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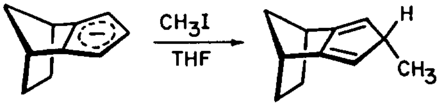
ELECTRONIC CONTROL OF STEREOSELECTIVITY. 20. CRYSTAL AND MOLECULAR STRUCTURE OF THE FERROCENE DERIVED FROM TRICYCLO[5.2.1.0^{2,6}]DECA-2,5,8-TRIENE[1]

Leh-Yeh Hsu,[2] Susan J. Hathaway, and Leo A. Paquette*

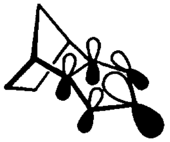
Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Summary: Reaction of the isodicyclopentadienide anion and its dehydro congener with Fe(II) leads to a stereochemically homogeneous ferrocene derivative in each instance. Through chemical correlation and X-ray analysis, above-plane complexation is established for both halves within the two sandwich compounds.

The isodicyclopentadienide anion (1) is now recognized to possess an ensemble of pπ orbitals intrinsically capable of face stereoselectivity toward diverse electrophilic reagents.[3-5] Its proclivity for below-plane bond formation is exemplified by the exclusive formation of 2 upon reaction with methyl iodide in tetrahydrofuran solution. This stereochemical preference parallels that generally observed for Diels-Alder cycloadditions to neutral isodicyclopentadienes.[6] Our interpretation of this behavior follows from INDO calculations[7] which reveal that high lying norbornyl σ orbitals in 1 are strongly coupled to the neighboring π fragment.



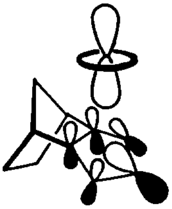
1 2



3

The result of this relatively substantive σ/π mixing is disrotatory tilting of the peripheral p lobes in ψ_1 toward the methano bridge as illustrated in 3. With particular reference to the seat of reaction, this tilting deformation leads to group overlap integrals more conducive to endo nucleophilic attack.

The unique orbital construct in 3 has prompted us to initiate investigations designed to elucidate the level of stereoelectronic control which can operate during metal complexation. Our considerations have revolved around the possible interplay of several interesting product-determinative options. Should overlap control be dominant and orbital tilting be restricted to the ψ_1 level, all metal ions might well prefer approach from above-plane because their d_{z^2}, s, and p_z orbitals (all of which are related to ψ_1 by symmetry) would, under these circumstances, be directed to the center of the more electron-rich cyclopentadienide core (see 4). Alternatively, it remains possible that the pπ orbitals in ψ_2 remain sufficiently tilted to override the effect of ψ_1, due to the customary greater importance of d_π-ψ_2 interactions relative to those of the d_σ-ψ_1 type. In this event, a metallic species with contracted $d\pi$ orbitals (i.e., a small metal or one in a high oxidation state) would likely favor top-side bonding (viz., 5), whereas one with diffuse $d\pi$ orbitals could engage in better overlap on the endo face (*cf* 6).



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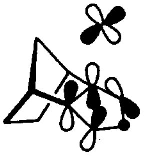

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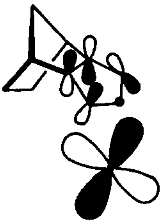
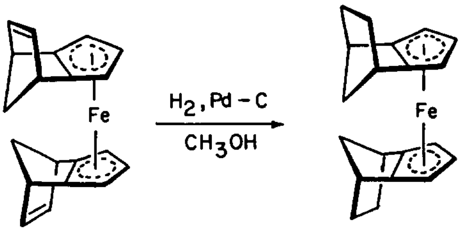


6

Because both hypotheses predict that an Fe(II) atom may prefer to coordinate to 1 from its exo surface *in direct contrast to the stereoselectivity of electrophilic capture*, preparation of the ferrocene derivative was undertaken.[8] Sequential reaction of isodicyclopentadiene with ethylmagnesium bromide and Fe(II)(acac)$_2$(py)$_2$ in xylene solution (2 days as 20°C, 1 h at 65-70°C) resulted in 33% conversion to a single ferrocene (8) which was isolated as golden plates, mp 167.5-169°C, from acetone. Its 200 MHz ^{1}H NMR spectrum [(CDCl$_3$) δ 3.95 (s, 2 H), 3.74 (s, 4 H), 2.85 (s, 4 H), 2.28 (d, J = 8 Hz, 2 H), 1.74-1.69 (m, 4 H), 1.35 (d, J = 8 Hz, 2 H), 1.02-0.95 (m, 4 H)] proved to be inadequately diagnostic of stereochemistry. When no crystals suitable for X-ray analysis could be grown, the analogous reaction was applied to its dehydro congener, tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene. The only detectable ferrocene was isolated as large yellow-brown prisms, mp 162.5-163.5°C, [9] and identified as 7 by X-ray diffraction studies. Furthermore, catalytic hydrogenation of 7 over 10% palladium on charcoal afforded 8, thereby establishing a common stereochemical infrastructure in the two complexes.



