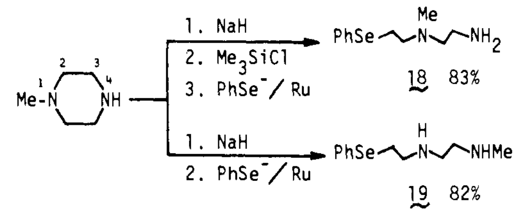
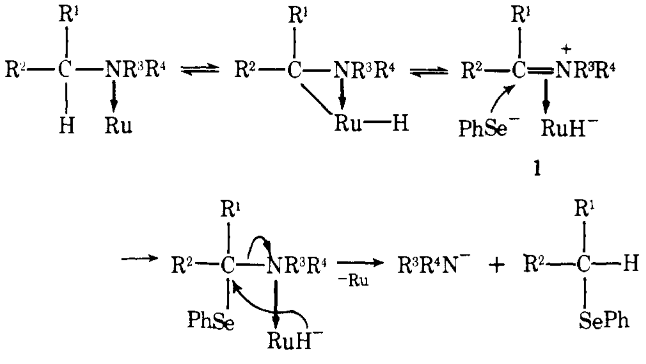
thoxy-2,3-methylenedioxy-14-phenylselenohexahydrodibenz[*c,g*]azecine (**15**) (mp 153 °C)[18] in 67% yield. Oxidation of **15** with *m*-chloroperbenzoic acid (CH_2Cl_2, −78 °C) gave azecine **16** (mp 131-132 °C, 61%).[19,20] It is noteworthy that intramolecular cyclization[21] of **16** with $PdCl_2(PhCN)_2$ catalyst gave (±)-**14** (mp 169-171 °C)[22] in 83% yield. Furthermore, chemoselective transformation of primary, secondary, and tertiary amines is performed. For instance, *N*-methylpiperazine undergoes either the bond cleavage between N_1-C_2 or N_4-C_3 exclusively, depending on the reaction condition employed. Thus, the ruthenium-catalyzed reaction of *N*-methyl-*N'*-trimethylsilylpiperazine (**17**) with lithium benzeneselenolate gave **18** (83% isolated yield), while that of *N*-methylpiperazine sodium amide gave **19** (82%) with no sign of the other possible opening product in either case.



Nucleophilic attack of selenolate anions on the iminium ion complex **1**,[23,24] formed from the insertion of ruthenium into a carbon-hydrogen bond adjacent to the nitrogen,[5,25] and subsequent reductive cleavage seem to operate as key steps.



Work is currently in progress on the extention of potential application of this transformation to other system and of use in the synthesis of natural products.

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(16) NMR ($CDCl_3$, δ) 1.57 (s, 3 H, (*Z*)-Me), 1.67 (s, 6 H, (*E*)-Me), 1.95 (d, 4 H, CH_2CH_2, $J = 3.5$ Hz), 3.50 (d, 2 H, $J = 8.0$ Hz, CH_2Se), 4.90–5.60 (m, 2 H, olefin), 7.13 (m, 3 H, Ph), 7.47 (m, 2 H, Ph).

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(18) NMR ($CDCl_3$, δ) 1.25 (s, 1, NH), 2.55–3.38 (m, 6), 3.61 (s, 1, H^8), 3.80 (s, 6, OCH_3), 4.08 (s, 1, H^8), 4.46 (t, 1, H^{14}, $J = 4.0$ Hz), 5.85 (s, 2, OCH_2O), 6.52 (s, 1, H^4), 6.67 (s, 1, H^{11}), 6.77 (s, 2, H^1, H^{12}), 7.17 (m, 3), 7.50 (m, 2 H); mass (*m/e*) 496, 495, 419, 340, 164, 156, 149, 77.

(19) NMR ($CDCl_3$, δ) 1.29 (s, 1 H, NH), 2.73 (t, 2 H, $J = 4.0$ Hz, H^6), 3.57 (t, 2, $J = 4.0$ Hz, H^5), 3.78 (s, 6, OCH_3), 3.90 (d, 2, $J = 1.5$ Hz, H^8), 5.85 (s, 3, OCH_2O), 6.41 (d, 1, $J = 16$ Hz, H^8, H^{13}), 6.52 (s, 1, H^4), 6.67 (s, 1, H^{11}), 6.77 (s 2, H^1, H^{12}), 7.07 (d, 1, $J = 16$ Hz, H^{14}).

