cyclohexane from the conformer with a pseudoaxial methyl group and/or as a twist boat from the conformer with a pseudoequatorial methyl group to avoid the approach of MCA from the same side of the ring as the 3-methyl group.

The α-halo esters formed in these ene reactions are useful synthetic intermediates. The halide can be displaced with inversion by a variety of nucleophiles. The use of these adducts for the synthesis of δ,ϵ-unsaturated amino acids will be reported shortly.

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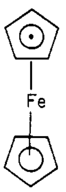
Received February 14, 1980

Bis(pentadienyl)iron Compounds: The "Open Ferrocenes"

Sir:

A great deal of the current interest in organometallic chemistry was spawned by the reports of the unusually stable compound ferrocene, $(C_5H_5)_2Fe$[1] (I). A very interesting molecular orbital scheme involving efficient covalent interaction of iron s, p, and d valence orbitals with the cyclopentadienyl ligands' molecular orbitals has been helpful in understanding the stability of these complexes and various chemical trends.[2]



I

It is here noted that the molecular orbitals of a *pentadienyl* anion in a "U" configuration are quite analogous in symmetry and orientation to those of the cyclopentadienyl ligand, although the energetic orderings do differ.[3] These considerations would seem to suggest that a large class of compounds should exist in which the pentadienyl ligand replaces its more familiar cyclic counterpart. In fact, however, only relatively few metal complexes with the pentadienyl ligand are known,[4] although there would seem to be substantial advantages to a more widespread implementation of these ligands in such complexes. For example, as this ligand is noncyclic, it should be much more prone to (reversibly) isomerize to η^3 (II) or η^1 (III) bonded configurations, a process likely to be of some chemical importance.[6] As a crude comparison in this regard, one can note the much greater versatility and application of the allylic ligands as compared to the cyclopropenyl ligands.[7] We have therefore set out to address some of the questions and possibilities raised herein by, as a first step, synthesizing "opened" analogues of the classic compound ferrocene.

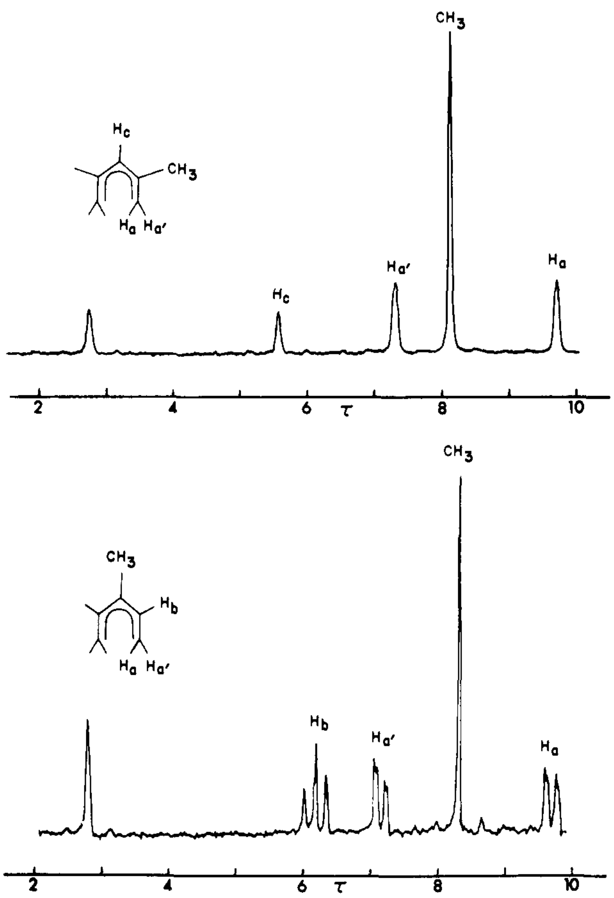
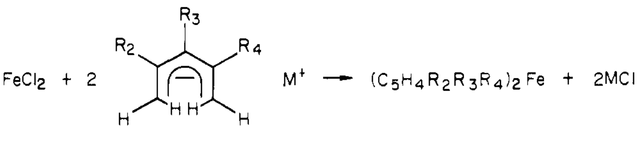


Figure 1. ^1H NMR spectra (C_6D_6 solvent, C_6D_5H internal standard) of (top) bis(2,4-dimethylpentadienyl)iron and (bottom) bis(3-methylpentadienyl)iron. The peaks at τ 2.77 are due to the C_6D_5H resonance.

