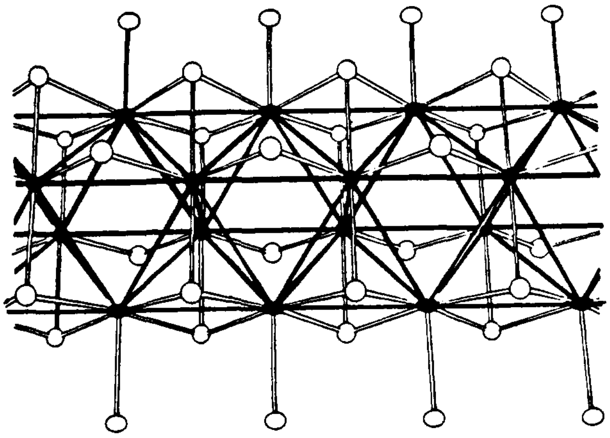
Chart I



A

at each vertex: $M_6(\mu_2\text{-}X)_{12}X_6$.[14]

The ^{1}H NMR spectrum of I recorded in benzene-d_6 at 22 °C, 500 MHz, reveals the presence of 13 O-*i*-Pr groups. Specifically, there are 12 septets (one signal of twice the intensity of the rest due to degeneracy) for the methyne protons. In addition, in the range δ 15–9 there are five signals assignable to hydride ligands. Each resonance shows coupling to ^{183}W ($I = {}^1/_2$, 14.5% natural abundance). From the relative intensities of the satellite spectra, we infer that one hydride is terminal (δ 10.01, $J_{^{183}W-^1H} = 130$ Hz) and four are edge bridging. The ^{183}W–^{1}H coupling constants for the bridging hydrides ($J_{W-H} = 88$–104 Hz) are comparable in magnitude to those observed for $[W_2(\mu\text{-H})(O\text{-}i\text{-Pr})_7]_2$[4b] and $W_2(\mu\text{-H})(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)$.[5] Two of the hydrides show a significant ^{1}H–^{1}H coupling, $J = 10.5$ Hz, and we suggest that those hydride ligands are mutually trans and occupy bridges between W(1)–W(4) and W(3)–W(4). The proposed disposition of μ-H ligands, with three on one face of the W_6 octahedron, generates only one such trans arrangement. By application of the program XHYDEX and the assumed W–H and W–μ-H distances given by Orpen,[15] each of these sites was found to be perfectly acceptable.

In conclusion, we have discovered the first of a potentially significant class of tungsten(III) alkoxide clusters, namely, that based on a W_6^{18+} octahedron. The specific presence of five hydrides and 13 alkoxides leads us to believe that other members of the family $W_6(H)_x(OR)_y$ where $x + y = 18$ will be discovered subsequently.

Finally it is worth noting that in many of the ternary oxides of molybdenum and tungsten in their lower oxidation states there are isolated or fused octahedral M_6 cluster units that bear a striking resemblance to the $W_6(H)_5O_{13}$ core found here. For example, a segment of one of the $[Mo_4O_6^-]_\infty$ chains in $NaMo_4O_6$ is shown in A (Chart I), where the dark and unshaded spheres represent Mo and O atoms, respectively.[16]

Further studies are in progress.[17]

Supplementary Material Available: VERSORT drawings, stereoviews, ORTEP drawings, atomic coordinates, anisotropic thermal parameters, complete listing of bond distances and bond angles, and NMR data for I (26 pages); listing of F_o and F_c values (16 pages). Ordering information is given on any current masthead page.

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(14) This is a common structure for lower valent metal halides of niobium and tantalum: Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 19 and references therein. The halides $W_6(X)_{12}X_6$, where X = Cl and Br, have been prepared by halogenation of the $W_6(X)_8X_4$ compounds and are presumably members of this structural family: Lange, U.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1986**, *542*, 207.

(15) Orpen, G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2509 and references therein.

(16) McCarley, R. E. In *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Ed.; Texas A&M University Press: College Station, 1989 and references therein.

