through base-promoted elimination of HCl from **3**. Initial attempts with *tert*-butyllithium, both in pentane and in ethers, produced a wide variety of products including those derived from nucleophilic addition to the π system and from displacement of chloride. Use of *N*-lithiohexamethyldisilazane also produced a complex product mixture. Although the silicon–carbon double bond is known to be trapped by dienes,[7] inclusion of excess butadiene in this reaction mixture yielded only a trace of material which could be tentatively identified by gas chromatography–mass spectroscopy as an adduct of the desired silabenzene (**6**) and butadiene.[8] However, when the *N*-lithiodisilazane **3** and excess perfluoro-2-butyne were combined in dry ether at −77 °C and the solution was allowed to warm to room temperature, there was obtained (after removal of a polymeric material generated from the base and the acetylene) a mixture which GC analysis showed to contain two major products, **7** and **8**.[9] Separation was accomplished by preparative GC.
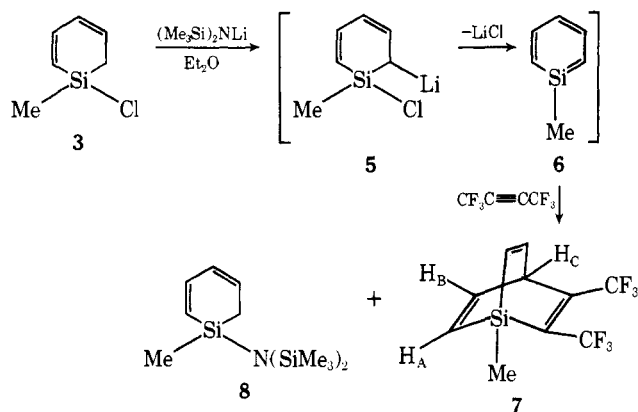
Adduct **7**, formed in 28% yield, was identified from its 60-MHz ^{1}H NMR spectrum ((C_6D_6) δ 0.4 (q, 3 H, SiMe, J_{HF} = 1.5 Hz), 4.85 (overlapped t of t, 1 H_C, J_{AC} = 1.5 Hz, J_{BC} = 7 Hz), 6.4 (d of d, 2 H_A, J_{AB} = 11 Hz), 7.15 (d of d, 2 H_B)), its ^{19}F NMR spectrum (($DCCl_3$) two quartets, 53.43 and 65.23 ppm from $CFCl_3$, J = 12.2 Hz), and its mass spectrum (M^+ 270.03005, calcd for $C_{10}H_8F_2Si$ 270.02995).

Like Jones,[1] we were unable to intercept an intermediate carbanion when a tenfold excess of trimethylchlorosilane was included in the reaction mixture, although the yield of **7** was reduced by half. Quenching the reaction with excess methyl iodide before workup resulted in no incorporation of methyl in any of the products. However, unlike Jones, we have never seen any evidence of the [2 + 2] silene dimer, the 1,3-disilacyclobutane.

It is of particular interest to compare our results with those of Ashe[10] who has synthesized by an analogous method arsabenzene, stibabenzene, and bismabenzene and found all of these heteroaromatics to readily react with perfluoro-2-butyne to afford adducts of the same type as **7**. Thus, while we cannot totally rule out a mechanism involving carbanionic attack on acetylene followed by intramolecular displacement of chloride, the absence of trimethylchlorosilane trapping combined with the precedents set by Jones[1] and Ashe[10] provide strong evidence for the intermediacy of 1-methyl-1-silacyclohexa-1,3,5-triene (**6**), the first silabenzene.

Work is presently in progress to study the photochemistry of **7** and to attempt the pyrolytic retro-Diels–Alder reaction of **7** back to **6**.