II

III

The reaction of ferrous chloride with an anionic source of a pentadienyl ligand[8] in THF at −78 °C leads to formation of deep, orange-red solutions containing the appropriate bis(pentadi-



M = Li, K IV, $R_2 = R_3 = R_4 = H$
V, $R_2 = R_4 = CH_3$; $R_3 = H$
VI, $R_2 = R_4 = H$; $R_3 = CH_3$
VII, $R_2 = R_3 = CH_3$; $R_4 = H$

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[1] (a) Kealy, T. J.; Pauson, P. L. *Nature (London)* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632. (c) Wilkinson, G. *J. Organomet. Chem.* **1975**, *100*, 273.

[2] (a) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (b) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *Ibid.* **1971**, *93*, 3603. (c) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980.

[3] Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists", Wiley: New York, 1961.

[4] (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1962**, *84*, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organmet. Chem.* **1968**, *12*, 551. (c) Rienacker, R.; Yoshiura, H. *Agnew Chem., Int. Ed. Engl.* **1969**, *8*, 677. (d) Krüger, C. *Ibid.* **1969**, *8*, 678. (e) A greater number of cyclohexadienyl metal complexes are known,[5] but their cyclized nature and ready reversion to arene complexes are likely to be detrimental with respect to their chemistry and σ/π-related isomerizations.

[5] For example, see: (a) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Barger, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (b) Mahler, J. E.; Pettit, R. *Ibid.* **1963**, *85*, 3955. (c) Calderazzo, F. *Inorg. Chem.* **1966**, *5*, 429. (d) Whitesides, T. H.; Lichtenberger, D. L.; Budnik, R. A. *Ibid.* **1975**, *14*, 68. (e) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1969**, 2024. (f) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, *4458*. (g) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777. (h) Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7209. (i) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1968**, 2257, 2261.

[6] (a) Tsutsui, M.; Courtney, A. *Adv. Organomet. Chem.* **1979**, *16*, 241. (b) Powell, J. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972**, *6*, 273.

[7] (a) Stone, F. G. A.; West, R., Eds. *Adv. Organomet. Chem.* **1979**, *17*, I. (b) See, however: King, R. B.; Ikai, S. *Inorg. Chem.* **1979**, *18*, 949.

[8] (a) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 199. (b) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

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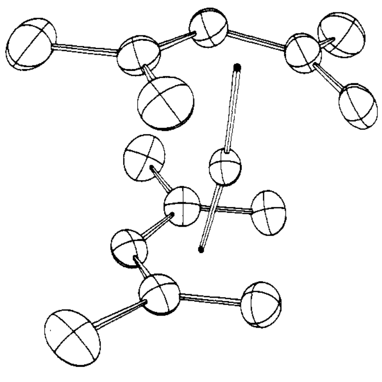
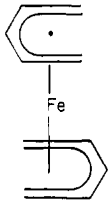
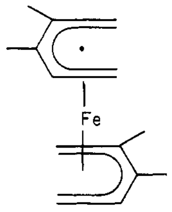


Figure 2. Perspective view of bis(2,4-dimethylpentadienyl)iron. The hydrogen atoms have been omitted for clarity. The 35% probability ellipsoids are shown.

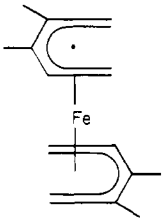
enyl)iron complexes, which were isolated and recrystallized and/or sublimed following pentane extraction. The methylated complexes are in many respects similar to ferrocene, being hydrocarbon soluble, sublimable, stable at and somewhat above room temperature, and air stable for at least several hours. They have been characterized by infrared, nuclear magnetic resonance, and mass spectroscopy, as well as analytically.[9]

The infrared spectra are devoid of C=C stretching bands, suggesting a η^5 mode of bonding. The appropriate parent ions and reasonable fragments are exhibited in the mass spectra.[10] ^{1}H NMR data are also consistent with the formulation of these compounds as "open sandwiches".[11] As prime examples, the ^{1}H NMR spectra of V and VI are shown in Figure 1. The assignments, relative intensities, and coupling constants[12] are consistent with those previously observed for various allyl and diene complexes of iron.[13] For compound VII, a very complex, unassignable ^{1}H NMR spectrum indicates the presence of two nonsuperimposable isomers, VIIa and VIIb.





