D forms, leading to poor binding interactions for hydrolysis in the D case. Neither the D nor the L *N*-ethyl derivative effectively inhibits the enzyme (Table I), a result most probably of the formation of diazoethane from the ethyl diazonium ion rather than the ethyl carbonium ion,[11] although the position of the group released may be involved as discussed in the case of L-Ia.

Our results indicate that mapping studies of enzyme active sites should be pursued with suitable derivatives of all stereoisomers.

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(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

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(5) (a) The low level of inhibition previously reported for L-Ia (ref 2) was due to contamination of the sample with a small amount of D-Ia. (b) Satisfactory elemental analyses were obtained for all compounds: for D-Ia, mp 110.5–111.0 °C dec; $[\alpha]^{26}_{D}$ −46.8° (*c* 1.30, CH_3CN); for L-Ia, mp 109.5–110.0 °C dec; $[\alpha]^{23}_{D}$ +47.1° (*c* 0.68, CH_3CN); for D-Ib, mp 95.8–96.2 °C dec; $[\alpha]^{21}_{D}$ −47.7° (*c* 1.47, CH_3CN); for L-Ib, mp 92.1–92.4 °C dec; $[\alpha]^{26}_{D}$ +47.0° (*c* 1.27, CH_3CN).

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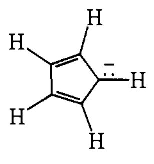
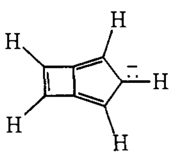
Synthesis, Nuclear Magnetic Resonance Observation, Basicity, and Reactions of Bicyclo[3.2.0]heptatrienideiron Complexes

Sir:

Because it may be viewed either as a perturbed cyclopentadienide (**1**) or cycloheptatrienide (**3**), bicyclo[3.2.0]heptatrienide[1] (**2**) occupies an important position on the borderline between conjugative stabilization and destabilization[2] of cyclic π-conjugated carbon anions. Although very dilute solutions of **2** have been prepared, its UV spectrum recorded and an approximate pK_a estimated, solutions concentrated enough for NMR or IR observation or extensive chemical study apparently cannot be obtained.[1b,d]



1



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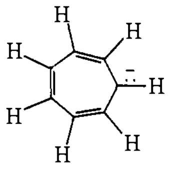
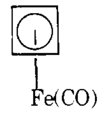


3

It seemed reasonable to us that complexation of **2** to an appropriate transition metal might provide a molecule stable enough for NMR observation and possibly isolation.[3] In addition, such complexation raises the interesting possibility of using the number of other ligands on the metal to determine whether it coordinates to the (4π electron) four-membered ring (analogy: cyclobutadiene(tricarbonyl)iron[3] (**4**)) or to the (6π electron) five-membered ring (analogy: η^5-cyclopentadienyl(dicarbonyl) ferrate[4] (**5**)). We now wish to report the preparation of surprisingly stable, spectroscopically observable solutions of two iron complexes of anion **2**, NMR and IR spectra of these materials, and certain of their chemical reactions. We also discuss the chemistry and pK_a's of their neutral precursors, the latter providing a quantitative evaluation of the effect of changing the metal-bound dative ligands upon the acidity of the complexed triene.