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(1) P. R. Jones and T. F. O. Lim, *J. Am. Chem. Soc.*, **99**, 2013 (1977).
(2) Previous attempts to prepare silabenzene derivatives are reviewed by P. Jutzi, *Angew. Chem., Int. Ed. Engl.*, **14**, 232 (1975).
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(4) This compound is conveniently prepared in our laboratory by the mercury-sensitized photolysis of methyldichlorosilane.
(5) Lower temperatures favor **4** over **3**.
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(7) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **201**, 1365 (1971).
(8) Also obtained in this reaction are products whose gas chromatography–mass spectrum correspond to an isomeric mixture of adducts of **6** and **8**. These adducts have to date defied separation and conclusive identification.
(9) In the absence of acetylene trap the yield of **8** was 10–20%, while with added trap it was always <5%. Silazane **8** was identified by spectral methods (molecular ion at m/e 269; δ 0.05 and 0.18 (21 H, SiMe), 1.5 (m, 2 H, CH_2), 5.8–6.8 (m, 4 H, vinyl). The possibility that at least some of **8** arises from attack on **6**, rather than simple displacement on **3**, cannot be excluded at this time.
(10) A. J. Ashe and M. D. Gordon, *J. Am. Chem. Soc.*, **94**, 7595 (1972).

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Preparation of the endo-6-Acetoxy and endo-6-Hydroxy Derivatives of η^5-(1,3-Cyclohexadienyl)iron Tricarbonyl Fluoroborate
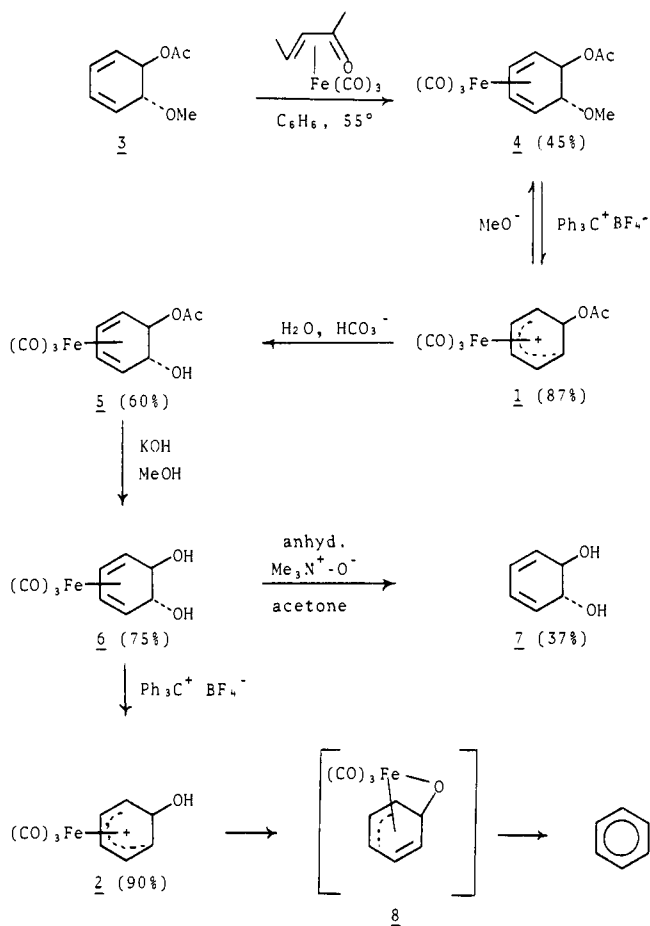
Sir:

We wish to report the stereospecific synthesis of η^5-(*endo*-6-acetoxy-1,3-cyclohexadienyl)iron tricarbonyl fluoroborate (**1**) and η^5-(*endo*-6-hydroxy-1,3-cyclohexadienyl)iron tricarbonyl fluoroborate (**2**). Since there are no previously reported cases of η^5-(1,3-cyclohexadienyl)iron tricarbonyl cations with a heteroatom substituent at C-6, it was of interest to determine whether **1** could be prepared as a stable salt in sufficient quantity to be useful as a synthetic intermediate. Salt **2** is particularly interesting since it represents a stable metal complex of the cationic intermediate in the rearrangement of oxepin–benzene oxide to phenol via the NIH shift,[1] and the complex shows no tendency to rearrange via the NIH shift pathway.

