C-4. The ^1H NMR of **2a** exhibits a singlet (δ 7.64) for the unique hydrogen at C-4. This resonance was not observed in the ^1H NMR of compound **3**. Likewise, a comparison of the $^{13}C\{^1H\}$ NMR of **2a** and **3** shows complete deuterium substitution at C-4. The $^{13}C\{^1H\}$ NMR of **3** exhibits a triplet (J_{CD} = 23.2 Hz) for the carbon at C-4.[19] The chemical shift of C-4 (δ 138.49) for **3** is slightly upfield of C-4 (δ 138.81) for **2a**. There have been many examples of this upfield deuterium isotope shift in ^{13}C NMR reported.[20]

These findings indicate that Fischer-type tungsten carbene complexes react with acetylenes under thermal conditions to give vinyl ethers and enones. The formation of these compounds can be explained by an exocyclic β-hydride elimination reaction followed by reductive elimination. We are continuing to investigate the reactions of tungsten carbene complexes with acetylenes and to develop their application in organic synthesis.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Professor J. Paukstelis for assistance with the NOE experiment. We thank the National Science Foundation for financial support to purchase the 400-MHz NMR spectrometer.

Registry No. **1a**, 91711-62-5; **1b**, 91711-63-6; **1c**, 91711-64-7; **1d**, 91711-65-8; **2a**, 38661-88-0; **2b**, 42968-14-9; **2c**, 91711-66-9; **2d**, 75391-07-0; **3**-*d*, 91711-67-0; **3**-d_2, 91711-68-1; **3**-d_3, 91711-69-2; $W(CO)_6$, 14040-11-0; $W(CO)_5[C(OMe)CH_3]$, 20540-70-9; $W(CO)_5[C(OMe)CH_2CH_3]$, 37956-78-8; $W(CO)_5[C(OMe)CO_3]$, 64784-31-2; PhC≡CMe, 673-32-5; PhC≡CPh, 501-65-5.

Supplementary Material Available: Partial ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100.6 MHz) spectra for compounds **2a** and **3** (2 pages). Ordering information is given on any current masthead page.

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[19] The magnitude of the ^{13}C–D coupling constant (J_{CD}) is equal to J_{CH}/6.5. "Interpretation of Carbon-13 NMR spectra"; Wehrli, F. W.; Wirthlin, T.; Heyden Press: New York, 1980; p 107. The observed ^{13}C–H coupling constant for C-4 of compound **2a** was 152.8 Hz.

[20] Feeney, J.; Partington, P.; Roberts, G. C. K. *J. Magn. Reson.* **1974**, *13*, 268. Stothers, J. B.; Tan, C. T.; Nickon, A.; Huana, F.; Sridhar, R.; Weylein, R. *J. Am. Chem. Soc.* **1972**, *94*, 8581. Bell, R. A.; Chan, C. L.; Sayer, B. G. *J. Chem. Soc., Chem. Commun.* **1972**, 67. Dodrell, D.; Burfitt, I. *Aust. J. Chem.* **1972**, *25*, 2239.

Cluster Mimetics. 2. The Preparation and Characterization of $(\mu\text{-H})(\mu\text{-CO})Fe_3(CO)_9BH_2$, $(\mu\text{-CO})Fe_3(CO)_9BH_2^-$, and $Fe_3(CO)_9BH_4^-$

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Summary: The preparation and characterization of $HFe_3(CO)_{10}BH_2$ and the related anions $Fe_3(CO)_{10}BH_2^-$ and $Fe_3(CO)_9BH_4^-$ are described. Measured ^{11}B NMR parameters demonstrate that the capping boron in $HFe_3(CO)_{10}BH_2$ is similar to the capping carbon in the isoelectronic $HFe_3(CO)_{10}CH$ cluster. However, in contrast to the CCH_3 derivative of this hydrocarbyl cluster, neither the neutral ferraborane nor the deprotonated anion undergoes ready reaction with H_2. The arrangement of hydrogens on $HFe_3(CO)_{10}BH_2$, compared to that in the analogous $H_3Os_3(CO)_9BCO$, emphasizes the important role of the M–H–M bond energy in these systems.

