Table I. Hfscs Observed in ENDOR Spectra of Spin Adducts in MHz

Adduct	β H	R[a]	Phenyl and *tert*-butyl
Methyl	10.20	1.41	0.40
Trideuteriomethyl	10.20		0.40
n-Butyl	10.36	1.33	0.41
Phenyl	5.67	0.47	0.47
Benzoyloxy	3.42	0.40	0.40

[a] R denotes adding group.

vation of the hfs of the adding group by means of electron nuclear double resonance (ENDOR) technique makes the assignment more accurate because of the characteristic ENDOR pattern for each spin adduct.

The addition of organolithium and Grignard compounds to the nitrone followed by air oxidation produces the corresponding nitroxide in high yield. This method has been sometimes used for the identification of spin adducts.[2] Most of the adducts used for the present study were synthesized by this method.

The ENDOR spectrum of methyl adduct of PBN in toluene shows three kinds of hfs from the hydrogens in it (Figure 1a). The largest hfs (10.20 MHz) is due to the β hydrogen which can be seen in the ESR spectrum. The hfs of the two groups of hydrogens which are hidden in the line width of the ESR spectrum appear in this spectrum around free proton frequency region. The trideuteriomethyl adduct shows only one hfs other than the β hydrogen which is shown in Figure 1b. The hfs of 1.41 MHz which appears in the spectrum of the methyl adduct completely disappears. This is because the frequency region of the present ENDOR spectrometer does not cover the resonance frequency of deuteron. The disappearance of the hfs in Figure 1b shows that 1.41 MHz hfs in Figure 1a can be ascribed to the methyl group of the adduct. The smallest hfs should be assigned to residual protons in phenyl and *tert*-butyl groups. The *n*-butyl adduct also produces a similar ENDOR pattern as methyl adduct (Figure 1c). The splitting of 1.33 MHz can be assigned to methylene hydrogens in the *n*-butyl group by analogy to the methyl adduct.

The phenyl adduct shows a rather different ENDOR pattern (Figure 1d). Around the free proton frequency region only one hfs is observed. The result is consistent with the fact that the hfs of the protons in the phenyl group in the methyl and *n*-butyl adducts is small. The small hfs of the phenyl protons in the phenyl adduct causes the overlap of the splitting from 19 hydrogens in phenyl and *tert*-butyl groups. The fact that the line width of the ESR spectra of alkyl spin adducts is usually wider than that of phenyl adduct is explainable by the larger hfs of the alkyl group.

Figure 1e shows the ENDOR spectrum in the thermal decomposition of benzoyl peroxide in the presence of PBN in toluene. The spectrum pattern around free proton frequency is similar to that of the phenyl adduct. However, the β hydrogen splitting is considerably smaller (3.42 MHz). This adduct has already been assigned to benzoyloxy adduct by Janzen and Blackburn.[3] The result of ENDOR does not contradict this assignment because the benzoyloxy group does not have significant hfs. The observed hfs of spin adducts determined by ENDOR are listed in Table I.

Actual radical reaction systems do not usually give a high enough concentration of spin adduct for the observation of a ENDOR spectrum. Presently the ENDOR technique is applicable only to limited examples of spin trapping systems because of the relatively low concentrations of spin adducts. Improvements in the experimental conditions of ENDOR are now in progress.

Throughout the observation of ENDOR spectra the optimum signal appeared at relatively higher temperatures (−30∼−50 °C) for protons which have smaller hfs and at lower temperatures (−60∼−90 °C) for β hydrogens. The external magnetic field was fixed at the central peak of the ESR spectrum during the sweep of the radiofrequency.

Details of the ENDOR spectrometer used are described elsewhere.[4]

References and Notes

(1) For reviews of this technique see E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971); C. Lagercrantz, *J. Phys. Chem.*, **75**, 3466 (1971); M. J. Perkins, *Chem. Soc. Spec. Publ.*, **No. 24**, 97 (1970).

(2) The magnitude of hfs of β hydrogen range ~2–3 G.

(3) E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, **91**, 4481 (1969).

(4) Y. Kotake and K. Kuwata, *Bull. Chem. Soc. Jpn.*, **45**, 2263 (1972).

