present in ^{12}C methyl groups ($^{12}CH_nD_{3-n}$) increases to its equilibrium value by a first-order process with a rate constant ($k_{obsd}^{H} = 2.9 \times 10^{-5}$ s^{-1}) approximately equal to k_{obsd}^{C} indicates that no intramolecular scrambling occurs—i.e., $Cp_2W(H)CD_3$ is converted to $Cp_2W(D)CHD_2$ by the same process that transfers deuterium from one molecule to another and converts $Cp_2W(H)^{13}CH_3$ into $Cp_2W(H)^{13}CH_2D$.

The tungsten hydride in $Cp_2W(H)CH_3$ can thus exchange with the C–H bonds in the methyl ligand of another molecule of the same material—at a rate that competes successfully with intramolecular methane elimination except in very dilute solution. Preliminary ^{2}D NMR experiments show similar exchange between $Cp_2W(D)CD_3$ and Cp_2WH_2. Similar exchange between arene hydrogens and M–H bonds of the early transition metals is common,[16] but the tungsten hydrides discussed herein are the first hydrides for which intermolecular exchange with an *aliphatic ligand* has been reported.

Acknowledgment. We thank NSF Grant CHE82-07597 for support of this work. We are grateful to M. Bradicich and K. Hennessy for preliminary work, to M. L. H. Green, N. J. Cooper, and B. Ladanyi for helpful discussions, and to the Colorado State University Regional NMR Center (NSF Grant CHE82-08821) for ^{2}D NMR spectra.

Registry No. $Na[D_2Al(OCH_2CH_2OCH_3)_2]$, 94370-28-2; $Cp_2W(CH_3)(OCOPh)$, 73210-66-9; $(\eta^5\text{-}C_5H_4D)(\eta^5\text{-}C_5H_5)W(H)CH_3$, 94370-29-3; $Cp_2W(D)CH_3$, 94370-30-6; $Cp_2W(H)CH_3$, 72415-89-5; $Cp_2W(H)CD_3$, 94370-31-7; $Cp_2W(H)^{13}CH_3$, 94370-32-8; $Cp_2W(D)CD_3$, 94370-33-9; $Cp_2W(\eta^2\text{-}CD_3CN)$, 94370-34-0; D_2O, 7789-20-0; CH_3D, 676-49-3; CD_3H, 676-80-2; $^{13}CH_4$, 6532-48-5; CD_4, 558-20-3; CD_2H_2, 676-55-1; CH_4, 74-82-8.

Supplementary Material Available: Determination of the equilibrium constant *K* for eq 5 from ^{1}H and ^{2}D NMR relative intensity measurements and determination of the equilibrium fraction of ^{13}C present in undeuterated methyl groups and the equilibrium fraction of ^{1}H present in ^{12}C methyl groups (4 pages). Ordering information is given on any current masthead page.

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(16) See footnote 13 of ref 3f for a list of leading references on this topic; see especially: Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

Formyl, Acyl, and Carbene Derivatives of $Fe_3(\mu_3\text{-}EPh)_2(CO)_9$ (E = N, P). Unique Examples of Carbene–Nitrene and Carbene–Phosphinidene Coupling

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The chemistry of phosphinidene-bridged (μ_3-PR) compounds is currently under active exploration.[1] Comparatively fewer nitrene-bridged (μ_3-NR) clusters have been prepared, and little is known about the chemistry of this bridging ligand.[2] The few studies do indicate that μ_3-nitrene ligands are relatively inert since they are not easily removed by hydrogenation to give amines or carbonylation to give isocyanates.[3] In our studies of the derivative chemistry of the μ_3-nitrene cluster $Fe_3(\mu_3\text{-}NPh)_2(CO)_9$ (**1**)[4] and its phosphinidene analogue $Fe_3(\mu_3\text{-}PPh)_2(CO)_9$ (**2**)[5] we have discovered unique examples of carbene–nitrene and carbene–phosphinidene coupling, details of which are described herein.