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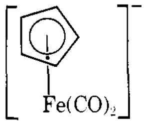
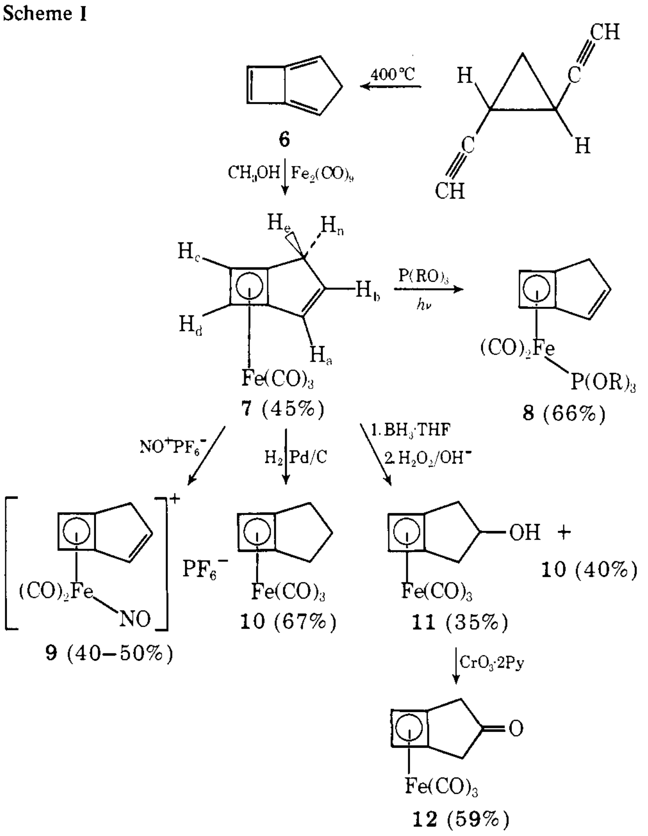


5

King and his co-workers recently found[5] that treatment of air-sensitive bicyclo[3.2.0]hepta-1,4-6-triene[1d,6] (**6**) with $Fe_3(CO)_{12}$ in refluxing hexane for 20 h led to substituted cyclobutadiene complex **7**. We have found that the presence of CH_3OH (a stabilizer normally added to commercial $Fe_3(CO)_{12}$ by the supplier) is required to make this reaction proceed efficiently. In fact, it is best carried out in CH_3OH as solvent; under these conditions either $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ may be used as the source of metal. The complex is isolated as a yellow oil by short-path distillation: NMR (THF-d_8) H_a δ 6.24 (d of t, J_d = 5 Hz; J_t = 2 Hz), H_b δ 6.02 (d of t, J_d = 5 Hz; J_t = 2 Hz), H_c, H_d δ 4.20 (s), H_e, H_n δ 3.06 (m); IR (hexane) 2050, 1980 cm^{-1}; mass spectral parent peak at *m/e* 229.967 (calcd: 229.967).

Complex **7** readily undergoes ligand substitution reactions, including nitrosation,[7] and the complexes shown in Scheme

Scheme I



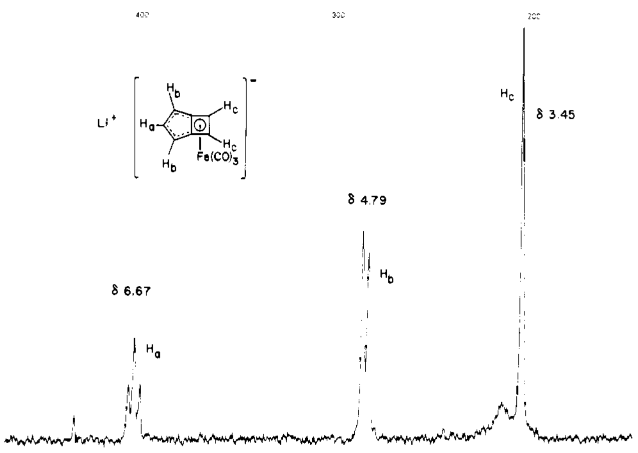
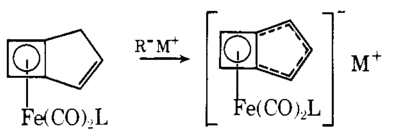


Figure 1. Proton NMR spectrum (60 MHz, 37 °C probe temperature) of $Li^+[C_7H_5{\cdot}Fe(CO)_3]^-$ (**13**) in THF-d_8.

