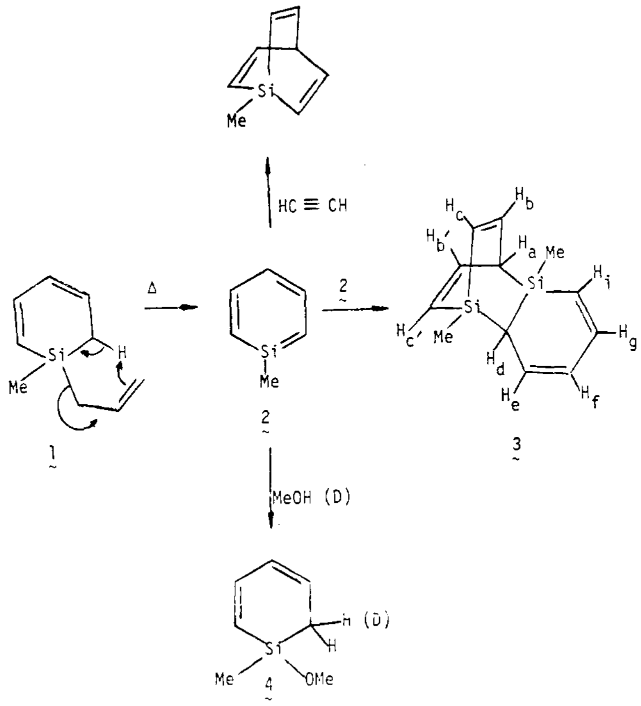
Spectroscopic Observation of Matrix-Isolated Silatoluene[1]

Sir:

In 1978, the first unambiguous evidence for the existence of a silabenzene was reported.[2] Evidence that 5-methyl-5-allyl-5-silacyclohexa-1,3-diene (**1**) underwent a thermally induced retro-ene extrusion of propene to afford silatoluene (**2**) included both precedent for such a process on silicon[3] and trapping of **2** by acetylenes. Subsequent to that report we have found that, in the absence of trapping agents, vacuum-flow pyrolysis (640 °C, 3×10^{-5} Torr, 18% isolated) of **1** yields the Diels–Alder dimer **3**[5] of **2** rather than the [2 + 2] dimer which had been predicted.[4]



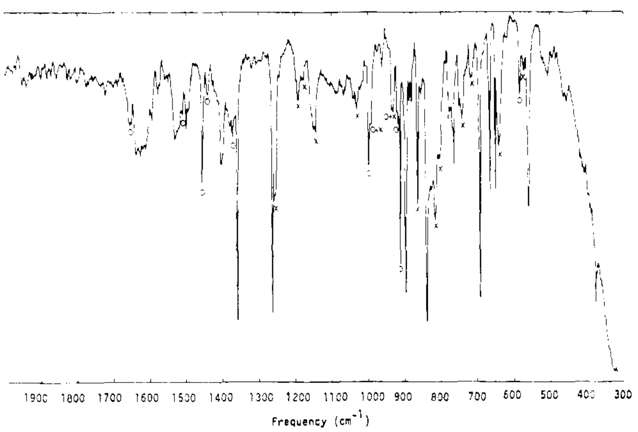


Figure 1. Infrared spectrum of silatoluene matrix isolated in argon at 23 K. Bands marked X are due to 5-methyl-5-allyl-5-sila-1,3-cyclohexadiene (**1**) and bands marked O are due to propene.