VIIa



VIIb

The parent complex, $(C_5H_7)_2Fe$, is a relatively less tractable material which readily decomposes to dipentadienyl and ferromagnetic iron byproducts, and thus, ^{1}H NMR characterization has not yet been achieved. Similar orange solutions of this compound in hydrocarbons could be prepared as described for the other complexes, and generally a semicrystalline material would be isolated, for which only crude analytical and mass spectral information could be obtained.[14] The compound itself decomposes on attempted sublimation. It is clear, then, that the presence of methyl substituents serves as the real key to the isolation and characterization of these compounds by imparting a great deal of (perhaps predominately kinetic) stability to the complexes, probably by sterically hindering the coupling process. Similar observations have been made concerning methylation of allylic ligands,[15] but these influences have generally not been exploited.

X-ray studies of some of these species have been complicated apparently by severe thermal disorder and/or polycrystallinity problems. The bis(2,4-dimethylpentadienyl)iron complex was actually synthesized with the hope of overcoming these problems through locking of the methyl groups in the lattice. Indeed, crystals of this compound, while of a generally poor nature, diffract sufficiently well that with Mo Kα radiation, slow scan rates (1°/min), wide scan ranges (ca. 3.3° in 2θ), and the collection of a large number of data, we have been able to obtain some meaningful information. The space group is C_i^1–$P\bar{1}$(No. 2): $a = 7.778$ (5), $b = 7.979$ (5), $c = 11.198$ (8) Å; $\alpha = 85.77$ (5), $\beta = 80.46$ (5), $\gamma = 68.48$ (5)°; $Z = 2$. The structure was solved and refined by standard Patterson, Fourier, and least-squares techniques. At the present stage of anisotropic refinement, the conventional R index[16] is 0.071 for the 2697 unique reflections ($0 < 2\theta < 60°$) having $I > 3\sigma(I)$. A perspective view of the molecule is presented in Figure 2. The compound indeed is seen to exist as an open sandwich with nearly planar pentadienyl ligands. In the solid state, the compound is observed in an essentially gauche-eclipsed conformation with methyl groups interlocked. The interior carbon–carbon bond distances are essentially equal at 1.410 (4) Å. Iron–carbon distances are shortest at 2.071 (3) Å for the carbon atoms in the 2,4-positions, and somewhat longer for the 3- and 1,5-positions at 2.084 (3) and 2.114 (8) Å, respectively.[17] These values can be compared to the slightly shorter iron–carbon distance of 2.033 (3) Å found in ferrocene.[18] Interestingly, however, it can be noted that the distance from the iron atom to the bonded ligand-fragment center of mass is *shorter* in the present case than in ferrocene (1.50 vs. 1.66 Å). These observations may be, to a large extent, of geometric origin. It is clear, however, that the above information demonstrates that the bis(pentadienyl)iron complexes are true structural analogues of ferrocene. We have found that a number of other metals form stable pentadienyl complexes, both "sandwich" and "nonsandwich", and these studies, as well as further chemical experimentation, are being actively pursued.

Acknowledgments. R.D.E. expresses his gratitude for partial support of this research through grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, from a Pennwalt Corporation Grant of Re-

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(9) Anal. Calcd for V: C, 68.31; H, 9.01. Found: C, 68.60; H, 8.86. Calcd for VI: C, 66.08; H, 8.32. Found: C, 65.11; H, 8.59. Calcd for VII: C, 68.31; H, 9.01. Found: C, 67.76; H, 8.96.

(10) Besides the parent mass peaks, other common fragments were those of iron, and in the case of 3-methylated complexes M–L–H.

(11) For convenience, the structures drawn are shown in opposing orientations. In solution or gaseous phase, facile rotation of the ligands is expected while in the solid phase other orientational isomers may be frozen out. However, ferrocene has been depicted in a staggered conformation.

(12) With the designations given in Figure 1, $J_{aa'} \approx 0$–2, $J_{ab'} \approx 9$, and $J_{ab} \approx 10$ Hz.

(13) (a) Fischer, E. O.; Werner, H. "Metal π-Complexes", Elsevier: Amsterdam, 1966. (b) Maddox, M. L.; Strafford, S. L.; Kaesz, H. D. *Adv. Organomet. Chem.* **1965**, *3*, 1. (c) T. J. Marks in "The Organic Chemistry of Iron", E. A. Koerner von Gustorf and F.-W. Grevels, Eds., Academic Press: New York, 1978; Vol. 1.