1 have been obtained in the yields indicated. The five-ring double bond may be selectively hydrogenated without loss of metal to give saturated complex **10.** Hydroboration-oxidation also occurs without loss of metal; however, both alcohol **11** and hydrocarbon **10** are obtained in this reaction.[8] Oxidation of partially purified **11** gives ketone **12.**

Complex **7** is stable in neutral CH_3OH or CH_3OD at room temperature. However, when a trace of $NaOCH_3$ is added to the CH_3OD solution, the NMR patterns of the vinyl and allylic hydrogens simplify considerably. Workup followed by NMR and mass spectral analysis confirms that *one* allylic hydrogen (presumably[3c,9] the exo; cf. Scheme I) is exchanged under these conditions. Encouraged by this result, a degassed solution of **7** in THF-d_8 was cooled to −78 °C, 1 equiv of *n*-BuLi added, and the resulting cherry-red solution warmed to room temperature. IR and proton NMR observation (Figure 1) showed complete conversion to a new, symmetrical anion (NMR H_a δ 6.67 ppm (t, J = 3 Hz), H_b δ 4.79 ppm (J = 3 Hz), H_c δ 3.45 ppm (s); IR (metal carbonyl region) 2040, 1960, 1885 cm^{-1}). The potassium salt of this anion may be prepared in dimethyl sulfoxide (Me_2SO) solution by treatment of **7** with $K^+CH_3SOCH_2^-$. In this medium it has IR absorptions at ν 1970 and 1875 cm^{-1} and NMR signals at δ 6.79 (t, J = 3 Hz), 4.81 (d, J = 3 Hz), and 3.40 (s) ppm.

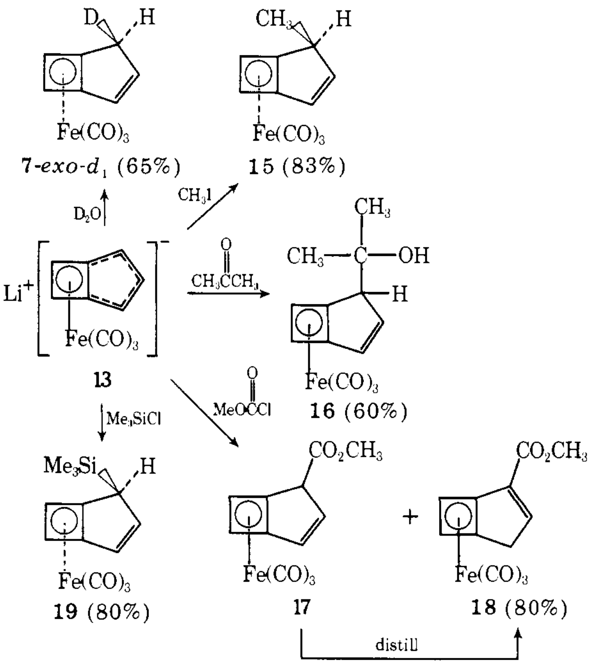
The relatively low IR frequencies suggest[10] that some negative charge is carried by iron in this complex (compare IR of cyclobutadiene iron tricarbonyl[11] at ν 2055 and 1985 cm^{-1}). However, the proton chemical shifts are similar to those observed in model allylic anion systems.[12] This allows assignment of structure **13,** having iron coordinated to the four-membered ring, to this complex. The neutral trimethyl phosphite-substituted complex **8** may also be converted to its corresponding anion (**14**) using KCH_2SOCH_3/Me_2SO: NMR δ 6.63 (t, J = 3 Hz), 4.66 (d of d, $J_{HH} \cong J_{PH}$ = 3 Hz), 3.20 (s), 3.23 (phosphite methyls, d, J = 12 Hz); IR 1910, 1840 cm^{-1}. The relative NMR chemical shifts of **13** and **14** suggest (as might be expected) that the π-ring carries somewhat more negative charge in the phosphite-substituted anion.