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Electron Impact Ionization of Phenylsilane. Evidence for the Formation of Phenylsilyl and Silacycloheptatrienyl Cations

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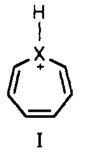
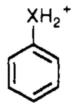
Since the original suggestion by Mayerson and co-workers[1] that hydrogen atom loss from the molecular toluene cation results in the formation of the cycloheptatrienyl cation (Ia), a number of studies[2] have attempted to elucidate the structure, energetics, and modes of formation of $C_7H_7^+$ isomers. It is now well understood that electron impact ionization of toluene yields both Ia and IIa. The relative yield of the two isomers is dependent on the internal energy content of the molecular toluene cation.[2a,f,i,j,m,n]



I

a: X = C
b: X = Si



II

a: X = C
b: X = Si

Interestingly, Fourier transform ion cyclotron resonance spectrometric studies[3] in our laboratory of the reactions of $C_6SiH_7^+$ (formed by electron impact ionization of phenylsilane) with the parent neutral indicate that this ion may be formed in two isomeric forms which are noninterconverting at room temperature.[4] As can be seen from Figure 1a, the abundance of $C_6SiH_7^+$ decays initially and then becomes constant at longer times. The initial decay of $C_6SiH_7^+$ is due to reaction process 1. Isolation of

$$C_6SiH_7^+ + C_6H_5SiH_3 \rightarrow C_{12}SiH_{11}^+ + SiH_4 \qquad (1)$$

$C_{12}SiH_{11}^+$ in neutral phenylsilane does not yield $C_6SiH_7^+$. Further, isolation of $C_6SiH_7^+$ at long times indicates that it is unreactive. These observations suggest that $C_6SiH_7^+$ consists of a reactive and an unreactive population of ions. In this communication, we provide evidence that suggests that the unreactive and reactive $C_6SiH_7^+$ ions are two structurally distinct forms of the ion: the

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(3) (a) The technique of ion cyclotron spectrometry and its chemical applications are discussed in the following: Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (b) FT-ICR spectrometry is reviewed in the following: Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316.

(4) At least on the order of seconds.

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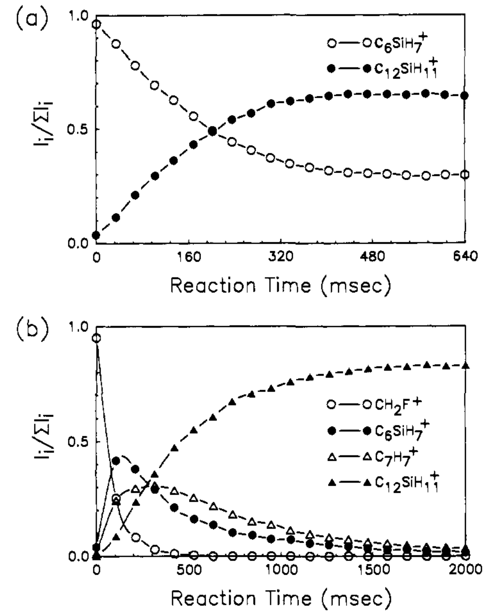

Figure 1. (a) Temporal variation of ion abundances following the isolation of $C_6SiH_7^+$ in phenylsilane at a pressure of 1.8×10^{-7} Torr (approximate value). The electron impact ionization energy was 20 eV. (b) Temporal variation of ion abundances following the isolation of CH_2F^+ in a 1:6 mixture of phenylsilane and CH_3F at a total pressure of 6.2×10^{-7} Torr (approximate value). The electron impact ionization energy was 30 eV. For purposes of clarity, in both the figures minor products arising from side reactions are not shown. These ions are, however, included in the total ion count.

silacycloheptatrienyl (Ib) and the phenylsilyl (IIb) cations.

Figure 1b shows the temporal variation of ion abundances following the isolation of CH_2F^+ in a 1:6 mixture of phenylsilane and CH_3F at a total pressure of $\sim 6 \times 10^{-7}$ Torr. Besides CH_2F^+, the other ions that participate in the reaction processes are $C_7H_7^+$, $C_6SiH_7^+$, and $C_{12}SiH_{11}^+$. Standard double resonance ion ejection techniques[5] enabled reaction processes 1-5 to be identified.

