with other adducts,[3-5] cycloaddition of **2** to C_{60} occurs across a 6,6 ring junction of the framework. The average bond lengths for the 5,6- and 6,6-junctions in the C_{60} framework, other than those related to atoms connected to C(30) and C(31), are 1.43 (4) and 1.39 (4) Å, respectively, in good agreement with the observed values for the osmylated and platinum complexes.[3b,4b] The four sp^2–sp^3 bond lengths C(22)–C(30), C(29)–C(30), C(31)–C(32), and C(31)–C(39) average 1.52 (4) Å, and the C(30)–C(31) bond length is 1.62 (4) Å. These values reproduce almost exactly those of the osmate adduct.[3b] It seems likely that the length of the C(30)–C(31) bond is greatly increased because the overall bending deformation of the sp^3 angles at C(30) and C(31) is accommodated at the cost of increased bond stretching. Figure 1 shows that the cyclohexene unit defined by C(30)–C(31)–C(61)–C(62)–C(63)–C(64) is clearly in a stable boat conformation. The ground-state conformation of cyclohexenes is generally a C_2-symmetrical half-chair.[14a] The angle between the two mean planes defined by C(61)–C(31)–C(30)–C(64) and C(61)–C(62)–C(63)–C(64) is 135.0 (3)°, and the corresponding dihedral angles are planar within ±5°.

The UV/vis spectrum of **1**[12] has absorption features virtually identical with those of the related dioxirane adduct.[5g] The LD-TOF mass spectrum of **1** shows that our working hypothesis is valid:[12] the parent ion P ($m/z = 1004$), although weak relative to that of C_{60} ($m/z = 720$), is clearly observed in contrast to other Diels-Alder adducts.[6,7,10] In the ^{13}C NMR spectrum of **1**,[12] the fullerene region of the spectrum (140–150 ppm) has three peaks corresponding to two carbon atoms and 11 corresponding to four carbon atoms (a broad signal at 145.9 ppm integrates to 12 carbons). The C(30) and C(31) carbon atoms appear at 66.3 ppm and the CH_3 and CH_2 groups at 18.0 and 42.1 ppm, respectively. Five signals are observed for the three tertiary and four quaternary aromatic carbon atoms of the diene component in the binary solvent systems used ($CS_2/CDBr_3$ and CS_2/acetone-d_6). However, the relative intensities of these peaks (for carbons with similar environments) imply overlap of some of the absorptions. Interestingly, the 500-MHz ^1H NMR spectrum of **1** at 26 °C displays a broad doublet centered at 4.73 ppm for the two methylene protons. The doublet coalesces at 35 °C, reflecting conformational exchange between the two boat forms of the molecule (the methyl groups appear as a sharp singlet at 2.29 ppm). Variable temperature experiments reveal that the ring inversion is in the slow exchange region below −20 °C, giving an AB quartet with a chemical shift difference of 94.8 Hz ($J = 13.8$ Hz).[15] Our experiments yield an activation energy $\Delta G^{*} = 14.6 \pm 0.1$ kcal/mol for the boat-to-boat barrier of inversion in **1**. If the transition state for this inversion is planar, the barrier is substantially higher than the calculated (MM3)[16] potential energy difference between the boat and planar conformations of cyclohexene (7.5 kcal/mol).[14] The high barrier of inversion in **1** can be attributed to severe torsional and angular constraints imparted by the rigidity of the C_{60} backbone.[17] Experimental and theoretical studies with model compounds are under way to further assess the origin of this effect.

Acknowledgment. We thank Professors Frank A. L. Anet, Craig A. Merlic, and Robert L. Whetten at UCLA for helpful discussions and the UCLA College of Letters and Sciences for a New Faculty Grant.

Supplementary Material Available: Experimental details of the crystal structure determination for **1**, fully labeled view of the structure, and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (15 pages); listing of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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Generation and Characterization of Isomeric Iron–Silylene and Iron–Silene Cationic Complexes in the Gas Phase

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Transition metal–silylene complexes ($L_nM{=}SiR_2$) are postulated intermediates in a number of transition metal-mediated transformations, including Rochow's direct process,[1] catalytic redistribution of silanes,[2] various silylene-transfer reactions,[3] and dehydrogenative coupling reactions of silanes with transition metals.[4,5] Although transition metal–carbene, –germylene, –stannylene, and –plumbylene complexes are well-known, the corresponding transition metal–silylene species have been synthetically elusive with silylene complexes being only recently generated and characterized.[6-8] The related transition metal–silene complexes ($L_nM(R_2Si{=}CR_2)$) have been proposed as intermediates in metal-mediated rearrangements of organosilicon ligands,[9,10] including β-hydrogen transfer of a bound silyl group.[9a,11] Stable transition metal–silene complexes have recently been synthesized and characterized.[12,13] The difficulty in synthesizing

