Os(3)–Os(4) bond at 3.092 (1) Å is believed to contain one of the two unobserved bridging hydride ligands. The second hydride ligand is believed to bridge the Os(1)–Os(3) bond.[20] There is a triply bridging sulfido ligand on one side of the cluster and a quadruply bridging acetylene ligand on the other side. The acetylene ligand is bonded to three of the metal atoms at the unsaturated C(12)–C(13) bond and is coordinated to the fourth metal through the oxygen atom O(12) of the carboxylate group, Os(2)–O(12) = 2.18 (1) Å. Thus, the acetylene ligand serves as a six-electron donor and the 66-electron complex is electron-precise.

Compound **2a** has not yet yielded crystals suitable for a structural analysis, but it reacts rapidly (30 min) with CO (25 °C) (1 atm) to form the adduct $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu\text{-}HC_2CO_2Me)(\mu\text{-}H)_2$ (**3**) in 86% yield.[8,21,22] Compound **3** has been analyzed by a X-ray diffraction analysis, and an Ortep drawing of this molecule is shown in Figure 3. The molecule consists of a chain of four osmium atoms with three metal–metal bonds.[23] The external bonds Os(1)–Os(4) = 2.941 (1) Å, and Os(2)–Os(3) = 2.924 (1) Å which are longer than the internal bond Os(1)–Os(3) = 2.803 (1) Å are believed to contain the two inequivalent bridging hydride ligands. There is a triply bridging sulfido ligand and triply bridging acetylene ligand that serve as four-electron donors. Thus, compound **3** like **2b** is electron precise. When heated to 125 °C, **3** loses both CO and hydrogen to regenerate **1** in 34% yield but also yields a small amount of **2b** by loss of CO alone. Compound **2b** adds CO to form **3**, but the reaction is much slower: 8 days; 25 °C (1 atm); 39% yield. The transformations observed for these compounds are summarized in Scheme I.

Details of the structure of **2a** have not been established yet, but the high stretching frequency (1712 cm^{-1}) of the carboxylate C=O bond indicates that this group is not coordinated in this molecule. The relatively low-field chemical shift (−8 to −10 ppm) for one of the hydride ligands in this molecule could be indicative of the presence of a terminally coordinated hydride ligand.[16]

The unsaturated clusters $M_4(CO)_{11}(\mu_4\text{-}PR)_2$(M = Fe,[24] Ru[25]) also undergo unusually facile ligand additions, but studies of their reactivity toward hydrogen have not been reported. The fact that **1** readily adds both hydrogen and donors would seem to make it a most attractive subject for hydrogenation catalysis.[2] These studies are in progress.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-8416460. We wish to thank Johnson-Matthey for a generous loan of osmium tetraoxide.

Registry No. 1, 102110-06-5; **2b**, 102110-07-6; 3, 102110-08-7; $Os_4(CO)_{12}[\mu_4\text{-}SC(CO_2Me)CH]$, 97919-67-0.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, interatomic distances, selected interatomic angles, and structure factor amplitudes for the structural analyses of compounds 1, **2b**, and 3 (61 pages). Ordering information is given on any current masthead page.

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(19) Selected interatomic distances (Å) and angles (deg) for **2b** are as follows: Os(1)–Os(2) = 2.803 (1), Os(1)–Os(3) = 2.803 (1), Os(2)–Os(4) = 3.092 (1), Os(3)···Os(4) = 3.943 (1), Os(1)–C(12) = 2.31 (2), Os(3)–C(12) = 2.11 (2), Os(1)–C(13) = 2.29 (2), Os(4)–C(13) = 2.14 (2), Os(2)–O(12) = 2.18 (1); C(12)–C(13) = 1.40 (2), C(14)–O(12) = 1.22 (2); Os(2)–Os(1)–Os(3) = 137.31 (3), Os(1)–Os(2)–Os(4) = 70.12 (2).

(20) This hydride ligand is believed to bridge the Os(1)–Os(3) bond in the large cavity that is circumscribed by the carbonyl ligands C(1)–O(1), C(2)–O(2),C(6)–O(6), and C(7)–O(7).

(21) Compound **3** was isolated by TLC on silica gel plates using a CH_2C_2/hexane (20/80) solvent mixture. IR (ν(CO) in hexane, cm^{-1}): 2113 w, 2093 s, 2082 vs, 2059 s, 2035 m, 2022 m, sh, 2018 s, 2005 w, 1995 w, 1989 w, 1709 w, br. Compound **3** exists in $CDCl_3$ solution as a mixture of two slowly interconverting isomers in a 3/4 ratio. ^1H NMR (δ in $CDCl_3$): minor isomer, 8.06 (s, CH), 3.74 (sCH_3), −16.48 (s, OsH), −18.28 (s, OsH); major isomer, 7.83 (s, CH), 3.79 (s, CH_3), −16.52 (s, OsH), −18.22 (s, OsH). Satisfactory elemental analyses have been obtained.

