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COFACIAL CYCLOPENTADIENES.
SYNTHESIS AND REACTIONS OF 1,8-BIS(CYCLOPENTADIENYL)NAPHTHALENE

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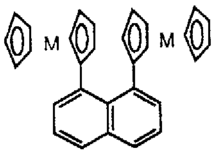
Summary: The reaction of Cyclopentadienylcopper·SMe_2 with 1,8-diiodonaphthalene gives 1,8-bis(cyclopentadienyl)naphthalene *3*, which undergoes a sigmatropic shift followed by an intramolecular Diels-Alder reaction, yielding the dicyclopentadiene *5*. Cycloreversion of *5* in the presence of sodium hydride, and trapping of the dianion with ferrous chloride, gives the bridged ferrocene *11*.

We recently reported the preparation of metallocenes *1* (M=Fe, Ru)[2] and of polymers *2*[3], and have examined the steric and electronic interactions between the cofacial metallocenes in these compounds.[4]



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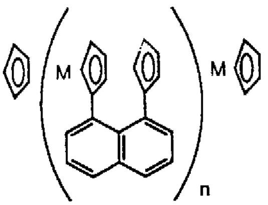

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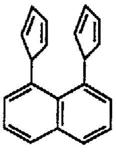
In order to extend the means by which such cofacial complexes might be obtained, we have sought to prepare the framework hydrocarbon 1,8-bis(cyclopentadienyl)naphthalene *3*. Although steric and electronic interactions in 1,8-diarylnaphthalenes have been examined[5], and the study of cofacial interactions of constrained π-systems forms an important part of the chemical literature[6], similarly interacting cyclopentadienyl ring systems have not apparently been examined. We report here the preparation of 1,8-bis(cyclopentadienyl)naphthalene through coupling of cyclopentadienylcopper[7], and the intramolecular cycloaddition and cycloreversion reactions of this substance.

Lithio cyclopentadienide (2.4 mmol), prepared in THF solution at room temperature from n-butyllithium and freshly cracked cyclopentadiene, was cooled to -78° and added to an equimolar suspension of CuBr·SMe_2 in THF, cooled to -78°. After the reaction was complete, the resulting solution was warmed to -20°, and a solution containing 0.8 mmol of 1,8-diiodonaphthalene in THF, also cooled to -20°, was added to this. After stirring the resulting red-orange solution overnight at -20°, solvent was removed and the residue was extracted with hexane. The product *5*, isolated in 40% yield, is a white crystalline material, mp 129-130°.

The initial coupling product *3* is stereochemically incapable of forming either an *endo-* or an *exo*-dicyclopentadiene adduct. However, a single sigmatropic [1,5] hydrogen shift,[8] results in the formation of *4* which can in principle undergo cycloaddition to give either *5*, *6* or *7*. Of these, MM2 calculations[9] show that *6* and *7* are both highly strained (bond bending strain energy associated with the aryl-ring bonds = 69.2 and 56.8 Kcal/mole respectively). Adduct *5* is significantly less strained (2.1 Kcal/mole). Furthermore, frontier orbital analysis[10] of *4* predicts that the aryl-conjugated cyclopentadienyl ring should function preferably as the dienophile rather than as the diene to give *5*. A second [1,5] sigmatropic shift in *4* would give *8* or *9*. Of these, the latter isomer is stereochemically incapable of yielding a cycloadduct. Compound *8* can in principle yield the cycloadduct *10*, which also shows low bond bending strain (1.9 Kcal/mole). Finally, none of the intermediates which result from two successive [1,5] sigmatropic rearrangements in one cyclopentadienyl ring and either one or two such processes in the second, is capable of giving a cycloadduct.



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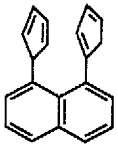

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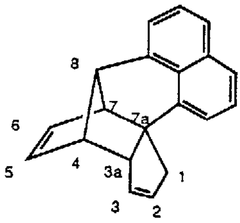

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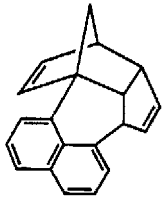

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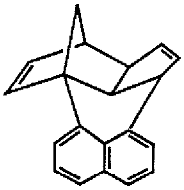

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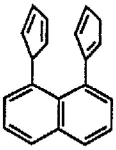

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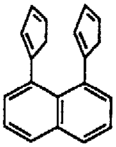

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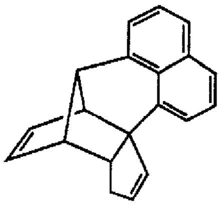

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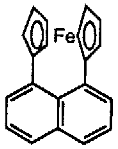
The structure of the cycloadduct, derived from ^{1}H NMR spectral analysis, may be shown to be best represented by *5*, since the product shows the presence of two dicyclopentadiene[11] bridgehead protons and of only one bridging methylene proton, thus excluding structures *6* and *7*. Structure *10* is excluded since the product shows typical long range coupling between the *exo-* and *endo*-methylene protons at C_1 and a proton at C_{3a}[11a]. Further HETCOR and COSY experiments provided full assignments for carbon and proton resonances, in accord with structure *5*.[12] Thus, *4*, formed from the initial coupling product *3* by a single sigmatropic rearrangement, is irreversibly trapped as its cycloadduct, precluding further sigmatropic change and the formation of the closely related product *10*.