(14) Anal. Calcd for $C_{10}H_{14}Fe$: C, 63.19; H, 7.43. Found: C, 64.33; H, 8.21. Due to the instability of the compound toward sublimation, a parent ion peak was not observed; however, the dominant peak observed was that due to C_5H_7 fragments. The material also exhibits a UV–vis spectrum similar to those of the methylated complexes.

(15) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 964.

(16) $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. All but one hydrogen atom have been located. All have been included in calculated or idealized locations. An absorption correction has not yet been applied, however.

(17) The Fe–C(1) and Fe–C(5) distances actually differ at 2.092 (5) and 2.135 (4) Å, respectively, where C(1) is the terminal carbon atom in the lower right.

(18) A result of 2.058 (5) Å was found by electron diffraction.[18b] (a) Seiler, P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1979**, *35*, 1068. (b) Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470.

(19) NSF Predoctoral Fellow, 1980.

(20) Camille and Henry Dreyfus Foundation, Summer 1979 Undergraduate Research Student.

search Corporation, and from the University of Utah Research Committee.

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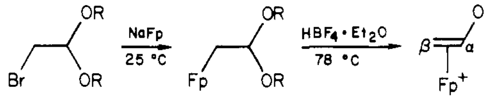
Enol Ether-Iron Complexes as Vinyl Cation Equivalents. Vinylation of Enolates

Sir:

While vinyl anion reagents are common synthetic components,[1] vinyl cations are known only as reactive intermediates in solvolysis reactions.[2] Cationic reagents which function as equivalents of vinyl cations would consequently provide a valuable charge-reversal complement in synthesis, especially for the vinylation of enolizable centers.[3] We report here on the use of Fp(alkyl vinyl ether), [Fp = $C_5H_5Fe(CO)_2$] complexes as vinyl cation equivalents for the regio- and stereospecific vinylation of enolates under mild conditions.

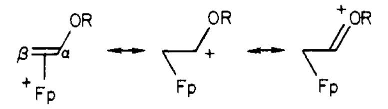
Fp(vinyl ether) complexes are readily available by metalation of α-bromo acetals or ketals by NaFp, followed by acid-promoted alcohol elimination (eq 1), and are obtained as yellow crystalline



(1)

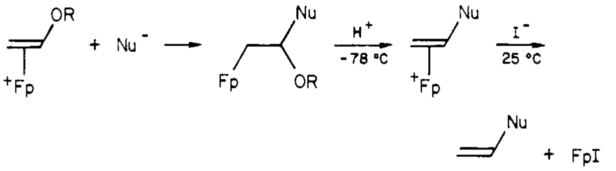
materials, which may be stored for prolonged periods of time at 0 °C without appreciable decomposition.[4]

By contrast with alkyl-substituted Fp(olefin) cations, which react with nucleophiles with low regiospecificity, nucleophilic addition to vinyl ether complexes occurs with high regiospecificity at the α carbon atom due to localization of charge at this site (eq 2).



(2)

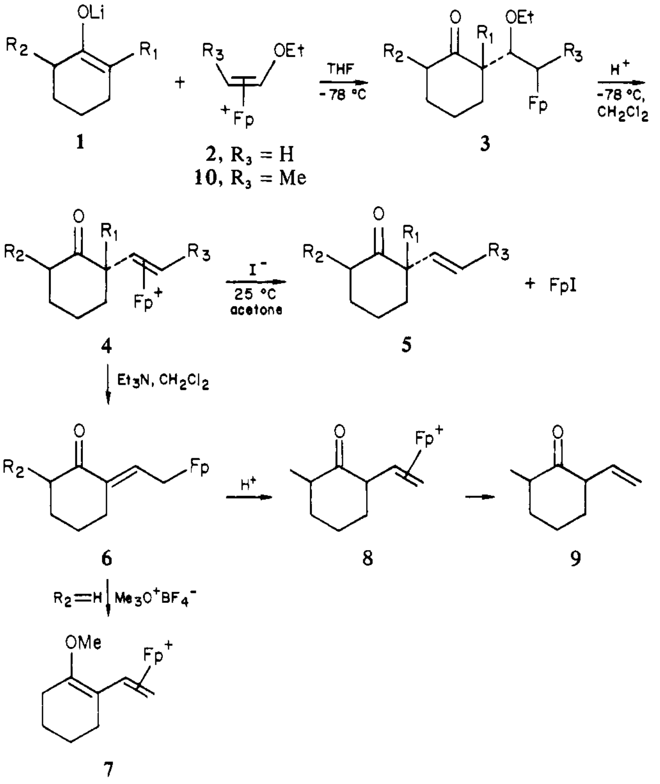
Transformation of the adduct to the vinylated product is then readily accomplished by low-temperature protonation, followed by brief exposure of the resulting cationic olefin complex to iodide (eq 3).