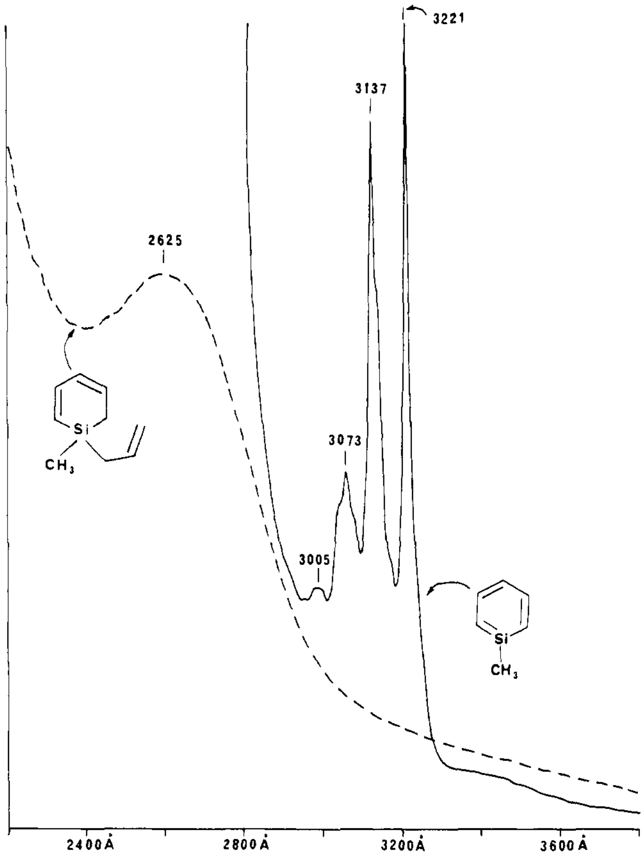


Figure 2. Ultraviolet spectra of silatoluene and the precursor (**1**) matrix isolated in argon at 26 K.

We report now the first spectroscopic evidence for a silabenzene.[6] Pyrolysis of **1** was accomplished either by passing a mixture of **1** in argon (1:500, v/v) through an evacuated quartz tube (5×10^{-6} Torr) heated to 610 °C, or by allowing **1**, cooled to −41 °C, to slowly vaporize through a 730 °C tube and mix with argon (1:250 to 1:1000, v/v) upon exit from the hot zone. To obtain the infrared spectrum, this mixture was deposited on a CsI window cooled to 23 K. Analysis of the resulting spectrum (Figure 1) and comparison with the spectra of matrix-isolated authentic samples revealed that both propene and the starting diene (**1**) were present. The additional bands are attributed to silatoluene (1530, 1500, 1410, 1360, 1268, 980, 965, 900, 890, 883, 842, 770, 697, 655, 563 cm^{-1}). No definitive assignments of these bands to specific vibrations are possible at this time.

To obtain the ultraviolet spectrum, the argon-diluted pyrolysis mixture was deposited on a sapphire window cooled to 26 K. While matrix-isolated **1** showed only one UV maximum at 2625 Å, the spectrum of the matrix-isolated pyrolysis mixture (Figure 2) possessed much longer wavelength absorption with considerable, well-resolved vibrational structure,[7] as would be expected for the electronic transition corresponding to the ${}^1L_b \leftarrow {}^1A$ (${}^1B_{2u} \leftarrow {}^1A_{1g}$) band in benzene. The bathochromic shift to 310 nm (relative to benzene, 256 nm) is in accord with expectation based on calculations for silabenzene.[4,8] The UV spectrum of **2** is in good agreement with the prediction[4,8] that silabenzene would be an aromatic system.

Conclusive evidence for the presence of **2** in the matrix was obtained by methanol trapping. Copyrolysis of **1** and methanol (456 °C, nitrogen flow, vertical, quartz-packed tube) gave 5-methoxy-5-methyl-5-silacyclohexa-1,3-diene (**4**) in 45% yield.[9] It was shown that **4** arises from 1,2 addition to **2**, rather than methanolysis of **1**, by performing the copyrolysis with MeOD, and obtaining only **4** with one methylene proton replaced by deuterium.[10] It is of considerable interest to note that **4** is also obtained (albeit in considerably reduced yield) when a flow pyrolysis of neat **1** is conducted with MeOH in a trap located ~20 cm downstream of the heating zone. After these experiments were performed, the flash pyrolysis and matrix isolation of **1** was repeated, and IR analysis showed the presence of silatoluene (**2**), propene, and **1**. The matrix was then coated with a layer of methanol (ca. half the thickness of the argon layer) and the CsI window was slowly warmed. At 180 K the deposited material completely evaporated, and the products were isolated in a liquid nitrogen cooled trap. Analysis by GC-MS revealed only two major components, methoxysilane **4** and **1** in a 1:12.5 ratio. Both components had identical retention times and mass spectra with those of authentic samples. Silatoluene (**2**) was stable to UV irradiation in the argon matrix. Warming the matrix produced a polymer which we did not characterize.