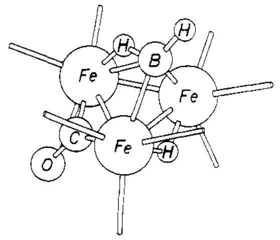
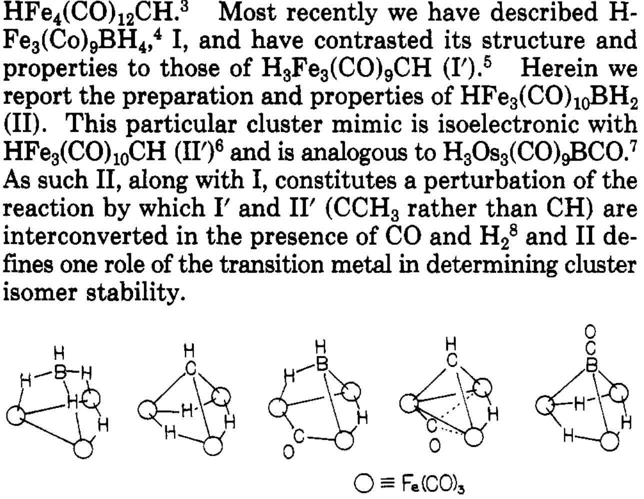


Figure 1. Proposed structure of $HFe_3(CO)_{10}BH_2$.

Isoelectronic compounds have provided a rich source of information upon which to base models of bonding. Examples of such compounds, differing only in the location of a single type of proton, are particularly fascinating in that the perturbation caused by moving a proton relative to the nuclear framework lends itself to simple physical descriptions.[1] In this vein, we have previously compared compounds in which BH replaces C in small systems, e.g., HBS vs. CS^2 as well as very large, e.g., $HFe_4(CO)_{12}BH_2$ vs. $HFe_4(CO)_{12}CH$.[3] Most recently we have described $HFe_3(Co)_9BH_4$,[4] I, and have contrasted its structure and properties to those of $H_3Fe_3(CO)_9CH$ (I′).[5] Herein we report the preparation and properties of $HFe_3(CO)_{10}BH_2$ (II). This particular cluster mimic is isoelectronic with $HFe_3(CO)_{10}CH$ (II′)[6] and is analogous to $H_3Os_3(CO)_9BCO$.[7] As such II, along with I, constitutes a perturbation of the reaction by which I′ and II′ (CCH_3 rather than CH) are interconverted in the presence of CO and H_2[8] and II defines one role of the transition metal in determining cluster isomer stability.



I I′ II II′ III

The reaction of $Na[Fe(CO)_4C(O)CH_3]$ in THF with 2 equiv of commercial $BH_3 \cdot THF$[9] and 2 equiv of $Fe(CO)_5$ at 70 °C for 1 h yields a red mixture of anionic ferraboranes and iron carbonyl hydrocarbyls. Removal of the solvent, followed by treatment with 80% aqueous H_3PO_4 and extraction with hexane, yields a brown extract. Compound II is a major component of this mixture and is isolated in 14% yield (based on total iron) by chromatography as a brown solid that is modestly air stable. The molecular composition of this material was established by mass spectrometry as $C_{10}H_3O_{10}BFe_3$.[10] The fragmentation be-

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[1] See, for example: Ballard, R. E. *Appl. Spectrosc. Rev.* **1973**, *7*, 183.

[2] Fehlner, T. P.; Turner, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7175.

[3] Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

[4] Vites, J.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.

[5] The ethylidyne derivative $H_3Fe_3(CO)_9CCH_3$ has been fully described (Wong, K. S.: Haller, K. J.; Dutta, T. K.; Chipman, D. M.; Fehlner, T. P. *Inorg. Chem.* **1982**, *21*, 3197. DeKock, R. L.; Wong, K. S.; Fehlner, T. P. *Ibid.* **1982**, *21*, 3203) and we have now fully characterized the methylidyne. Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P., to be submitted for publication.

