene remained in the reaction mixture, and the major product was 1-cyclopentadienyl-8-iodonaphthalene

(33) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932. Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113.

(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 148–150.

(35) Frenz, B. A. et al. The program package SDP, Enraf-Nonius Corporation, Delft, Netherlands, and Bohemia, New York, 1985.

(36) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 1954.

by ^{1}H NMR analysis. At that point d_5-CpCu·SMe$_3$, prepared from 0.4 mL of perdeuteriocyclopentadiene in the same way as described above, was added to the reaction mixture. The reaction was allowed to proceed overnight at −23 °C. It was then poured into a saturated solution of ammonium chloride, extracted with ether, dried over magnesium sulfate, and chromatographed on a TLC silica gel plate with hexane. The main product was **3** (0.072 g, 18%). A ^{1}H NMR spectrum showed a vinyl proton ratio of $H_{2,3}/H_{5,6}$ = 1.7.

In a second experiment, the sequence in which labeled and unlabeled cyclopentadienylcopper reagent was added in the reaction was reversed. After workup, 0.093 g (23%) of **3** was obtained which showed a vinyl proton ratio $H_{2,3}/H_{5,6}$ = 1.8.