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References and Notes

(1) Portions of this work have been presented at the A. C. Cope Award Symposium, 176th National Meeting of the American Chemical Society, Miami, Fla., Sept 1978 (O. L. Chapman), and in a plenary lecture at the 5th International Symposium on Organo-Silicon Chemistry, Karlsruhe, West Germany, Aug 1978 (T. J. Barton).

(2) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978,** *100,* 5246.

(3) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978,** *100,* 1630–1632.

(4) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975,** *97,* 1311–1318.

(5) Spectral data: NMR (CCl_4) δ 0.12 (s, 3 H, SiMe), 0.57 (s, 3 H, SiMe), 0.80 (d, J_{de} = 6 Hz, collapses to s with $h\nu$ at δ 6.04, 1 H_d), 3.66 (overlapped d of d of d of d, 1 H_a, $J_{ab} \sim J_{ab'} = 7$, $J_{ac} \sim J_{ac'}$ = 2 Hz, collapses to broad s with $h\nu$ at δ 7), 6.04 (d of d, $J_{ef} = 10$, J_{de} = 6 Hz, collapses to d with $h\nu$ at δ 0.8, 1 H_e), 7.09 and 6.93 (each d of d, $J_{bc} \sim J_{b'c'}$ = 12 Hz, each collapses to a d with $h\nu$ at δ 3.66, 1 H_b and 1 $H_{b'}$), 6.60 (d of d, $J_{gi} = 6$, J_{fg} = 14 Hz, 1 H_g), 5.52–5.93 (partially resolved m, 4 H, H_c, $H_{c'}$, H_i, H_f); mass calcd for $C_{12}H_{16}Si_2$ 216.07906, measured *m/e* 216.07909, base peak *m/e* 108.

(6) Professor H. Bock has now obtained the photoelectron spectrum of **2** in the gas phase (private communication).

(7) The UV bands observed for **2** under conditions for maximum resolution are at 3228, 3225, 3221.5, 3218, 3214, 3210, 3185, 3181.5, 3178, 3163, 3160, 3156.5, 3153.5, 3149.5, 3139, 3135, 3132, 3129, 3124.5, 3120, 3115.5, 3095.5, 3093, 3090, 3086.5, 3078.5, 3075, 3071.5, 3069, 3065.5, 3062.5, 3060, 3054, 3050.5, 3046.5, 3042, 3039, 3012, 2998, 2973, and 2935 Å. Figure 2 shows the UV spectrum under lower resolution conditions to save space.

(8) Schlegel, H. B.; Coleman, B.; Jones, J., Jr. *J. Am. Chem. Soc.* **1978,** *100,* 6499–6501.

(9) Spectral data: NMR (CCl_4) δ 0.17 (s, 3 H, SiMe), 1.56 (m, 2 H, $SiCH_2C{=}$), 3.37 (s, 3 H, OMe), 5.95 (m, 3 H, vinyl), 6.95 (m, 1 H, vinyl); mass calcd for $C_7H_{12}SiO$ 140.0658, measured *m/e* 140.0652.

(10) Comparison of the relative intensities of the *m/e* 141 and 126 (loss of methyl) ions shows 93% deuterium incorporation; calcd for $C_7H_{11}DSiO$ 141.07202, measured *m/e* 141.07203.