[6] Although we have prepared this compound, it has already been reported. Kolis, J. W.; Holt, E. M.; Shriver, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 7307.

[7] Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

[8] Vites, J.; Fehlner, T. P. *Organometallics* **1984**, *3*, 491.

[9] A method for the in situ generation of reactive iron carbonyl anion fragments. Vites, J. C., unpublished observations.

[10] $^{56}Fe_3{}^{10}B^{12}C_{10}{}^{16}O_{10}{}^{1}H_3$: calcd 460.790 amu; obsd 460.788 amu. Sequential loss of 10 CO molecules from the parent ion is observed as well as a p − 1 ion (peak matched) of 25% of the intensity of the parent ion.

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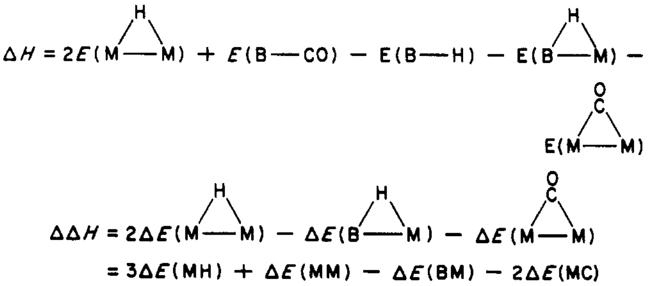
havior suggests a BFe_3 cluster core.

The principal features of the structure of II are clearly revealed by the IR and NMR spectra of the compound.[11] The IR reveals the presence of a bridging carbonyl, and the terminal CO stretching region is consistent with a $Fe_3(CO)_9$ fragment having low symmetry. The proton NMR spectrum demonstrates the presence of one terminal BH, one FeHB and one FeHFe interaction, and the selectively decoupled ^{11}B spectrum shows normal BH (terminal) and BH (bridge) coupling constants. The proposed structure, shown in Figure 1, is a cluster consisting of a BH capped $Fe_3(CO)_9$ fragment with one CO bridging a FeFe edge, one H bridging a FeFe edge, and one H bridging a FeB edge. Of the possible locations for these bridging moieties, the arrangement illustrated in the Figure 1 is that which seems most probable based on models using structural parameters from known related molecules.[12]

The new ferraborane II is seen to be related to the isoelectronic II′ by moving, in a formal sense, a proton from the nucleus of the capping carbon of II′ to bridging a boron–iron edge. The existence of correlations between ^{11}B and ^{13}C NMR data[13-15] allows one to compare the chemical environment of the capping atom in II′ with that of its ferraborane mimic II. Doing so suggests that the capping atom is bound to the metal triangle in a similar fashion in both cases, i.e., $\delta(^{11}B)$ 56 (obsd), 57 (calcd),[16] J_{BH}(terminal) = 145 Hz (obsd), 114 Hz (calcd).[17] Note that this is not the case for I and I′ ($\delta(^{11}B)$ 2 (obsd), 47 (calcd), J_{BH}(terminal) = 75 Hz (obsd), 113 Hz (calcd)[4,18] where it is clear from the solid-state structural parameters that compared to I′ the capping atom of I has been lifted off the metal triangle by the three FeHB bridging hydrogens. Also note that the ^1H NMR spectrum of II, in contrast to that of I, shows no evidence of fluxional behavior below 20 °C. The proton on the capping carbon of II′ is found at low field. Likewise, the terminal resonance of the BH proton of II appears at markedly lower field than that of other cage boranes.[20] This corroborates the suggestions of similar chemical environments for the capping atoms of II and II′. Like II′, II is easily deprotonated. The anion has been isolated and characterized[21] showing loss of the FeHFe proton from II. Removal of the proton does not cause large pertubations in the spectroscopic parameters nor, presumably, in the structure.