$$CH_2F^+ + C_6H_5SiH_3 \longrightarrow C_6SiH_7^+ + CH_3F \qquad (2)$$

$$CH_2F^+ + C_6H_5SiH_3 \longrightarrow C_7H_7^+ + SiH_3F \qquad (3)$$

$$C_7H_7^+ + C_6H_5SiH_3 \longrightarrow C_6SiH_7^+ + C_7H_8 \qquad (4)$$

$$C_6SiH_7^+ + CH_3F \longrightarrow C_7H_7^+ + SiH_3F \qquad (5)$$

Isolation of $C_6SiH_7^+$ produced by electron impact ionization of phenylsilane in the same mixture of phenylsilane and CH_3F indicates that the fraction of $C_6SiH_7^+$ which is unreactive with phenylsilane is unreactive with CH_3F as well, while the reactive fraction of $C_6SiH_7^+$ is seen to undergo both reactions 1 and 5. These observations strongly suggest that $C_6SiH_7^+$ generated by reaction 2 is the same reactive species generated from phenylsilane by electron impact. In a mixture of CF_4 and phenylsilane, the reactive isomer of $C_6SiH_7^+$ is exclusively generated by the reaction channel of CF_3^+ with phenylsilane which is analogous to process 2. It is entirely reasonable that "soft" chemical ionization processes such as hydride abstraction (by CH_2F^+, $C_7H_7^+$, and CF_3^+) are likely to generate the phenylsilyl cation. We therefore, propose that the reactive isomer of $C_6SiH_7^+$ is the phenylsilyl cation (IIb).

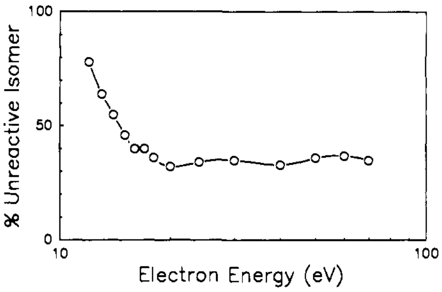

Figure 2. Variation of the percentage of the unreactive $C_6SiH_7^+$ isomer as a function of electron impact ionization energy (uncorrected) of phenylsilane at a pressure of 5.5×10^{-8} Torr (approximate value). The fraction of the unreactive $C_6SiH_7^+$ isomer is defined as the ratio of the steady-state (measured between 1500 and 2000 ms) abundance of $C_6SiH_7^+$ to the abundance of $C_6SiH_7^+$ measured 5 ms after the electron beam pulse. The width of the electron beam pulse was ~20 ms.

From Figure 2 it can be seen that the unreactive isomer of $C_6SiH_7^+$, which is the dominant product at electron energies below 14 eV, decreases monotonically until the ratio of the unreactive to reactive isomers attains a constant value of ~0.5 at electron energies greater than 20 eV. Such behavior is qualitatively similar to the analogous process in toluene (as studied by ion cyclotron resonance spectrometric techniques[2l,m]), where the ion analogous to the unreactive isomer of $C_6SiH_7^+$ is Ia ($\Delta H_f \approx 206$ kcal mol^{-1} [6]) while the ion analogous to the reactive isomer of $C_6SiH_7^+$ is IIa ($\Delta H_f \approx 217$ kcal mol^{-1} [6]). This leads us to propose that the unreactive isomer of $C_6SiH_7^+$ is the silacycloheptatrienyl cation (Ib). The greater yield of Ib at low electron impact energies indicates that it is perhaps more stable than IIb. Further studies are in progress in our laboratory to quantitatively determine the relative stabilities of the $C_6SiH_7^+$ isomers and the energetics of their interconversion.

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Registry No. Ib, 139732-71-1; IIb, 139732-72-2; $PhSiH_3$, 694-53-1; CH_3F, 593-53-3; CF_4, 75-73-0.

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An Unusually Rapid Intramolecular General-Base Catalysis. Relevance to Enzymology

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Intramolecular general-base catalyses are notoriously inefficient;[1] "effective molarities" in organic systems rarely exceed 10 M. Contrast this with chymotrypsin, an enzyme that operates via a general-base mechanism worth 10^8 in rate acceleration.[2] Few comparisons in bioorganic chemistry are more humbling.

We have proposed that enzyme-like rates are possible when two reactive species are held rigidly at "contact distances" too short to accommodate intervening solvent.[3] The question arose whether "spatiotemporal" factors could, in part, also explain the general-base disparity between enzymes and their chemical models. An opportunity to explore this possibility arose when an article by R. L. Harlow et al.[4] came to our attention half a decade after its publication.

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