The cycloadduct *5* can be shown to undergo thermal reversion in refluxing decalin solutions. Thus, when *5* (0.16 mmol) is heated in decalin solution at 190° for 20 hours, in the presence of sodium hydride (34 mmol), and the mixture is subsequently treated with anhydrous ferrous chloride (1.6 mmol), the unique bridged ferrocene *11*[13] is formed (22%). An examination of the structure and chemistry of *11* an the use of *5* in the preparation of polymeric cofacial metallocenes is in progress.



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REFERENCES

1. Present address Nalco Chemical Company, Naperville, Illinois. 1.
2. Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539.
3. Arnold, R.; Matchett, S. A.; Rosenblum, M. *Organometallics* **1988**, *7*, 2261.
4. Arnold, R.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 1253.
5. Claugh, R. L.; Pierre, M.; Roberts, J. D. *J. Org. Chem.* **1976**, *41*, 2252. House, H. O.; Koepsel, D. G.; Campbell, W. *ibid.* **1972**, *37*, 1003. House, H. O.; Campbell, W. J.; Gall, M. *ibid.* **1970**, *35*, 1815. House, H. O.; Magin, R. W. *ibid.* **1963**, *28*, 2403. Zweig, A.; Galivan, J. B. *J. Am. Chem. Soc.* **1969**, *91*, 260.
6. *Cyclophanes*; Keehn, P. M.; Rosenfeld, S. M., Ed.; Academic Press; New York, 1983.
7. Nilsson, M.; Wahren, R.; Wennerström, O. *Tetrahedron Lett.* **1970**, 4583.
8. Roth, W. R.; *Tetrahedron Lett.* **1964**, *17*, 1009. McLean, S.; Haynes, P. *ibid.* **1964**, *17*, 2385. Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* 1973, *19*, 1939. Alder, K.; Ache, H.-J. *Chem. Ber.* **1970**, *103*, 426.
9. MM2 and MMX, used on a VAX, was obtained from Serena Software, 489 Serena Lane, Bloomington, IN 4 Updated versions of MODEL, obtained from Prof. Midland, University of California, Riverside, and Prof. Steliou, University of Montreal, were used for structure input and analysis.
10. Fleming, I. *Frontier Orbitals And Organic Chemical Reactions*; J. Wiley and Sons: New York, 1976. Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions In Chemistry;* J. Wiley and Sons; New York, 1985. Streitwieser, A.; Brauman, J. I.; Coulson, C. A. *Dictionary of π-Electron* Calculations, Pergamon press: Oxford, 1965, Vol. 2.
11. a. Sergeyev, N. M.; Avramenko, G. I.; Korensky, V. A. *Org. Mag. Res.* **1972**, *4*, 39. b. Foster, R. G.; McIvor, M. C. *J. Chem. Soc.* (B) **1969**, 188.

12. ^1H-^1H homonuclear correlated 2-D (COSY) and ^1H-^{13}C heteronuclear correlated 2-D (HETCOR
were performed using pulse sequences and parameter sets supplied by Varian VMX version 6.2
For numbering, see structure <u>5</u>.

^1H NMR (300 MHz, $CDCl_3$); 2.07-2.17 (d of d of m, 1H, $J_{1X,1Y} = 18.0$ Hz, $J_{1X,3a} = 3.6$ Hz,
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 (d of d of m, 1
18.0 Hz, $J_{1Y,3a} = 2.4$ Hz, H_{1Y}), 3.23-3.26 (m, 1H, H_{8S}), 5.52-5.58 (d of d of m, 1H, $J_{2,3} =$
2.1 Hz, H_2), 5.62-5.68 (d of d of m, 1H, $J_{3,2} = 6.0$ Hz, J = 2.1 Hz, H_3), 6.25-6.30 (d of d
$J_{5,6} = 6.0$ Hz, $J_{5,4} = 3.3$ Hz, $J_{5,7} = 0.9$ Hz, H_5), 6.33-6.38 (d of d of d, 1H, $J_{6,5} = 6.0$ H
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,
7.71 (m, 1H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$); 34.21 (C7a), 34.99 (C1), 52.24 (C4), 54.61 (C7), 64.17 (C8), 6
117.51 (Ar), 124.17 (Ar), 125.33 (Ar), 125.50 (Ar), 125.62 (Ar), 126.52 (Ar), 129.53 (C2),
133.67 (Ar-quat.), 133.85 (C6), 135.74 (Ar-quat.), 138.48 (Ar-quat.), 138.95 (C5), 145.35

13. ^1H NMR (300 MHz, $CDCl_3$); 4.23 (t, 4H, J = 1.8 Hz, Cp), 4.29 (t, 4H, J = 1.8 Hz, Cp), 7.
7.5, 8.4 Hz $ArH_{3,6}$), 7.61 (dd, 2H, J = 7.2, 1.5 Hz $ArH_{2,7}$), 7.89 (dd, 2H J = 8.4, 1.5 Hz A
^{13}C NMR (75 MHz, $CDCl_3$); 70.02 (Cp), 71.38 (Cp), 86.94 (Cp-quat), 116.46 (Ar-quat), 124.17
124.21 (Ar-quat), 128.82 (Ar), 130.90 (Ar), 131.39 (Ar-quat).

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