7, L = CO
8, L = P(OMe)$_3$

13, L = CO
14, L = P(OMe)$_3$

Scheme II



Anion **13** is extremely air-sensitive and its salts decompose rapidly in the solid state. However, it is indefinitely stable in solution at room temperature and chemical reactions may be carried out conveniently by treating solutions of **13** with various reagents (Scheme II). We have found in this way that reaction with D_2O occurs (again apparently exclusively from the exo side) to give **7**-*exo*-d_1, and reaction with methyl iodide gives only one methyl compound, **15.** The anion reacts readily with ketones to give alcohols (e.g., **16**) which do *not* dehydrate under the reaction conditions. Carboxylation occurs to give a mixture of esters **17** and **18; 17** is then converted completely to **18** during workup. Reaction with chlorotrimethylsilane provides alkenylsilane **19.**

A quantitative indication of the stability of anion **13,** and of the effect of metal-bound ligands upon this stability, may be obtained by estimation of the basicity of **13** and **14.** Attempts to measure the pK_a of **7** directly have been frustrated by the fact that **7** and **13** undergo irreversible decomposition when both are present in solution at room temperature. However, an estimate may be obtained by rapid quenching[1b,13] of **13** with carbon acids of varying pK_a. These experiments were carried out in Me_2SO solution, for which an extensive acidity scale has recently been developed.[14] We find that **13** may be protonated by fluorene (pK_a = 22.6), indene (p$K_a \cong$ 20), and cyclopentadiene (pK_a = 18.1), but *not* by dimethyl malonate (pK_a = 15.8). It appears to be *partially* protonated by nitromethane (pK_a = 17.2), and under these conditions **7** and **13** coexist in solution for a short time. We thus estimate the pK_a of **7** to be 17 ± 1. In an analogous way, we have determined the pK_a of **8** to be 21.5 ± 1, indicating that substitution of $P(OMe)_3$ for CO at the metal costs about 4 pK_a units in acidity of the π-ligand. In contrast, it is apparently much more difficult to generate an anion from saturated complex **10.** In $CD_3SOCH_2^-K^+/Me_2SO$-d_6 this complex undergoes no exchange, indicating that the α-hydrogens in **10** are at least 18 pK_a units less acidic than those in **7.** The fact that **7** is comparable in acidity to cyclopentadiene is strong evidence that cyclic π-electron delocalization plays an important role in its unusual stability.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. CA-15006) for financial support of this work, to Professor R. B. King for providing us with details of his preparation of complex **7** prior to publication, and to Professor F. G. Bordwell for providing recently measured pK_a data for a number of carbon acids.

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(12) See D. H. O'Brien, C. R. Russell, and A. J. Hart, *Tetrahedron Lett.*, 37 (1976), and references cited there.

(13) In order to ensure that the protonations described in the text reflect equilibrium (rather than kinetic) effects, in each case where an acid HA was observed *not* to reconvert **13** to 7, we demonstrated independently that its conjugate base A^- did in fact convert **7** to **13**.

(14) (a) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975); (b) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *ibid.*, **97**, 3226 (1975); see also (c) C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 (1968); (d) F. G. Bordwell, private communication.

(15) National Science Foundation predoctoral fellow, 1973-1976.