Complex **1** reacts with $Li[BHEt_3]$ to give a relatively stable formyl derivative $Li[Fe_3(\mu_3\text{-}NPh)_2(CO)_8(CHO)]$ (**3**),[6] which at

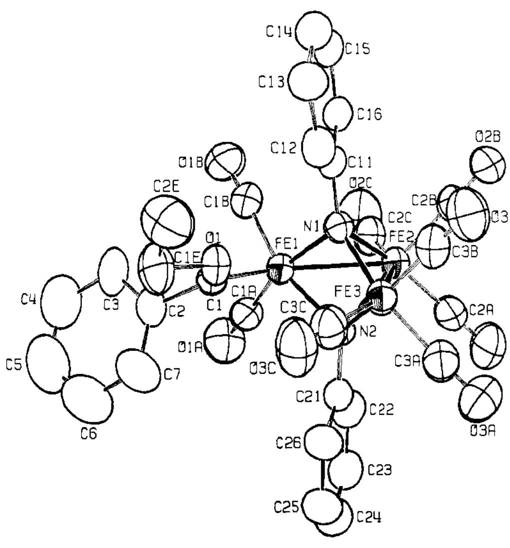
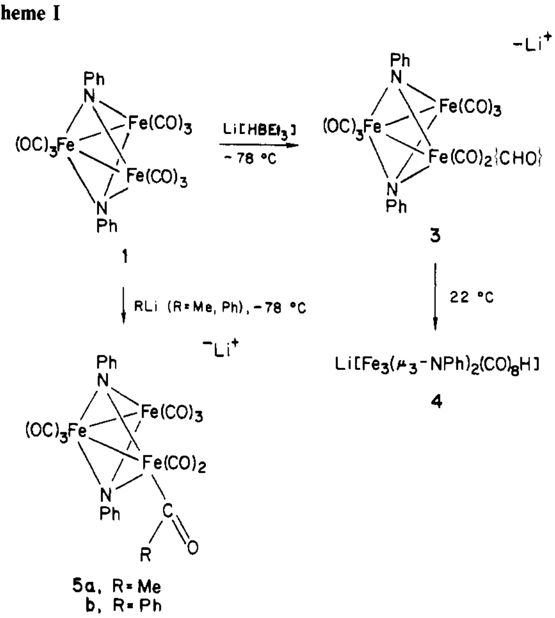


Figure 1. ORTEP drawing of $Fe_3(\mu_3\text{-}NPh)_2(CO)_8\{C(OEt)Ph\}$ (**6**). Relevant bond distances (Å) and angles (deg): Fe(1)–Fe(2), 2.498 (1); Fe(2)–Fe(3), 2.419 (1); Fe(1)–N(1), 1.937 (4); Fe(1)–N(2), 1.929 (4); Fe(2)–N(1), 1.980 (4); Fe(2)–N(2), 1.988 (4); Fe(3)–N(1), 1.944 (4); Fe(3)–N(2), 1.939 (4); Fe(1)–C(1), 1.856 (5); Fe(1)–Fe(2)–Fe(3), 77.04 (3).

Scheme I



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(1) (a) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219–1239. (b) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251–1252. (c) Mays, M. J.; Raithby, P. R.; Taylor, P. L.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 959–967.

(2) For reviews, see: (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (b) Cenin, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.

(3) (a) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255–7259. (b) Dawoodi, Z.; Mays, M. J.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 433–440. (c) Bernhardt, W.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 381. (d) Coupling of μ_3-NPh and H ligands on a Ru_3 cluster has recently been reported, see: Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; Jones, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765–1767.

(4) Stanghellini, P. L.; Rossetti, R. *Atti. Accad. Sci. Torino, Cl. Sci. Mat. Nat.* **1970**, *105*, 391.

(5) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367–374.

(6) **3**: IR (THF) 2050 m, 2004 s, 1997 s, 1975 m, 1938 m, 1595 m cm^{-1}; ^{1}H NMR δ 14.52 (s, CHO).

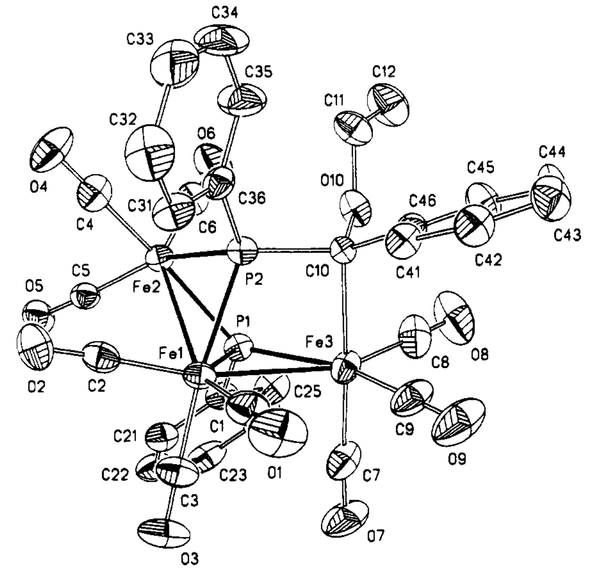
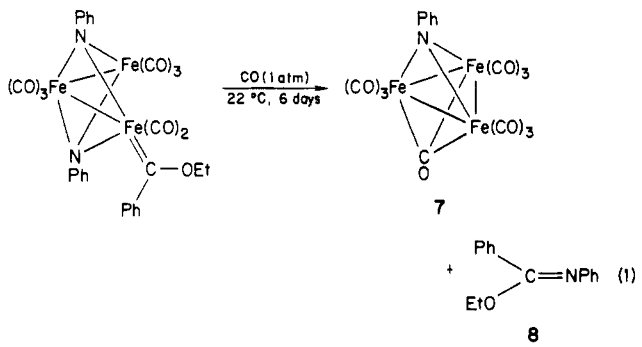