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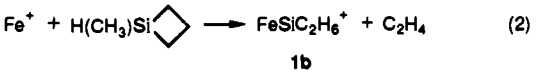
stable metal–silene and –silylene complexes has prevented detailed studies concerning their involvement in organosilane chemistry. In this report we describe the first examples of generation and characterization of isomeric iron–silylene and –silene cationic complexes ($FeSiCH_4^+$ and $FeSiC_2H_6^+$ isomers) in the gas phase.

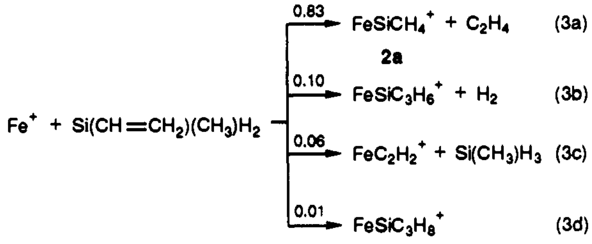
Experiments were performed on a Nicolet FTMS-1000 Fourier transform mass spectrometer.[14–16] Fe^+ was generated by laser desorption/ionization from a high-purity iron foil.[17] Precursor organosilanes were admitted into the vacuum chamber at either a static pressure or by a pulsed solenoid inlet valve.[18] A static argon pressure of 1×10^{-5} Torr was maintained throughout these experiments and served both to facilitate ion thermalization prior to reaction and as the target for collision-activated dissociation (CAD).[19,20]

$FeSiC_2H_6^+$ ions are generated exclusively by reactions 1 and 2. $Si(CH_3)_2D_2$ yields exclusive loss of D_2 with Fe^+, suggesting formation of a silylene complex, $Fe{=}Si(CH_3)_2^+$.[21] Reaction 2 may produce the corresponding silene complex, $Fe(H(CH_3)Si{=}CH_2)^+$, by initial insertion into a strain-weakened Si–C bond[22] to yield a silametallacyclopentane[23] followed by ethene extrusion.[24] Although Fe^+ is inert with $Si(CH_3)H_3$,[21] $FeSiCH_4^+$ is produced by reactions 3a and 4.[25] Reaction 3a may produce either a silene or a silylene complex, depending on the mechanism for ethene elimination. By analogy to reaction 2, a silene complex, $Fe(H_2Si{=}CH_2)^+$, is presumably formed in reaction 4. Exclusive loss of C_2H_4 with 1-silacyclobutane-*1,1-d*$_2$, reaction 5, is consistent with silene formation in reaction 4.

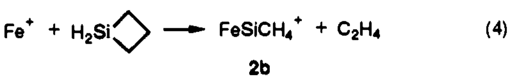
$$Fe^+ + Si(CH_3)_2H_2 \longrightarrow \underset{\mathbf{1a}}{FeSiC_2H_6^+} + H_2 \qquad (1)$$



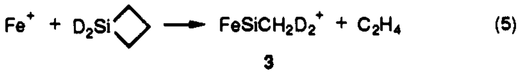
1b (2)



$$Fe^+ + Si(CH{=}CH_2)(CH_3)H_2 \begin{cases} \xrightarrow{0.83} \underset{\mathbf{2a}}{FeSiCH_4^+} + C_2H_4 & (3a) \\ \xrightarrow{0.10} FeSiC_3H_6^+ + H_2 & (3b) \\ \xrightarrow{0.06} FeC_2H_2^+ + Si(CH_3)H_3 & (3c) \\ \xrightarrow{0.01} FeSiC_3H_8^+ & (3d) \end{cases}$$



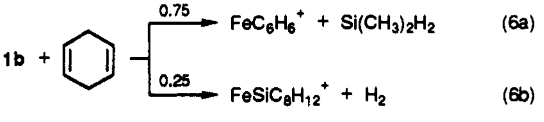
2b (4)



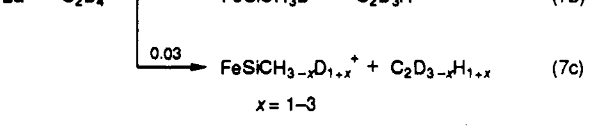
3 (5)