The more sensitive probe of chemical reactivity, however, shows a significant difference between II and II′. The CCH_3 derivative of the latter reacts readily with H_2 to form I′ in a process that has been demonstrated to be a facile equilibrium at 60 °C.[8] However, treating II at up to 75 °C and 3 atm of H_2 pressure produces no detectable quantities of I. At the highest temperature substantial deomposition to $Fe_3(CO)_{12}$ occurs. Likewise I does not react with CO (75 °C, 1 atm) to produce II. While appreciating the negative character of these results, they nevertheless suggest that the conversion of C to BH in going from II′ to II has raised the activation energy for the interconversion reaction; i.e., either I or II must be the thermodynamically more stable isomer and conditions underwhich I′ and II′ interconvert do not interconvert I and II. Keister and co-workers have shown for the ruthenium analogue of II that CO dissociation precedes the rate-determining oxidative addition of H_2.[22] As the loss of CO should occur as readily from II as for II′, the oxidative addition must be less favorable for II than for II′. The anion of II is no more reactive with respect to H_2 than is II itself. Likewise, the anion of I, prepared by a small modification of the above route and characterized separately,[23] decomposes more rapidly at 60 °C than it reacts with CO.

Finally, the new ferraborane II is analogous to $H_3Os_3(CO)_9BCO$ recently reported by Shore and co-workers.[7] On heating we have observed no tendency for II to rearrange into the iron analogue having structure III. Note that $HOs_3(CO)_{10}CH$, the analogue of II′, rearranges on heating to $H_2Os_3(CO)_9CCO$ (the carbon analogue of III).[24] This suggests that in going from iron to osmium, the energetics favor structure III vs. II. A simple analysis of the energetics in terms of bond energy contributions[8] yields:



$$\Delta H = 2E(\overset{\mathrm{H}}{\mathrm{M{-}M}}) + E(\mathrm{B{-}CO}) - E(\mathrm{B{-}H}) - E(\overset{\mathrm{H}}{\mathrm{B{-}M}}) - E(\overset{\overset{\mathrm{O}}{\mathrm{C}}}{\mathrm{M{-}M}})$$

$$\Delta\Delta H = 2\Delta E(\overset{\mathrm{H}}{\mathrm{M{-}M}}) - \Delta E(\overset{\mathrm{H}}{\mathrm{B{-}M}}) - \Delta E(\overset{\overset{\mathrm{O}}{\mathrm{C}}}{\mathrm{M{-}M}})$$
$$= 3\Delta E(\mathrm{MH}) + \Delta E(\mathrm{MM}) - \Delta E(\mathrm{BM}) - 2\Delta E(\mathrm{MC})$$

$\Delta\Delta H$ is the difference in enthalpies (ΔH) for the isomerization III → II and ΔE(M–X) (X = M, H, B, C) is the change in the two-center MX bond energy contribution in going from osmium to iron. Assuming that the E(M–X) terms increase similarly as one goes from iron to osmium,[25] then the greater number of positive terms suggests $\Delta\Delta H > 0$. Apparently, the change is sufficiently large to tip the balance in favor of III for osmium. In turn, reasonable numbers for the energy parameters for the ruthenium analogue of II suggest that both isomeric forms might be found.

Trimetal methylidyne complexes have been suggested by Muetterties and others as models for CH fragments bound to metal surfaces.[26] We have previously suggested

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(11) NMR: ^1H ($C_6D_5CD_3$, −60 °C) δ 5.9 (br, 1 H), −13.7 (br, 1 H), −25.6 (s, 1 H); ^{11}B (C_6D_6, 20 °C) δ 56 (br, d), {^1H} (br, fwhm = 130 Hz), J_{BH} = 145 Hz (terminal), $J_{BH} \sim 50$ Hz (bridge). IR (hexane, cm^{-1}): 2106 w, 2073 s, 2054 vs, 2041 sh, 2031 m, 2022 m, 2010 m, 1995 m, 1868 m.

(12) Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57. Grimes, R. N., Ed. "Metal Interactions with Boron Clusters"; Plenum Press: New York, 1982.

(13) Spielvogel, B. F.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 1609. Spielvogel, B. F.; Purser, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4418.

(14) Noth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3089.