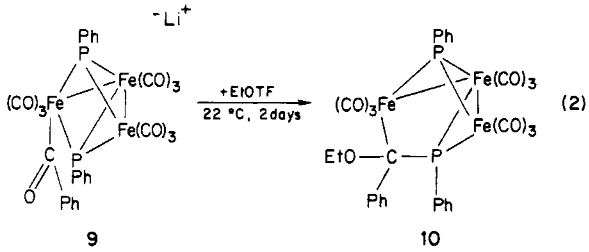
Figure 2. ORTEP drawing of $Fe_3(\mu_3\text{-}PPh)\{\mu\text{-}PhPC(OEt)Ph\}(CO)_9$ (**10**). Relevant bond distances (Å) and angles (deg): Fe(1)–Fe(2), 2.671 (2); Fe(1)–Fe(3), 2.750 (1); Fe(1)–P(1), 2.256 (2); Fe(1)–P(2), 2.240 (2); Fe(2)–P(1), 2.198 (2); Fe(2)–P(2), 2.211 (2); Fe(3)–P(1), 2.192 (2); Fe(3)–C(10), 2.139 (6); P(2)–C(10), 1.800 (6); Fe(2)–Fe(1)–Fe(3), 90.31 (8); Fe(1)–P(2)–Fe(2), 73.7 (1); Fe(1)–P(1)–Fe(3), 76.4 (1); Fe(1)–P(2)–C(10), 107.9 (2); Fe(2)–P(2)–C(10), 115.6 (2); Fe(3)–C(10)–P(2), 96.5 (3); Fe(3)–C(10)–O(10), 104.7 (4); P(2)–C(10)–O(10), 114.7 (5); [Fe(1)–Fe(2) P(1)]–[Fe(1)–Fe(3)–P(1)], 130.1.

22 °C slowly deinserts with $t_{1/2} \approx 1.5$ h[7] to give $Li[HFe_3(\mu_3\text{-}NPh)_2(CO)_8]$ (**4**)[8] (Scheme I). Cluster **1** also yields stable acetyl (**5a**[9]) and benzoyl (**5b**[9]) derivatives when treated with the appropriate RLi reagent (Scheme I). Alkylation of the benzoyl complex **5b** with $EtOSO_2CF_3$ yields the novel carbene–nitrene complex **6**.[10] Complex **6** has been structurally characterized (Figure 1)[11a] and to our knowledge is the only cluster compound containing both nitrene and carbene ligands. As shown in Figure 1, the nitrene and carbene ligands are well separated with the carbene having formally replaced one of the original cluster carbonyls.

Although the carbene and nitrene ligands do not interact in **6**, they couple and are eliminated when this complex is exposed to CO (eq 1). The products of this reaction are the known cluster **7**[3a] (67% isolated yield) and the imidate **8**[12] (48% yield by ^{1}H NMR).