Structures of $FeSiCH_4^+$ and $FeSiC_2H_6^+$ ions were probed by both CAD and ion/molecule reactions. **1a** and **1b** yield identical CAD breakdown curves as well as **2a** and **2b**. This similarity implies that either common structures are formed for $FeSiCH_4^+$ and $FeSiC_2H_6^+$ or rearrangement to common intermediates precedes fragmentation. Although CAD does not structurally distinguish these ions, reaction with ethene (isotopically labeled) clearly establishes distinct isomeric structures. **1a**, **1b**, **2a**, and **2b** react with ethene to yield exclusive adduct formation with rate constants (k) of $(1.3 \pm 0.4) \times 10^{-11}$, $(1.5 \pm 0.4) \times 10^{-11}$, $(6.2 \pm 1.9) \times 10^{-11}$, and $(8.0 \pm 2.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.[26,27] The adducts are presumably stabilized by infrared radiative emission.[28] Adducts **1a**(C_2H_4) and **2a**(C_2H_4) add a second ethene ($k \approx 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}), while adducts **1b**(C_2H_4) and **2b**(C_2H_4) are inert with ethene ($k < 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}), suggesting different $FeSiC_2H_6^+$ and $FeSiCH_4^+$ structures.

Additional structural information is obtained by studying isotopic exchange reactions. **1a** and **2b** both react with ethene-d_4 and ethene-$^{13}C_2$ to yield exclusive, initial adduct formation (*no* isotopic exchange occurs). Following adduct formation, a *double* H/D exchange occurs with ethene-d_4 (i.e., sequential H/D exchange is *not* observed) and a *single* $^{12}C/^{13}C$ exchange occurs with ethene-$^{13}C_2$. The ethene-d_4 adduct of $FeSiCH_2D_2^+$ (**3**) yields double H/D exchange with ethene-d_4, whereas **3**(C_2H_4) does not yield H/D exchange with C_2H_4. These results are consistent with formation of either Fe(silene)$^+$ or iron–alkylidene–silylene $(HRSi{=}Fe{=}CH_2)^+$ (**4**) complexes in reactions 2, 4, and 5 where *methylene* exchange occurs between the iron complex and ethene. 1,4-Cyclohexadiene reacts with **1b** to yield primarily $Si(CH_3)_2H_2$ elimination, reaction 6, with similar results observed with **2b**. These results provide compelling evidence against structure **4**, which is predicted to yield both CH_4 and $Si(CH_3)H_3$ eliminations and strongly supports a silene structure for **1b** and **2b**.



1a reacts with ethene-d_4 to produce mainly an adduct (ca. 0.64) as well as three H/D exchanges (ca. 0.12 for each H/D exchange). The adduct, **1a**(C_2D_4), undergoes *exclusive* addition of a second ethene-d_4 unit (*no* H/D exchange observed). In addition, CAD of the adduct, **1a**(C_2D_4), yields elimination of isotopically scrambled ethene. **1a** reacts similarly with ethene-$^{13}C_2$ to yield both $^{12}C/^{13}C$ exchange (0.56) and adduct formation (0.44). Ethene-d_4 yields a *rapid* single H/D exchange with **2a** followed by a small amount of exchange of the remaining three hydrogen atoms and adduct formation (process 7). The adduct, **2a**(C_2D_4), yields exclusive addition of a second ethene-d_4 (no exchange). These results indicate one unique and readily exchangeable hydrogen atom for **2a** with three other distinct hydrogen atoms. Exclusive elimination of D_2 with $Si(CH_3)_2D_2$, reaction 1, combined



$$\mathbf{2a} + C_2D_4 \begin{cases} \xrightarrow{0.12} \mathbf{2a}(C_2D_4) & (7a) \\ \xrightarrow{0.85} FeSiCH_3D^+ + C_2D_3H & (7b) \\ \xrightarrow{0.03} FeSiCH_{3-x}D_{1+x}^+ + C_2D_{3-x}H_{1+x} & (7c) \end{cases}$$

$x = 1–3$

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with the above results strongly supports formation of silylene complexes in reactions 1 and 3a.

The above results provide compelling evidence for formation of stable Fe–silene and Fe–silylene cationic complexes in the gas phase. These isomers do not interconvert, even upon formation of the ethene collision complex (ca. 40 kcal/mol excess energy).[29] High-level ab initio theory has revealed that $SiCH_4$ isomers (silene and silylene) have nearly identical stability (less than 10 kcal/mol difference).[30] Furthermore, there is a significant barrier (ca. 40 kcal/mol) for interconversion of these $SiCH_4$ isomers.[31,32] There is clearly a prohibitive barrier for this interconversion mediated by Fe^+. The ability to generate stable iron–silene and –silylene cations in the gas phase allows for studies concerning their role in important chemical transformations of silicon compounds.