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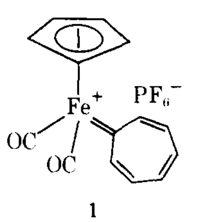
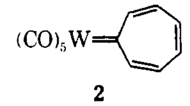
Synthesis and Crystal Structures of Cycloheptatrienylidene Complexes of Iron

Sir:

We recently reported the synthesis of **1** and **2**, the first examples of transition metal complexes of cycloheptatrienylidene (CHT).[1] At this time we report the application of the same method to the synthesis of two benzannelated CHT complexes **3** and **4**, as well as the X-ray crystal structures of **1** and **4**.



1



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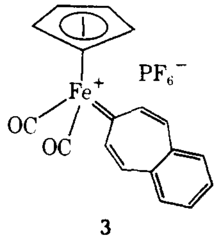

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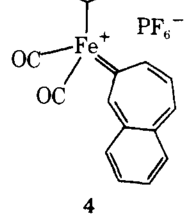

4

Bromide **6**, prepared in accordance with Scheme I and previously successful procedures,[1,2] was converted into **7**, as shown, and then to yellow-brown complex **8**[3] by treatment with

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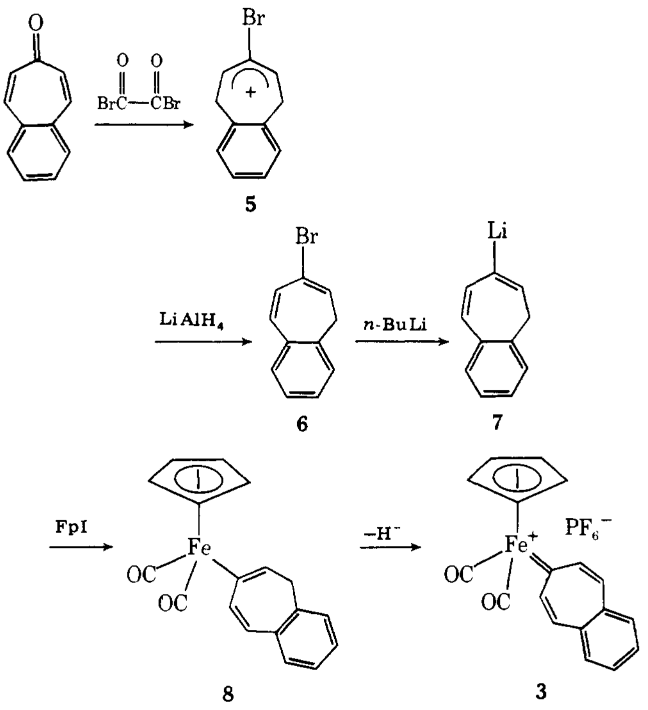
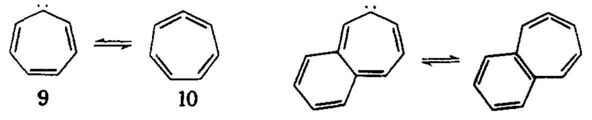
Scheme I



a cold solution of (η^5-C_5H_5)(CO)$_2$FeI (FpI). Elution of **8** with a pentane-benzene mixture over alumina, followed by oxidation, gave a red solution which, after warming to room temperature and addition of ether, afforded **3**[4] as a fairly air-stable red-brown solid.

It has long been assumed that the seven-membered ring intermediate on the C_7H_6 energy surface could be represented by a planar carbene (**9**).[5] Recently, however, evidence has accumulated which supports the existence of an isomeric twisted allene form **10** that may be of lower energy.[6,7] Furthermore, INDO calculations[8] predict that benzannelation as in **11** should favor the allene form over its carbene isomer **9** by ~45 kcal/mol.[9] We therefore undertook the synthesis—outlined in Scheme II—of a carbene complex benzannelated as in **4** to test this prediction.