The coupling of carbene with phosphinidene ligands is much more facile than the above-mentioned nitrene–carbene coupling. Treatment of the phosphinidene complex **2** with PhLi generates the benzoyl complex **9**.[13] When this species is treated with $EtOSO_2CF_3$ at 22 °C in an attempt to generate a phosphinidene–carbene complex analogous to **6**, a complex reaction occurs to give a mixture of products but with the major component being complex **10**,[14] which was isolated in 37% yield (eq 2). The X-ray structure of **10**[11b] (Figure 2) shows the presence of a coordinated PhP=C(OEt)Ph ligand which results from coupling of phosphinidene and carbene ligands. With the inclusion of the remaining μ_3-PPh ligand, the molecule is best described as a "butterfly" structure with the μ-PhP=C(OEt)Ph ligand bridging the open face of the butterfly. In solution, complex **10** exists in two diastereomeric forms which differ according to whether or not the OEt substituent lies on the same side of the molecule as P(1) (Figure 2) or on the other side. ^{1}H and ^{31}P NMR data show both diastereomers to be present in equal amounts. The ^{1}H NMR spectrum of **10** shows two OCH_2CH_3 resonances at δ 3.74 (dq, J(PH) = 7.2 Hz) and 3.60 (dq, J(PH) = 7.2 Hz), along with one OCH_2CH_3 resonance at δ 1.07 (t, J(HH) = 7.2 Hz). The ^{31}P NMR spectrum shows downfield resonances at δ 163.7 (d, J(PP) = 28 Hz) and 142.7 (d, J(PP) = 23 Hz) assigned to the μ-PhP=C(OEt)Ph ligand of the two diastereomers. The μ_3-PPh ligands appear within normal ranges at δ 301.1 (d, J(PP) = 28 Hz) and δ 289.6 (d, J(PP) = 23 Hz). Note that formation of **10** requires an additional CO which is apparently scavenged from other Fe_3 clusters that decompose, an observation that also accounts for the modest yield of **10**. Although bridging RP=CR(R′) ligands have not been previously described,[15] several mononuclear complexes containing these ligands are known.[16]



To our knowledge these are the first reported examples of nitrene–carbene and phosphinidene–carbene coupling reactions of any type, and they imply that these capping ligands may have as rich a derivative chemistry as that now developing for μ_2-PPh_2 ligands.[17] This and other aspects of the comparative chemistry of **1** and **2** are under exploration.

Acknowledgment. We gratefully acknowledge the Department of Energy, Office of Basic Energy Sciences, for support of this

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(7) The only other cluster formyl of comparable stability is $[Os_3(CO)_{11}(CHO)]^-$. See: Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559–2564.

(8) **4**: ^{1}H NMR δ −20.48 (s br, FeH).

(9) **5a**: IR (Et_2O) 2047 m, 2002 s, 1989 m, 1973 m, 1938 m, 1929 m, 1592 w cm^{-1}; ^{1}H NMR δ 2.56 (s, $COCH_3$). **5b**: IR (Et_2O) 2050 m, 2006 s, 1989 m, 1979 m, 1947 m, 1931 m, 1543 w cm^{-1}.

(10) **6**: IR (hexane) 2064 m, 2027 s, 2017 m, 2000 m, 1984 m, 1955 m, 1948 m cm^{-1}; ^{1}H NMR δ 3.98 (q, OCH_2CH_3, J = 7.0 Hz), 0.99 (t, OCH_2CH_3, J = 7.0 Hz); m/z 708 (M^+).

(11) (a) **6**: orthorhombic, P_{bca}, a = 13.668 (6) Å, b = 17.588 (7) Å, c = 25.644 (8) Å, V = 6164 Å^3, Z = 8. The structure refined to $R_f = 0.060$ and $R_{wf} = 0.075$ for the 2982 reflections with $F_o \geqslant 2\sigma(F_o)$. Crystallographic details are given in the supplementary material. (b) **10**: triclinic, $P1$, a = 9.241 (2) Å, b = 10.233 (3) Å, c = 19.564(5) Å, α = 84.53 (2)°, β = 84.43 (2)°, γ = 76.41 (2)°, V = 1784.7 (8) Å^3, Z = 2. Of 4643 unique reflections collected, 3710 with $F_3 \geqslant 3.0\sigma(F_o)$ were used in direct methods solution and refinement. $R_f = 0.0557$, $R_{wf} = 0.0602$, GOF = 1.252. Severely distorted molecules of hexane (no atom occupancies greater than 0.3) were located about the inversion centers, but not included. Crystallographic details are given in the supplementary material.

(12) **8**: IR (THF) 1657 cm^{-1}; ^{1}H NMR δ 4.29 (q, OCH_2CH_3, J = 7.2 Hz), 1.30 (t, OCH_2CH_3, J = 7.2 Hz), mass spectrum, m/z calcd for $C_{15}H_{15}NO$ 225.1154 found 225.1145 (M^+). Ta-Shma, R.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1977**, *659*–667.

(13) **9**: IR (Et_2O) 2041 m, 2022 w, 1997 s, 1973 s, 1951 w, 1933 w, 1535 w cm^{-1}; ^{31}P NMR δ 226.83 (s br).