Methoxy acetate **3**[2] reacted with (3-penten-2-one)iron tricarbonyl[4] in benzene at 55 °C to afford η^4-(*endo*-5-acetoxy-*exo*-6-methoxy-1,3-cyclohexadiene)iron tricarbonyl (**4**) in 45% yield.[5,6] Only the one isomer was observed. Other workers have observed similar stereoselectivity with an ester function in the molecule and have suggested that the reaction proceeds by initial complexation of the intermediate metal carbonyl species with the ester carbonyl oxygen atom and subsequent intramolecular transfer of the metal atom to the same side of the molecule.[7,8] Reaction of **4** with trityl fluoroborate in methylene chloride afforded cation **1** in 87% yield.[6] The stereochemistry of **1** was established unambiguously by conversion of **1** to **4** with methoxide in methanol.[9]

Cation **1** reacted with water containing sodium bicarbonate to afford **5** (60%),[6] the ester group of which was hydrolyzed in methanolic potassium hydroxide to afford **6**.[6] Removal of the $Fe(CO)_3$ protecting group of **6** was effected with anhydrous trimethylamine *N*-oxide[11] to give the known diene diol **7** (37%).[3]

Reaction of **6** with trityl fluoroborate in methylene chloride afforded the fluoroborate salt of **2** (90%).[6,12] The fluoroborate salts of **1** and **2** are stable, crystalline substances that show no

s, 1 H, exchanged with D_2O), 3.95 (m, 1 H), 4.38 (br s, 1 H), 5.51 ppm (m, 2 H). **6**: IR (CHCl₃) 3590, 2060, 1985, 1005 cm⁻¹; NMR (acetone-d_6) δ 2.93–3.2 (m, 3 H, 1 exchanged with D_2O), 3.63 (br s, 1 H), 3.82 (m, 1 H), 3.94–4.36 (m, 1 H, exchanged with D_2O), 5.56 ppm (m, 2 H).

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(8) A. J. Birch and I. D. Jenkins in "Transition Metal Organometallics in Organic Synthesis", Vol. 1, H. Alper, Ed., Academic Press, New York, N.Y., 1976, p 1–82.

(9) Nucleophilic addition to η⁵-(1,3-cyclohexadienyl)iron tricarbonyl cation under normal conditions affords the exo product resulting from kinetic control, but exceptions have been observed.⁸ Addition of methoxide affords the exo product, but, under conditions of equilibration, isomerization to an equilibrium mixture (35% exo:65% endo) is observed.¹⁰ Similar results are observed with hydroxy,⁸ ethoxy,¹⁰ and malononitrile¹⁰ adducts.

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tendency to decompose on exposure to the atmosphere. When **2** is dissolved in acetone-d_6 containing a trace of water or in CD_3OD, effervescence is observed and, within 60 min, the salt has undergone quantitative conversion to benzene. No phenol or $Fe(CO)_3$ complex of cyclohexadienone is observed. We assume the decomposition occurs via **8**. A similar intermediate has been suggested for the formation of naphthalene from **9**.¹³
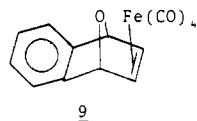
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(5) Reaction of **3** with Fe₃(CO)₁₂ gave **4** in 30% yield.