(3)

The use of this sequence for the vinylation of ketones is illustrated with cyclohexanone-derived enolates (Scheme I). Thus, cyclohexenone lithium enolate[5] (**1a**) reacts rapidly in THF solution at −78 °C with Fp(ethyl vinyl ether)BF_4 (**2**)[4] to give the adduct **3a** as amber crystals (89%) as a single stereoisomer.[6] Protonation

Scheme I



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$, $R_2 = Me$
c, $R_1 = Me$, $R_2 = R_3 = H$
d, $R_1 = R_3 = Me$, $R_2 = H$

of **3a** in CH_2Cl_2 solution at −78 °C with $HBF_4{\cdot}Et_2O$ gave the salt **4a** as an unstable yellow solid (90%), and this on brief exposure to NaI (acetone, 25 °C, 0.5 h) liberated the free vinyl ketone[7-9] (**5a**, 68% isolated). The proton at C-2 in **4a** is highly acidic due to activation by the adjacent cationic and carbonyl centers, so that brief treatment with 1 equiv of triethylamine (CH_2Cl_2, 25 °C) converts it entirely to the conjugated enone **6a**.[10] While pro-

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(1) Seyferth, D., Ed. "New Applications of Organometallic Reagents in Organic Synthesis", Elsevier: Amsterdam, 1976.

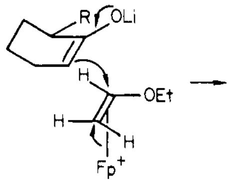
(2) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. Hanach, M. *Ibid.* **1976**, *9*, 364.

(3) A few uncharged vinyl cation equivalents are known, and the vinylation of lithium ester enolates, employing vinyl halides and a nickel catalyst, has recently been described: Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993. Eisch, J. J.; Galle, J. E. *Ibid.* **1976**, *41*, 2615. Oishi, T.; Takechi, H.; Ban, Y. *Tetrahedron Lett.* **1974**, 3757. Metcalf, B. W.; Bonilavri, E. *J. Chem. Soc., Chem. Commun.* **1978**, 914. Millard, A. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 4833.

(4) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381.

(5) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(6) On the basis of the ^1H and ^{13}C NMR spectra of the adduct. The stereochemistry assigned to this substance at C-2 and C-7 (II; R = H, Me) is based on the assumption of a sterically preferred orientation (I) of reacting components in the transition state.



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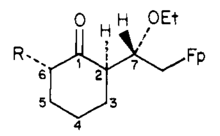


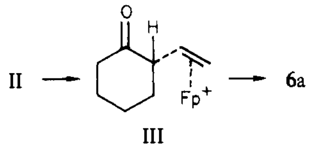
II

(7) (a) Marvell, E. N.; Russay, R. *J. Org. Chem.* **1977**, *42*, 3336. (b) Crandall, J. K.; Arrington, J. P.; Hen, J. *J. Am. Chem. Soc.* **1967**, *89*, 6208.

(8) IR (CH_2Cl_2) 1700, 1630, 990, 930 cm^{-1}; NMR ($CDCl_3$) δ 6.0 (q, $|J_{Ax} + J_{Bx}| = 28$ Hz, CH=), 5.05 (t, $J_{AB} < 1$ Hz, CH_2=).

(9) A satisfactory elemental analysis was obtained for this substance.

(10) This substance exhibits vinyl proton resonance at δ 7.15 (t, $J = 9$ Hz), which may be compared with resonances reported for *cis*- and *trans*-2-ethylidenecyclohexanone (δ_{cis} 5.6; δ_{trans} 6.6).[7b] The exclusive formation of the anti-isomer as a kinetic product is plausible in terms of the relative configurations assigned to the two chiral centers in II (R = H).[6] Trans elimination of ethanol[11] from it would give a vinyl complex with stereochemistry III, and stereospecific trans deprotonation[12] of this gives **6a**.



III