7 8

Data collection for 7 was carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer and the structure was solved[10] by MULTAN 82.[11] As the ORTEP drawing in Figure 1 reveals, the two C$_{10}$H$_9$ residues are enantiomerically related and possess individual pseudo-mirror planes. The two cyclopentadienide moieties are fully planar and virtually parallel to each other (dihedral angle = 3.6°). The centers of the five-membered rings are 3.31(7) Å

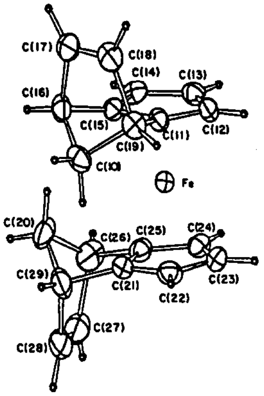


Figure 1. A computer-generated perspective side view of the final X-ray model of **7**.

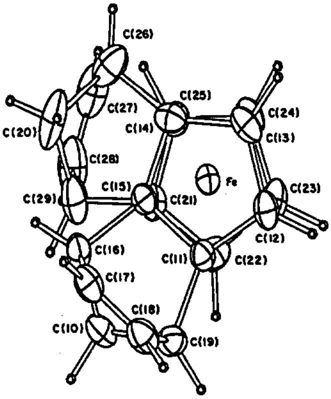


Figure 2. A computer-generated perspective top view of the final X-ray model of **7**.

apart, mirroring the situation in ferrocene itself,[12] with the Fe atom equidistant between them.

When the sandwich complex is viewed from above (Figure 2), one set of cyclopentadienide carbon atoms is seen to be positioned almost directly above the other. This effect, which may be the norm for ferrocene systems,[12,13] is best reflected in the torsion angle of 60° observed between the C(11)-C(15) and C(21)-C(25) bonds. Since the distance between C(10) and C(20) is large (4.287 Å) and van der Waal compression is not at issue, steric factors appear unimportant. The proximity of the two methano carbons may arise from intermolecular crystal packing forces and/or intramolecular attractive (London) forces.

A final point of interest is the dihedral angle relationship of the ethano bridge [the C(16)-C(15)-C(11)-C(19) plane] to the cyclopentadienide moiety in the top half (10.1°) relative to the state of affairs in the lower segment (θ = 9.3°). All of the other bond angles and distances are normal.

With establishment of the three-dimensional structure of **7**, specific attention must next be given to isodicyclopentadienide complexation with low valent metals of larger atomic dimensions. In question is whether a crossover to below-plane stereoselectivity will develop or above-plane preference will persist. We hope to report on these developments in the near future.

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References and Notes

(1) Part 19: Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642.

(2) Author to whom inquiries concerning the X-ray crystal structure analysis should be directed.

(3) Paquette, L. A.; Charumilind, P. *J. Am. Chem. Soc.* **1982**, *104*, 3749; Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *Ibid.* **1983**, *105*, 3126.

(4) Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* 1983, *105*, 100.

(5) Paquette, L. A.; Charumilind, P.; Gallucci, J. *J. Am. Chem. Soc.*, in press.

(6) Gleiter, R.; Paquette, L. A. *Accounts Chem. Res.* 1983, *16*, 328 and references cited therein.

(7) Böhm, M. C.; Gleiter, R. *Theor. Chim. Acta*, in press.

(8) The chemical transformation in question was actually disclosed for the first time in a brief report [Reimschneider, R. *Z. Naturforschg.* 1962, *17b*, 133]. Although a relatively sharp melting product was isolated after extensive purification, no mention was made of possible isomer distribution or of stereochemical considerations.

(9) 17.4% conversion; 200 MHz ^{1}H NMR (CDCl$_3$) δ 6.43-6.41 (m, 4 H), 4.02 (br s, 2 H), 3.82 (br s, 4 H), 3.41 (br s, 4 H), 2.97 (d, J = 7 Hz, 2 H), 2.23 (d, J = 7 Hz, 2 H); *Anal.* Calcd for $C_{20}H_{18}Fe$: C, 76.45; H, 5.78. Found: C, 76.47; H, 5.84.

(10) MoKα radiation; a = 9.137(1), b = 11.692(1), c = 7.348(2) Å; α = 93.62(2)°, β = 105.31(2)°, γ = 69.53(1)°; centrosymmetric P_I space group, Z = 2, ρ_{calcd} = 1.472; μ = 10.507 cm^{-1}; R_f = 0.026 and R_{wf} = 0.038.

(11) Frenz, B. A. Enraf-Nonius SDP User's Guide, 1982.

(12) See for example: (a) The parent molecule: Seiler, P.; Dunitz, J. D. *Acta Cryst.* 1979, *B35*, 1068; Seiler, P.; Dunitz, J. D. *Ibid.* 1979, *B35*, 2020; Takusagawa, F.; Koetzle, T. F. *Ibid.* 1979, *B35*, 1074. (b) Ferrocenedicarboxylic acid: [Palenik, G. J. *Inorg. Chem.* 1969, *8*, 2744]. (c) Diacetyl ferrocene: [Palenik, G. J. *Ibid.* 1970, *9*, 2424].

(13) Eclipsing is especially encountered when an interlocking bridge is present, e.g. as in 1,1-(1",3"-cyclopentylene)ferrocene [Batail, P.; Grandjean, D.; Astruc, D.; Dabard, R. *J. Organometal. Chem.* 1975, *102*, 79].

(14) *Note Added in Proof:* Subsequent to the submission of this paper, Professor P. D. Bartlett called to our attention the fact that the corresponding nickelocene was prepared several years ago [Scroggins, W. T.; Rettig, M. F.; Wing, R. M. *Inorg. Chem.* 1976, *15*, 1381] and shown by X-ray analysis to involve above-plane complexation to both halves, in agreement with our theoretical analysis.

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