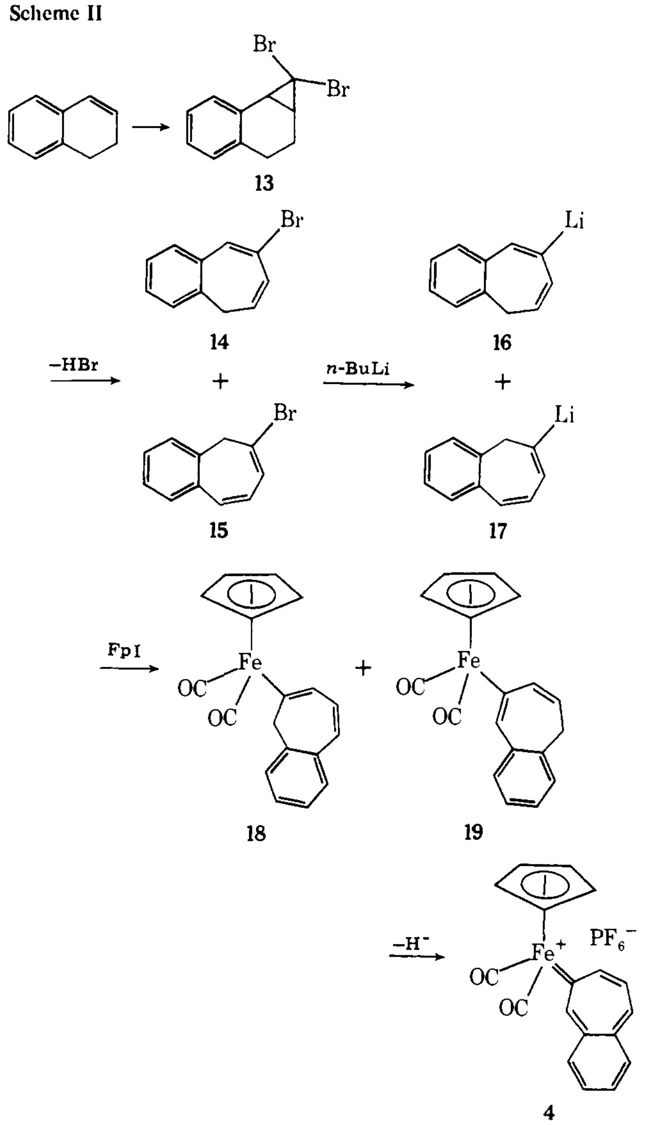


9 **10** **11** **12**

Reaction of dihydronaphthalene with dibromocarbene[10] gave the cyclopropane adduct **13** which upon distillation lost HBr to yield isomers **14** and **15**. Treatment with *n*-butyllithium formed **16** and **17**, which when added to a cold solution of FpI and chromatographed on alumina (pentane-benzene) gave isomers **18** and **19** as a yellow-brown oil.[11] After this mixture was oxidized with (Ph_3C)PF_6 and warmed to room temperature, **4** was precipitated with ether as a stable violet solid.[12]

The structures of the iron complexes of **1** and **4**, as determined by X-ray crystallography,[13] are shown in Figures 1 and 2. Both complexes are cationic iron-carbene species with pseudotetrahedral geometries, if the positions of the η^5-C_5H_5 centroids (Cp$_c$) are considered, which differ principally in the nature of the CHT ligand. In both complexes the CHT rings are planar and, although there is considerable variation in the C-C distances about the rings, the mean values in **1** [1.398 (28) Å] and **4** [1.387 (19) Å] do not differ significantly. Hence, the CHT ligand in **4** shows no tendency toward an allene structure. The bond angles about the carbene carbon atom, C$_{carb}$, in **1** and **4** are within 3° of the idealized value of 120° for sp^2 hybridization. The dihedral angle between the plane of the CHT ring and the plane of the C$_{carb}$, Fe, and Cp$_c$ positions is 87.6° in **1** and 89.5° in **4**; hence, the acceptor pπ orbitals of the CHT rings lie virtually in the plane of the C$_{carb}$, Fe, and Cp$_c$ positions, suitably oriented to back-bond with filled dπ orbitals of Fe. These orientations of the CHT ligands are essentially 90°

Scheme II



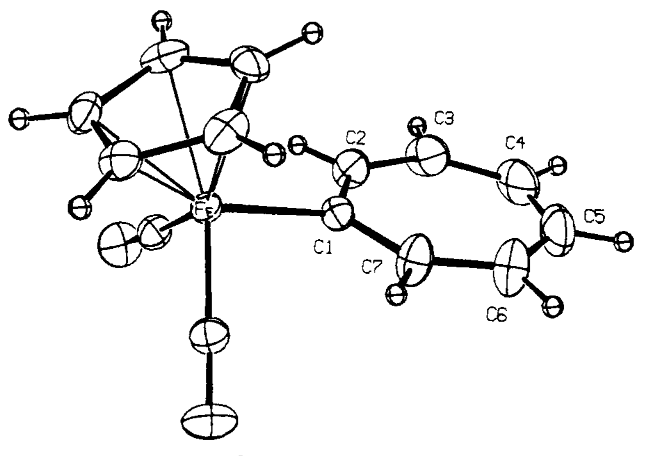


Figure 1. A view of the [(η^5-C_5H_5)(CO)$_2$Fe(C_7H_6)]$^+$ ion. Selected bond lengths (angstroms): Fe-C(1) = 1.979 (3), C(1)-C(2) = 1.393 (5), C(2)-C(3) = 1.395 (6), C(3)-C(4) = 1.410 (8), C(4)-C(5) = 1.358 (9), C(5)-C(6) = 1.387 (7), C(6)-C(7) = 1.363 (7), C(7)-C(1) = 1.406 (5). Selected angles (degrees): Fe-C(1)-C(2) = 118.6 (3), Fe-C(1)-C(7) = 118.9 (3), C(2)-C(1)-C(7) = 122.3 (3).