(14) **10**: IR(Et_2O) 2072 w, 2049 s, 2019 s, 2008 m, 1995 w cm^{-1}; mass spectrum m/z 770 (M^+).

(15) **Note Added in Proof**: Such a μ-RP=CR(R′) ligand was recently described: Knoll, K.; Huttner, G.; Wasiucionek, M.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 739–740.

(16) (a) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 3737–3738. (b) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132–1133.

(17) See references in: (a) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 1519–1521. (b) Henrick, K.; Iggo, J. A.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1984**, 209–211.

research and the Eastman Kodak Co. for fellowship support. The National Science Foundation is acknowledged for a grant which contributed to the purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of crystallographic data for **6** and **10**, positional parameters and temperature factor expressions for **6**, and atomic coordinates and temperature factors for **10** (6 pages). Ordering information is given on any current masthead page.

Synthesis and Thermal Ring Expansion of 2-Methylene-1,1-dimethylsilacyclobutane

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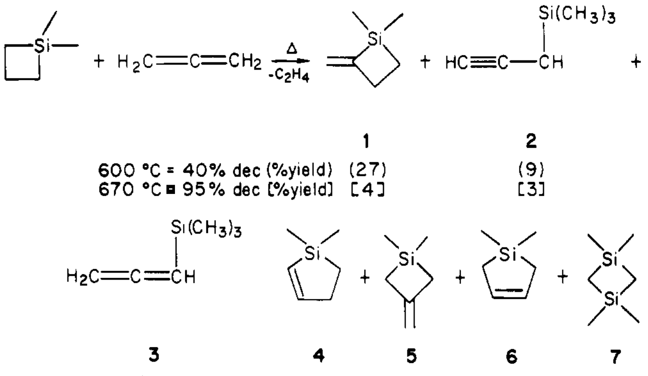
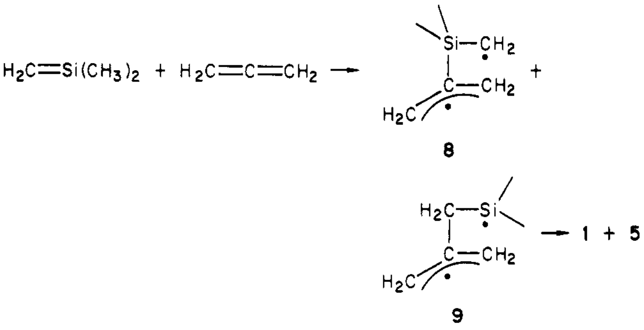
Early studies of the degenerate rearrangement of methylenecyclobutane[1] provided new insight into the influence of substituents on the thermal isomerization[2] of four-membered rings. Difficulty with the synthesis of the analogous methylenesilacyclobutanes, however, has impeded progress toward understanding the role of a metal atom on the course of isomerizations of metallocyclobutanes. We report herein the first synthesis of a 2-methylenesilacyclobutane **1**, which thermally isomerizes via an unexpected ring expansion to the isomeric silacyclopentenes.

Low-pressure flow pyrolysis[3] of 1,1-dimethylsilacyclobutane in an eightfold excess of allene at 600 °C affords a 27% yield of **1**[4] along with smaller amounts of six other products:[5] **2**, **3**, **4**, **5**,[6] **6**, and the dimethylsilene dimer **7**. When the pyrolysis temperature is raised from 600 to 670 °C, the combined yields of isomers **1** and **5** decrease from 31% to 5% while formation of **4** and **6** increases from 10% to 19%. With higher temperature and therefore higher concentration of dimethylsilene the yield of **7** increases as expected for dimerization. The ratio of total cyclic to acyclic silanes, 2.0 at 600 °C, however, shows little change at higher temperature, 1.8 at 670 °C.

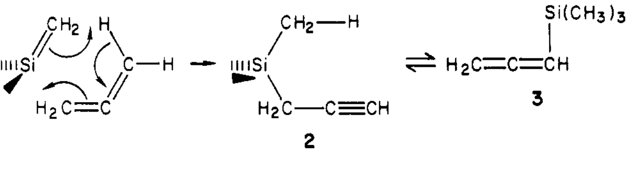


The major product at the lower temperature is the previously unknown 2-methylene-1,1-dimethylsilacyclobutane (**1**). Predominant formation of the 2-isomer is consistent with initial approach of the silicon atom of the silene to C2 of allene with concomitant development of the allylic-type resonance in the carbon frame. Since there is good evidence in the literature that fragmentation of a silacyclobutane commences at a carbon–carbon bond,[7] it is most likely that the reverse pathway, cycloaddition, starts with formation of a slightly stronger silicon–carbon bond[8] as represented below by diyl **8**. The symmetrical 3-methylenesilacyclobutane **5** is formed in lower yield (4.1% at 600 °C and 1.2% at 670 °C) than **1** presumably because formation of a somewhat weaker carbon–carbon bond in **9** is required in developing the transition state.