(15) Williams, R. E.; Field, L. D. "Boron Chemistry-4"; Parry, R. W., Kodama, G., Eds.; Pergamon Press: New York, 1980; p 131.

(16) The relationship used is as follows: $\delta(^{11}B) = {}^1/_3\delta(^{13}C) - 30$;[15] $\delta(^{13}C)$ 264.[6]

(17) A linear correlation $J_{BH} = 0.68J_{CH}$ has been found. See; Onak, T.; Leach, J. B.; Anderson, S.; Frisch, M. J.; Marynick, D. *J. Magn. Reson.* **1976**, *23*, 237 (J_{CH} = 168 Hz).[6]

(18) $\delta(^{13}C)$ 233 (J_{CH} = 166 Hz).[5]

(19) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(20) Eaton, G. R.; Lipscomb, W. N. "NMR Studies of Boron Hydrides and Related Compounds"; W. A. Benjamin: New York, 1969.

(21) $[Fe_3(CO)_{10}BH_2]$PPN: ^1H NMR $CD_3C(O)CD_3$, 20 °C) δ 7.73–7.57 (m, 30 H), 6.0 (br, 1 H), −11.1 (br m, 1 H); ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C) δ 57.4 (br, d), {^1H} J_{BH} = 130 Hz (terminal) $J_{BH} \simeq 50$ Hz (bridge); IR (toluene, cm^{-1}) 2051 w, 1989 vs, 1963 s 1935 m, 1790 w.

(22) Bavaro, L. M.; Montangero, R.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977.

(23) $[Fe_3(CO)_9BH_4]$PPN: ^1H NMR ($CD_3C(O)CD_3$, −90 °C), δ 7.73–7.56 (m, 30 H), 3.8 (br q, $J_{BH} \simeq 100$ Hz, 1 H), −13.1 (br m, 3 H); {^{11}B} 3.8 (q, $J_{HH} = \delta$ 20 Hz), −13.1 (d, J_{HH} = 20 Hz); ^{11}B NMR ($CD_3C(O)CD_3$, 20°C) δ 6.2 (br qd), {^1H} J_{BH} = 96 Hz (terminal), J_{BH} = 58 Hz (bridge); IR (toluene, cm^{-1}); 2045 m, 1990 sh, 1983 vs. 1954 s, 1933 m. Protonation of this anion yields I.

(24) Shapley J. R.; Strickland, D. S.; St. George, G. M.; Churchill, M. R.; Bueno, C. *Organometallics* **1983**, *2*, 185.

(25) Evidence for this assumption exists. See: Connor, J. A. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; p 345.

(26) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

I as a model for CH_4 chemisorbed on a trimetal site.[4] The ferraborane II, then, constitutes a possible model for chemisorbed CH_2 in the act of being dehydrogenated to CH on a trimetal site. Further studies on these and related compounds are in progress.

Acknowledgment. The support of the National Science Foundation under Grant CHE 81-09503 is gratefully acknowledged. The NMR facility was purchased with the support of the National Institutes of Health (Grant No. CM 25845-02S1).

Kinetics and Mechanism of Pyrolysis of Hydridosilacyclobutanes

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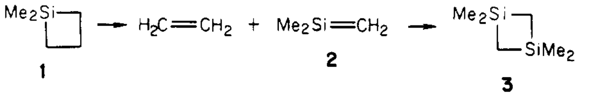
Summary: The thermal decomposition of hydridosilacyclobutanes was examined kinetically by low-pressure pyrolysis and stirred-flow reactor techniques, independent generation of proposed intermediates, and deuterium labeling. It was concluded that RSiH and propene arise from an initial rearrangement to *n*-propylsilylenes and not from the previously assumed sequence of homolytic cleavages.