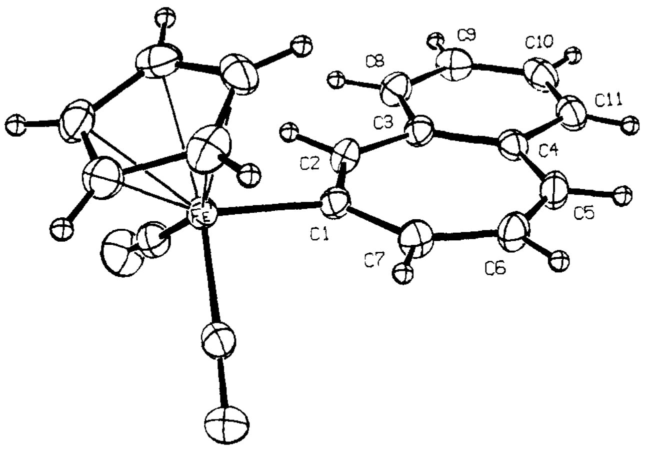


Figure 2. A view of the $[(\eta^5\text{-}C_5H_5)(CO)_2Fe(C_{11}H_8)]^+$ ion. Selected bond lengths (angstroms): Fe-C(1) = 1.996 (2), C(1)-C(2) = 1.395 (3), C(2)-C(3) = 1.416 (3), C(3)-C(4) = 1.435 (3), C(4)-C(5) = 1.400 (3), C(5)-C(6) = 1.373 (3), C(6)-C(7) = 1.388 (3), C(7)-C(1) = 1.407 (3), C(3)-C(8) = 1.429 (3), C(8)-C(9) = 1.358 (3), C(9)-C(10) = 1.402 (4), C(10)-C(11) = 1.346 (4), C(11)-C(4) = 1.429 (3). Selected angles (degrees): Fe-C(1)-C(2) = 119.4 (1), Fe-C(1)-C(7) = 117.7 (2), C(2)-C(1)-C(7) = 122.6 (2).

from that predicated[14] for the simplest carbene $:CH_2$ and observed in two Ta-CHR (R = H or Ph) complexes.[15,16] Comparison of the $Fe\text{-}C_{carb}$ distances of 1.979 (3) and 1.996 (2) Å in the cations of **1** and **4** with the $Fe\text{-}C(sp^2)$ distances of 2.025 (6) Å *in* cation $\{(\eta^5\text{-}C_5H_5)(CO)_2Fe[\eta^1\text{-}C(Ph_3P)\text{-}CH(Ph)]\}^+$ [17] and 1.996 (8) Å in uncharged $(\eta^5\text{-}C_5H_5)(CO)_2Fe[\overline{CC(CH_3)S(O)(OC}H_2)]$[18] suggests some degree of metal-ligand multiple bonding, particularly in **1**.

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(3) Analytical and spectroscopic data for **8**: 26% yield; mp 114.5–115.5 °C dec; NMR ($CDCl_3$) δ 3.0 (saturated CH, d, J = 7 Hz, 2 H), 4.6 (Cp, s, 5 H), 5.6 (C_1, t, J = 7 Hz, 1 H), 6.62 (C_3, C_4, s, 2 H), 7.2 (aromatic, m, 4.5 H); IR (KBr) in carbonyl region 2010, 1935, 1960 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2Fe$: C, 67.95; H, 4.44. Found: C, 67.99; H, 4.47.

(4) Analytical and spectroscopic data for **3**: 93% yield; mp 177–178 °C dec; ^1H NMR (0°C, CD_3CN) δ 9.58 (C_2, C_{11}, d, J = 11 Hz, 2 H), 8.26 (C_3, C_{10}, d, J = 11 Hz), 8.58–8.08 (C_5–C_8, m) (total area of C_3, C_{10}, C_5–C_8, 6 H); ^{13}C NMR (0 °C, CD_3NO_2) δ (from Me_4Si) 265.9 (C_1), 212.7 (CO), 158.5, 141.6, 140.3, 137.8, 137.1 (C_2–C_6), 89.5 (Cp); IR (CH_2Cl_2) in carbonyl region 2045, 2000 cm^{-1}; UV–visible (CH_2Cl_2) λ_{max} 500 (log ϵ 3.47), 468 (3.52), 330 (sh), 315 (sh), 282 (sh), 272 (4.21), 233 (4.20). Anal. Calcd for $C_{18}H_{13}O_2FePF_6$: C, 46.79; H, 2.84. Found: C, 46.78; H, 2.86.