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Biosynthesis of the Brevianamides: Quest for a Biosynthetic Diels–Alder Cyclization[†]

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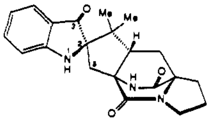
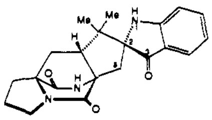
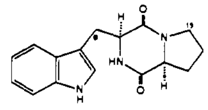
The brevianamides A (**1**) and B (**2**) are the simplest representatives of a curious class of mycotoxins[2] which also includes the paraherquamides[3] and the marcfortines.[4] While **1** has been shown to possess antifeedant and insecticidal effects,[5] several members of the structurally related paraherquamide family have potent antiparasitic properties.[3] In 1974, Birch and collaborators found that [15-^{3}H,8-^{14}C]brevianamide F (**3**) is biosynthetically incorporated into **1**[2e] and postulated[2b,c,e] a biosynthetic pathway, subsequently modified by us[6] to accommodate the observed absolute stereochemistries of **1** and **2**. The proposed biogenesis involved the formation of hexacyclic indole **4**, via a key [4 + 2] cycloaddition.[7]



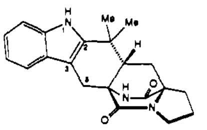
1, *(+)-BREVIANAMIDE A*



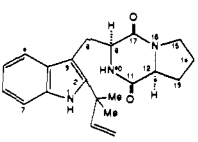
2, *(+)-BREVIANAMIDE B*



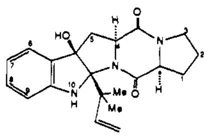
3, *BREVIANAMIDE F*



d,l-4



5, *DEOXYBREVIANAMIDE E*



6, *BREVIANAMIDE E*

In order to validate the proposed biosynthetic pathway, we synthesized *d,l*-[8-^{13}C]-**4** by using our synthesis,[8] only starting with *d,l*-proline and >90% ^{13}C-labeled gramine.[9,10] When fermentation extracts of *Penicillium brevicompactum* were screened for the production of **4**, this substance could not be found. Furthermore, the biosynthetic feeding of *d,l*-[8-^{13}C]-**4** gave cultures in which **1** showed no significant enhancement of C-8 in its ^{13}C NMR spectrum, indicating no incorporation.

We then synthesized [8-^{3}H]deoxybrevianamide E ([8-^{3}H]-**5**)[11] and [8-^{3}H]brevianamide E ([5-^{3}H]-**6**), following Kametani's synthesis.[12] Feeding experiments performed with [8-^{3}H]-**5** (16.5 mg with an activity of 1.605 μCi, and specific activity of 37.3 μCi/mmol) led to significant incorporation of the radioactivity into both **1** (7.8% specific incorporation, 0.125 μCi, 6.12 μCi/mmol) and **2** (0.93% specific incorporation, 0.015 μCi, 10.8 μCi/mmol). The specific activities of both **1** and **2** are comparable, thus confirming their common biosynthetic origin. As expected, **6** also showed significant incorporation (24.9% specific incorporation, 0.40 μCi, 32.0 μCi/mmol). The high values for the specific incorporations indicate that **5** is a biosynthetic precursor of **1**, **2**, and **6**. To check the possible intermediacy of **6** we obtained [5-^{3}H]-**6** from [8-^{3}H]-**5** as previously described.[12] In this case, however, the feeding experiment with [5-^{3}H]-**6** (17 mg; 1.60 μCi, 37.3 μCi/mmol) gave **1** and **2** with no significant incorporation. It thus seems that **6** does not lead to **1** or **2**.

The biosynthetic pathways leading to **1** and **2** proposed thus far[2b,c,e,6] do not explain the appearance of **6**, the presence of which in *P. brevicompactum* appears to be significant. It has been speculated that **6** may just be an artifact, because autoxidation of **5** leads to the production of **6**.[13] However, **5** was quite stable under the culture conditions in our feeding experiments. Moreover, **5** has been isolated from cultures of *Aspergillus ustus*,[11] while **6**, however, was not found in those cultures. In our opinion, this points to the conclusion that **6** is not an artifact. The results of our feeding experiments, together with these facts, lead us to

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[†] This manuscript is dedicated to Professor A. I. Meyers on the occasion of his 60th birthday.

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