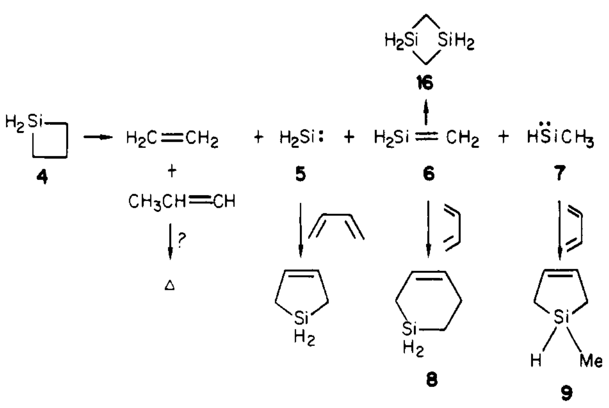
Pyrolysis of 1,1-dimethyl-1-silacyclobutane (1) is a clean, unimolecular reaction giving ethene and dimethylsilene (2) that can either be trapped or allowed to dimerize to 1,3-disilacyclobutane 3.[1]



However, gas-phase pyrolysis of the parent system 4 is far more complex as considerable formation of H_2 and propene is observed.[2] Conlin[3] has elegantly demonstrated through butadiene trapping that three silicon-reactive intermediates are formed in this pyrolysis: silylene (5), silene (6), and methylsilylene (7) (Scheme I).

Although the formation of methylsilylene (7) is easily rationalized by isomerization of silene (6) via 1,2-hydrogen migration,[4] it could also be accounted for[5] by a sequence of C-C bond homolysis in 4, 1,2-H migration to form either the 1,3 diradical 11 or silacyclopropane 12, and extrusion of :SiHMe as shown in Scheme II.

Scheme I



Scheme II

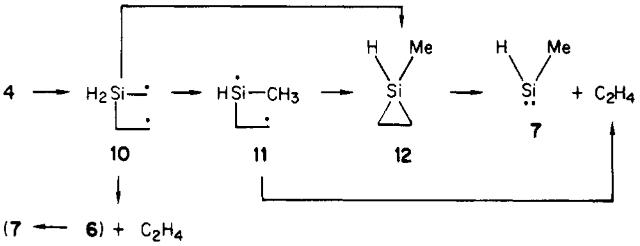
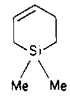
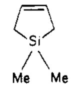
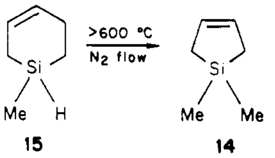


Table I. Arrhenius Parameters and Rate Constants for Decomposition of Silacycloalkenes

compd	log A, s^{-1}	E_a, kJ mol^{-1}	$k_{900\ K}$, s^{-1}
 13	14.1 ± 0.5	252 ± 8	0.298
 14	13.5 ± 0.6	255 ± 11	0.050

To distinguish between these two pathways, Conlin[3] noted that the process with the lowest activation entropy is the isomerization of 10 to 11 (as opposed to fragmentation of 10 to ethene and 6). Thus, if the multistep diradical process were operative, increasing temperature should favor formation of 6 over 7. His experiments indicated the opposite, as increasing temperature *increased* the 9/8 ratio. Therefore, it was reasonably concluded that only 5 and 6 are primary products from 4, and 7 must be derived from isomerization of 6.

This conclusion, while quite possibly correct, cannot be made from these data since silacyclohexenes are not thermally stable under the conditions required for decomposition of 4. For example (Table I), dimethylsilacyclohexene 13 decomposes six times more readily than dimethylsilacyclopentene 14 at 900 K. Indeed, both we and Conlin[6] have independently found that above 600 °C (vertical N_2 flow) hydridosilacyclohexene 15 begins to isomerize to silacyclopentene 16. Thus, the observed increasing 9/8 ratio is to be expected regardless of the mechanism of silacyclobutane decomposition.



15 14

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[1] Flowers, M. C.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 428, 1396.
[2] Maltsev, A. K.; Khabasheku, V. N.; Nefedov, O. M. Dokl. *Akad. Nauk SSSR* **1979**, *247*, 383.
[3] Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 618.
[4] Yoshioka, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 7366.
[5] Barton, T. J.; Burns, S. A.; Burns, G. T. *Organometallics* **1982**, *1*, 210.
[6] Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1984**, *3*, 918.