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Conversion of the Cyanocyclohexadienyl Ligand in the Cation $[(\eta^5\text{-}RC_6H_5CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^+$ (R = H or Me) into a π-Cyanoarene Ligand. Electrochemical Evidence for a Two-Electron Oxidation–Proton Elimination Mechanism

Sir:

The addition of a nucleophile to a π-complexed arene ligand to give a cyclohexadienyl transition metal complex is a well-established reaction.[1] Further reaction with a strong oxidizing agent in the case of cyclohexadienyl complexes derived from a carbon nucleophile has proved useful for the synthesis of free, substituted arenes.[2] The latter reaction suggested to us that complexes containing a substituted π-arene ligand might also be synthesized by the oxidation of a cyclohexadienyl complex under controlled conditions. Such a reaction would be useful for the synthesis of substituted π-arene complexes not obtainable by conventional methods and might also lead to the establishment of a general mechanism for the direct nuclear substitution of arenes catalyzed by transition metal complexes. We report here the novel conversion of a cyanocyclohexadienyl ligand in the cation $[(\eta^5\text{-}RC_6H_5CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^+$ (R = H or Me) into a π-cyanoarene ligand along with electrochemical evidence for a two-electron oxidation–proton elimination mechanism.

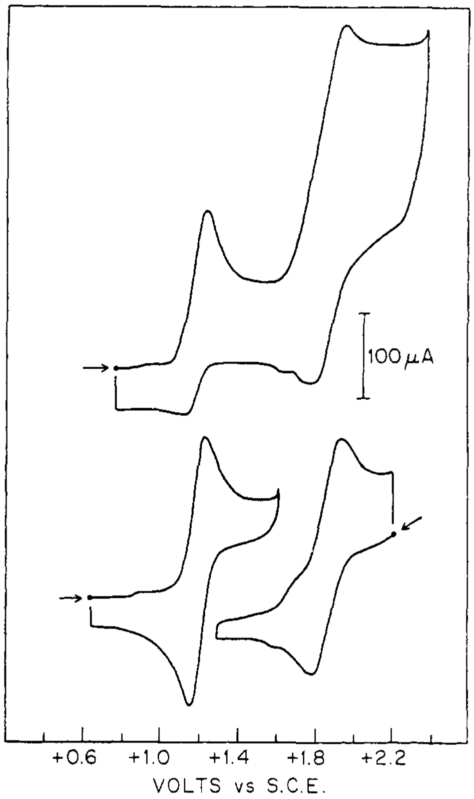

Figure 1. Cyclic voltammogram for the oxidation of $[(\eta^5\text{-}C_6H_6CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}C_6H_6)]^+$ in 0.1 M $(Et_4N)PF_6$-propylene carbonate at Pt vs. SCE (25 °C). The scan rate is 200 mV/s.

The previously reported cation $[(\eta^6\text{-}RC_6H_5)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^{2+}$ (R = H or Me) (**1**)[3] adds 1 equiv of the sodium salts of the nucleophiles ^-CN and ^-OMe in acetonitrile solution affording a stable cation of the type $[(\eta^5\text{-}RC_6H_5Nu)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^+$ (**2**) in essentially quantitative yield.[4]

The cyclic voltammogram of **2** (R = H; Nu = CN) at a platinum electrode in propylene carbonate with $(Et_4N)PF_6$ as supporting electrolyte is shown in Figure 1. A partial scan (lower curve) shows a reversible oxidation wave with $E_{1/2}$ = +1.17 V vs. SCE. Coulometry showed that this wave is associated with a one-electron transfer. Exhaustive electrolysis of the cyanide adduct at a controlled potential of +1.3 V in propylene carbonate gave a dark red solution which on standing for several hours at 25 °C reverted back to the original orange color. A cyclic voltammetry investigation on the solution immediately after exhaustive electrolysis indicated that the oxidation product $[(\eta^5\text{-}RC_6H_5CN)Mo(\mu\text{-}SMe)_4Mo(\eta^6\text{-}RC_6H_5)]^{2+}$ (**3**) has a half-life of at least 1 h at 25 °C. Workup of the solution after the red color had disappeared afforded **1** in high yield along with ~0.5 equiv of HCN which was distilled from the solvent on a high vacuum line and identified by its mass spectrum. The above observations are consistent with a mechanism in which a cyano radical is slowly eliminated from **3** giving **1**. Hydrogen abstraction from the solvent by the reactive cyano radical would then account for the HCN formed. IR studies showed that small quantities of solid cyano compounds are also formed in the reaction; however, these products have not yet been identified. A second one-electron

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