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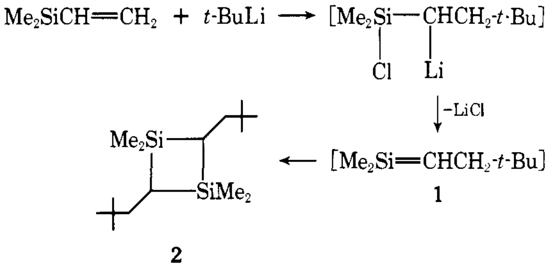
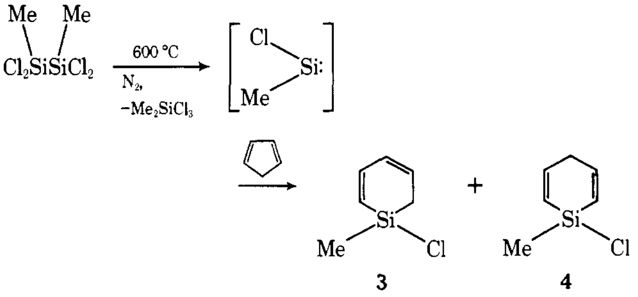
Evidence for the Generation and Trapping of a Silabenzene

Sir:

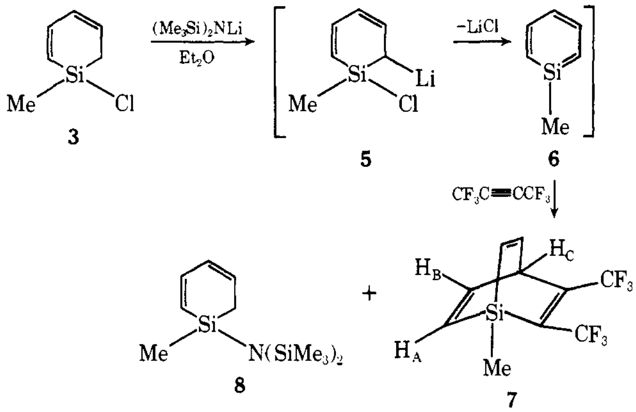
Jones and Lim[1] have recently reported that the addition of *tert*-butyllithium to vinyldimethylchlorosilane resulted in products presumably arising from silene (**1**) intermediacy. Formation of dimer **2**, coupled with the inability to trap the intermediate α-halosilyl carbanion with excess trimethylchlorosilane, strongly suggests the formation of **1** in this reaction.



We now wish to report a similar reaction which appears to proceed through the intermediacy of a long-awaited silabenzene.[2] Silacyclohexadienes are most conveniently prepared through the reaction of silylenes (the silicon analogues of carbenes) and cyclopentadiene with concomitant ring expansion.[3] Thus copyrolysis at ~600 °C (N_2 flow) of 1,1,2,2-tetrachloro-1,2-dimethyldisilane[4] and cyclopentadiene produced a mixture of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene (**3**, major isomer) and the nonconjugated isomer (**4**, minor)[5] which could be separated by preparative GC.



Metalation of silacyclohexadienes with alkyllithium to produce the corresponding pentadienyl anion is a well-established process.[6] Thus we thought to generate a silabenzene 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**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (Grant GM 16689) for their support of this work.

References and Notes

(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).

(3) E. A. Chernyshev, N. G. Komalenkova, and S. A. Bashkirova, *Dokl. Akad. Nauk SSSR*, **205**, 868 (1972); R.-J. Hwang, R. T. Conlin, and P. P. Gaspar, *J. Organomet. Chem.*, **94**, C38 (1975).

(4) This compound is conveniently prepared in our laboratory by the mercury-sensitized photolysis of methyldichlorosilane.

(5) Lower temperatures favor **4** over **3**.

(6) P. Jutzi, *Z. Naturforsch.*, **24b**, 354 (1969); *J. Organomet. Chem.*, **22**, 297 (1970); G. Märkl and P. L. Merz, *Tetrahedron Lett.*, 1303 (1971); E. A. Chernyshev et al., *Zh. Obshch. Khim.*, **44**, 226 (1974).

(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