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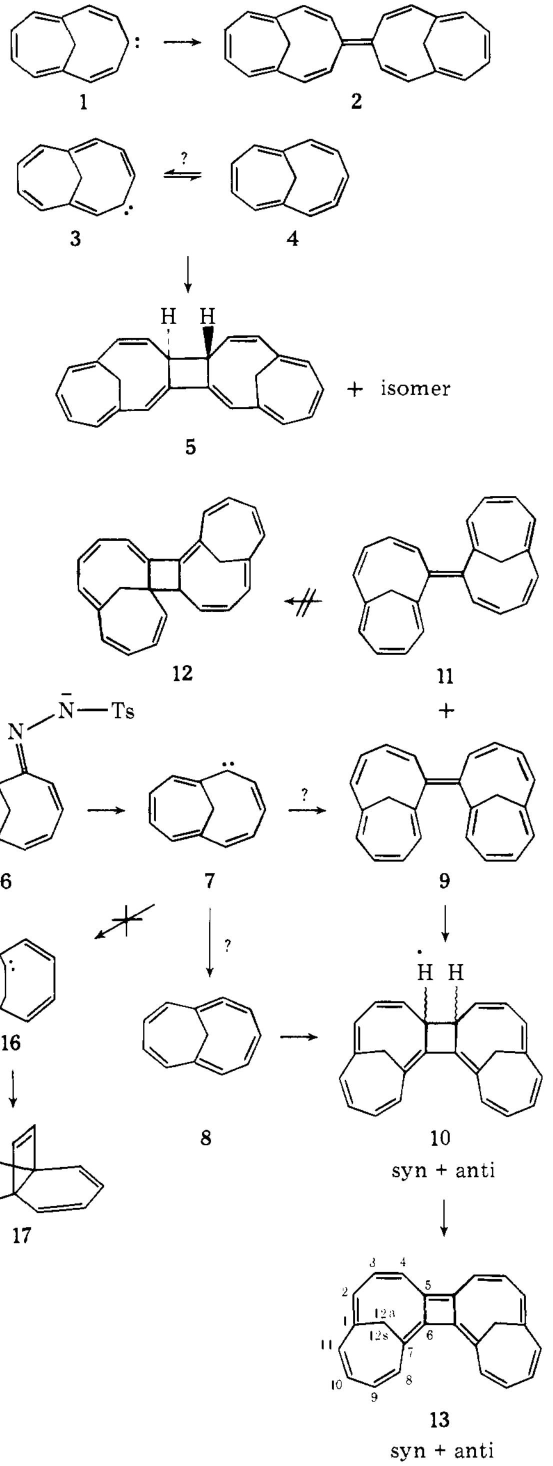
Bridged 22π Annulenes from 6,11-Methano[11]annulenylidene

Sir:

We have recently reported the generation and some of the chemical properties of **1**[1,2,5,6] and **3**,[3-6] two of the five possible methano[11]annulenylidenes in which the vacant orbital of the carbene may be an integral component of a carbocyclic aromatic π-system. At this time, we report the synthesis and pyrolysis products of the tosylhydrazone sodium salt **6**, a reaction which should give a third isomeric methano[11]annulenylidene **7**. This carbene was of particular interest because, in contrast to **1** and **3**, the proximity of the methano bridge in **7** introduces the possibility of a carbene-carbene rearrangement to **16**, a carbene that would be expected to undergo facile hydrogen migration to give the known [4.4.2]propellane **17**.[7] In fact, as in the case of **1** and **3**, in the absence of substrates the presumed carbene from **6** gave only products believed to originate from carbene (or allene) dimers; no **17** was detected. However, the dimers from **7** were found to be exceptional in that the probable intermediates (**10**) spontaneously lose hydrogen to give the totally unsaturated hydrocarbons **13** (syn and anti). To the best of our knowledge, these are the first recorded bridged [22]π annulenes.[8] *syn-* and *anti-* **13** show the further remarkable characteristic of existing in the unexpected localized forms shown.



The ketone[9] required for preparing **6** was synthesized from 2-bromo-1,6-methano[10]annulene[10] in two steps (1.5% overall yield) by the method developed by Vogel.[11] Conversion to the tosylhydrazone (~55%) (mp (CH_3OH/hexane 2:1) 106-108 °C; NMR $\delta(CDCl_3)$ 8.05-5.36 (12 H, m), 4.28 (1 H, part of AB system, $J = 11.5$ Hz), 2.35 (3 H, s), 1.20 (1 H, part of AB system, $J = 11.5$ Hz), N-H varies; high resolution MS (calcd 338.1088, found 338.1089)) was effected by refluxing (2 h) an ethanol solution of the ketone, tosylhydrazide,