Other reaction pathways to be considered include those leading to **2** and **3**. Both acyclic products were previously observed from the reaction of dimethylsilene and propyne[9] where it was shown that **2** resulted from isomerization of a primary product, **3**. The temperature dependence of the silene/allene reaction suggests a similar type of analysis. Since the ratio of the **2** to **3** *increases* from 0.3 to 0.7 as the pyrolysis temperature is *lowered* from 670 to 600 °C in the flow system, it is likely that **2** is a primary reaction product. The well-characterized, 1,3-trimethylsilyl shift converts the **2** to the thermodynamically more stable **3**. At 670 °C the ratio of **2** to **3**, 0.3, approaches the equilibrium value, 0.16, reported by Slutsky and Kwart.[10]

When propyne was the dimethylsilene trap, acyclic silanes **2** and **3** were the major products, formed in 5–7 times greater yield than the cyclic adduct 1,1,3-trimethylsilacyclobutene. In contrast, cycloadducts **1** and **4**–**6** are the major products of the silene/allene reaction. The acyclic products, **2** and **3**, arising from the intermolecular silene ene reaction, are formed in lower yield with allene because vinylic C–H bonds are stronger and less reactive than the propargylic C–H bonds of propyne. Transfer of a vinylic hydrogen of allene to the methylene portion of the silene can be described by a concerted ene pathway.



The presence of dimethylsilacyclopentenes among the reaction products is without parallel for simple 2 + 2 cycloadditions in hydrocarbon chemistry. Since higher temperature increases the

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[1] Doering, W. v. E.; Gilbert, J. C. *Tetrahedron, Suppl.* **1966**, *No. 7*, 397.

[2] For a comprehensive review, see: Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

[3] For experimental conditions, see ref 9.

[4] **1**: ^{1}H NMR (neat) δ −0.19, (s, 6 H, $(CH_3)_2Si$), 0.50 (br t, J = 8.5 Hz, CH_2Si), 2.25 (m, 2 H, CCH_2C), 4.90 (m, 1 H, =CH), 4.68 (m, 1 H, =CH); ^{13}C NMR (neat) δ −1.11 (q), 10.68 (t), 31.73 (t), 118.42 (t), 157.11 (s); GC/MS, *m/e* (% rel intensity) 112 (9), 97 (50), 85 (12), 84 (100), 83 (13), 72 (25), 71 (18), 68 (16), 58 (19), 58 (80); mass spectrum, calcd for SiC_6H_{12} 112.0709, *m/e* found 112.0709.

[5] Compounds **2**, **3**, **4**, **6**, and **7** were identified by comparison with authentic samples. Product yields were based on the quantity of decomposed 1,1-dimethylsilacyclobutane as measured by an inert internal standard.

[6] **5**: ^{1}H NMR (neat) δ −0.14, (s, 6 H, $(CH_3)_2Si$), 1.34 (app t, 4 H, J = 1.8 Hz, $(CH_2)_2Si$), 4.26 (app t, J = 1.8 Hz, CH_2=); ^{13}C NMR (neat) δ −2.99 (s), 26.66 (t), 107.36 (t), 152.23 (s); GC/MS, *m/e* (rel intensity) 112 (10), 97 (56), 84 (100), 83 (15), 72 (26), 71 (17), 69 (18), 59 (20), 58 (80), 53 (20), 44 (20), 43 (76). Since base-line separation of **5** and **6** could be achieved only on a capillary GC column, an elemental analysis on the mixture of isomers was not obtained.

[7] Barton, T. J.; Marquardt, G.; Kilgour, J. A.; *J. Organomet. Chem.* **1974**, *85*, 317. Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *97*, 8678. Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *24*, 3543.

[8] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[9] Conlin, R. T.; Kwak, Y.-W.; Huffaker, H. B. *Organometallics* **1983**, *2*, 343.

[10] Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

0002-7863/85/1507-0731$01.50/0