(5) Cf. Jones, W. M.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J. Am. Chem. Soc.* **1977,** *99*, 6379.

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(11) Analytical and spectroscopic data for **18** and **19:** 37% yield; ^1H NMR ($CDCl_3$) δ 2.9, 3.45 (saturated CH, d, s, 2 H), 4.9 (Cp, s, 5 H), 5.35, 6.2, 6.7, 7.2 (olefinic and aromatic, all complex multiplets, 8 H); IR in carbonyl region 2020, 1950 cm^{-1}; high resolution mass spectrum of mixture, *m/e* 318.03302 (theory, 318.03410).

(12) Analytical and spectroscopic data for **4**: 88% yield; mp 176–177 °C dec; ^1H NMR (8 °C, CD_3NO_2) δ 10.4 (1 H, d, J = 2Hz), 9.92 (1 H, d, J = 10.6 Hz), 9.23 (1 H, d of m, J = 10.6, 0.5 Hz), 8.50, 8.16 (5 H, m, J = 10.6 Hz); ^{13}C NMR (0 °C, CD_3NO_2) δ (from Me_4Si) 215 (CO), 201 (C_1), 176, 174, 155, 145, 139, 138, 138, 137, 136, 133 (C_2–C_{11}), 89 (Cp); IR (CH_2Cl_2), carbonyl region 2037, 1992 cm^{-1}; UV–visible (CH_2Cl_2) λ_{max} 380 (log ϵ 3.52), 313 (sh), 380 (4.36), 232 (4.28). Anal. Calcd for $C_{18}H_{13}O_2FePF_6$: C, 46.79; H, 2.84. Found: C, 46.68; H, 2.86.

(13) Single crystals of **1** and **4** form from CH_2Cl_2 solutions at ca. −15 °C in space group $P1$ with a = 7.981 (4), b = 14.378 (3), c = 7.133 (1) Å, and α = 98.52 (1), β = 100.75 (1), γ = 93.33 (1)° for **1** and a = 8.2987 (6), b = 15.238 (2), c = 7.4361 (8) Å, and α = 90.509 (7), β = 104.396 (5), γ = 94.676 (6)° for **4**. The structures were solved by heavy-atom methods and refined by full-matrix least-squares procedures; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.057 and 0.041 for **1** and **4**, respectively. Experimental procedures are essentially as previously delineated: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B.* **1976,** *32*, 381.

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Stereospecific Alkylation of a Carbanion in the Solid State

Sir:

Reactions in organic compounds are more selective when performed in the solid state rather than in solution.[1-3] For instance, the elimination in some halides is highly stereospecific when performed in the crystalline state.[4,5] The regiospecificity is drastically altered when the alkylation of some phenolate anions is performed in heterogeneous medium.[6-8] Similar findings have been described for the alkylation of pyrazole anion.[9] Optical induction has been observed during the reaction of chiral monocristals of chalcone with bromine,[10] and the higher reactivity of one enantiomer of a cristalline carboxylic acid with an optically active amine has been noted.[11]

The stereoselectivity of the lithiated carbanion derived from methyl benzyl sulfoxide[12-14] has been proposed to be due to internal chelation of the lithium cation by sulfoxide oxygen.[15-18] This chelation favors one of the diastereoisomeric carbanions and the reaction of these carbanions has been proposed to occur with inversion at the carbanionic center for nonchelating reagents such as alkyl halides and with retention in the case of chelating reagents such as water.[16] However, further studies are difficult because of the rapid equilibration of the species present in solution. We thought that in the solid state the reactivity may be more selective owing to the presence of a single diastereoisomer and to a fixed solvation state.

When a 1.1 M solution of the lithiated carbanion derived from racemic benzyl methyl sulfoxide **1** in tetrahydrofuran (THF) was cooled from −78 to −100 °C, a white precipitate was obtained. After removal of the solvent and washing several times with pentane (−100 °C), the solid was dried under vacuum. At 25 °C, liquid methyl iodide was added to the solid and after workup the ratio of the diastereoisomeric methylated products [r = **2**(R,S) + **2**(S,R)/**3**(R,R) + **3**(S,S)] was determined by ^1H NMR[19] to be 5:1. However, if a mixture of

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