(6) Satisfactory analytical data have been obtained for 1 and 2. Complexes **4, 5**, and **6** are obtained as oils that undergo slow decomposition at room temperature. Spectral data for **1, 2**, and **4–6** follow. **1**: IR (KBr) 2110, 2060, 1975, 1730, 1235, 1050 cm⁻¹; UV max (EtOH) 216 nm (sh) (ε 24 800); NMR (CF₃CO₂H) δ 2.47 (s, 3 H), 4.26 (br d, 2 H, J = 7 Hz), 5.18 (br d, 1 H), 6.05 (br t, 2 H, J = 6 Hz), 7.36 ppm (br t, 1 H, J = 6 Hz). **2**: IR (Nujol mull) 2120, 2070, 1310, 1240, 1165, 1070 cm⁻¹; NMR (CF₃CO₂H) δ 4.23 (d, 2 H, J = 7 Hz), 4.62 (s, 1 H), 5.95 (t, 2 H, J = 6 Hz), 7.30 ppm (t, 1 H, J = 6 Hz). **4**: IR (CHCl₃) 2060, 1985 (br), 1728, 1371, 1240 cm⁻¹; UV max (EtOH) 216 nm (ε 14 000), 239 (8600); NMR (CDCl₃) δ 2.12 (s, 3 H), 3.00 (m, 2 H), 3.26 (s, 3 H), 3.64 (m, 1 H), 4.68 (m, 1 H), 5.50 ppm (m, 2 H). **5**: IR (CHCl₃) 2060, 1985, 1720, 1374, 1250, 1030 cm⁻¹; UV max (EtOH) 216 nm (ε 18 600), 244 (sh) (3800); NMR (CDCl₃) δ 2.13 (s, 3 H), 2.72–3.16 (m, 2 H), 3.36 (br,

Fluorescence from 2,2′-Bipyridine. Evidence for Covalent Hydrate Formation¹

Sir:

There are many tantalizing reports in the literature concerning anomalous properties of 2,2′-bipyridine (bipy) and its coordination complexes in aqueous solution.² Recently, a proposal has been made about possible formation of covalent hydrates by reaction of H_2O or OH^- with coordinated or free bipy to account for these anomalies.³ Some consideration has been given to the role these species may play in the ground-state chemistry of tris-bipy complexes of transition metals,⁴⁻⁶ and there is reason to believe that covalent hydration is implicated in some excited-state chemistry;⁷ a covalent hydrate intermediate has been proposed in the photochemistry of pyridine.⁸ However, up to this time, direct evidence for the formation of covalent hydrates of bipy has not been advanced, although covalent hydrate formation is well established for 1,3-diazanaphthalenes and other aromatic N heterocycles.⁹ In this paper we report spectral (absorption and emission) evidence for such species.

The ground-state absorption spectra of bipy free base (B), monocation (BH^+), and dication (BH_2^{2+}) and their associated acid–base equilibrium constants in aqueous solution ($pK_a(BH_2^{2+}) = -0.5$; $pK_a(BH^+) = 4.5$) are well documented.²ᵇ,¹⁰ The first strong absorption band of B with λ_{max} 281 nm in aqueous solution has been assigned as a $\pi-\pi^*$ transition.¹¹ An additional unassigned band at 306 nm, seen only in aqueous solution, has also been reported.¹² Figure 1 shows the absorption spectrum of bipy in neat CH_3CN and in an H_2O-rich CH_3CN solution at constant [bipy].¹³ Because the absorption band in the 308-nm region is seen only in the presence of H_2O, in neat or mixed aqueous solutions (CH_3CN/H_2O, CH_3OH/H_2O, DMF/H_2O), rather than showing a red shift in nonhydrogen bonding and nonpolar solvents,¹⁵ it cannot be assigned as an n-π^* transition of B.

No fluorescence is detected from solutions of bipy in neat DMF, CH_3CN, benzene, cyclohexane, methanol, or ethanol. In neat H_2O or a neutral solution of bipy in CH_3CN/H_2O (or CH_3OH/H_2O or DMF/H_2O), a strong, structured emission is observed with λ_{max} 328 nm (Figure 2, lower curve) which increases in intensity with increasing mole fraction of H_2O.