(22) Yellow platelike crystals of **3** were grown by slow evaporation of solvent from CH_2Cl_2/hexane solutions at −20 °C: space $P2_1/n$; $a = 13.674$ (5) Å, $b = 10.253$ (5) Å, $c = 17.746$ (4) Å; $\beta = 103.42$ (2)°; $Z = 4$; $\rho_{calcd} = 3.34$ g/cm^3. The structure was solved by direct methods (MULTAN) and was refined with 2366 reflections to the final values of the residuals R = 0.040 and R_w = 0.042. The hydrogen atoms were not observed and were thus ignored.

(23) Selected interatomic distances (Å) and angles (deg) for **3** are as follows: Os(1)–Os(3) = 2.867 (1), Os(1)–Os(4) = 2.941 (1), Os(2)–Os(3) = 2.924 (1), Os(1)–C(13) = 2.31 (2), Os(1)–C(14) = 2.43 (2), Os(2)–C(14) = 2.16 (2), Os(4)–C(13) = 2.11 (2), C(13)–C(14) = 1.37 (2); Os(3)–Os(1)–Os(4) = 83.66 (3), Os(1)–Os(3)–Os(2) = 81.19 (3).

(24) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219.

(25) (a) Field, J. S.; Haines, R. J.; Smit, D. N. *J. Organomet. Chem.* **1982**, *224*, C49. (b) Field, J. S.; Haines, R. J.; Smit, D. N.; Natarajan, K.; Scheidsteger, O.; Huttner, G. *J. Organomet. Chem.* **1982**, *240*, C23.

Reactivity of Unsaturated Clusters. Multiple Additions of Unsaturated Hydrocarbons to $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$

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Summary: The unsaturated cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ (**1**) undergoes facile multiple addition reactions with phenylacetylene or allene at 25 °C to form the products $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)\text{-}C{\equiv}CCO_2Me]$ (**2**) or $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}C(H)C(CH_2)_2](\mu_3\text{-}S)$ (**3**) in 34% and 46% yields, respectively. Compounds **2** and **3** have been characterized by X-ray diffraction analyses and were found to consist of opened clusters of metal atoms in which the methyl acetylenecarboxylate ligand in **1** has been coupled to one of the added ligands by carbon–carbon bond formation.

Coordination unsaturation in metal complexes is a feature that has played a very critical role in the development of the field of homogeneous catalysis.[1] Coordination unsaturation in polynuclear metal complexes is uncommon because electron deficiencies are usually eliminated by the formation of metal–metal bonds.[2] Recent reports have described the synthesis and reactivity of the new tetranuclear clusters $M_4(CO)_{11}(\mu_4\text{-}L)(\mu_4\text{-}L')$ (M = Fe, Ru; L = L′ = PR) which consist of a square-planar arrangments of four metal atoms.[3] These compounds contain only 62 valence electrons and are thus electron deficient (EAN rule) by the amount of two electrons. Accordingly, they readily engage in ligand addition reactions and may be the prototypes for a general class of cluster complexes that exhibit high reactivity toward ligand additions.[3] In our recent studies we have synthesized the new tetraosmium cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu\text{-}HC_2CO_2Me)$ (**1**).[4] This cluster

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(1) (a) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136. (b) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

(2) (a) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (b) Kaesz, H. D. In *Metal Clusters in Catalysis*, Knozinger, H., Gates, B. C., Guczi, L., Eds.; Elsevier: Amsterdam, 1986, in press.

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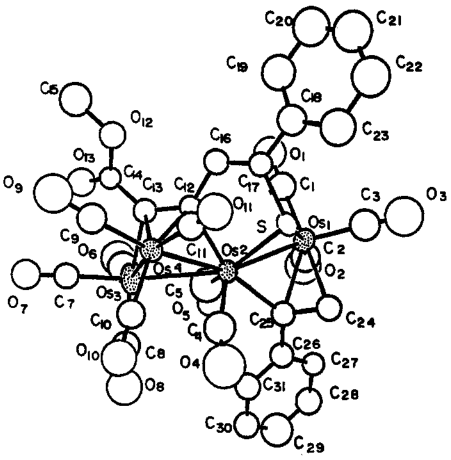

Figure 1. An ORTEP diagram of $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C{\equiv}CCO_2Me]$ (2) showing 50% probability thermal ellipsoids.

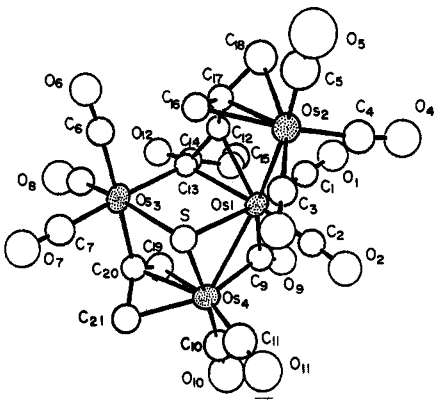

Figure 2. An ORTEP diagram of $Os_4(CO)_{11}[\mu\text{-}C(CH_2)][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}C(H)C(CH_2)](\mu_3\text{-}S)$ (3) showing 50% probability thermal ellipsoids.

also has only four metal–metal bonds and 62 valence electrons and is likewise electron deficient by the amount of two electrons.[5] We have recently reported that 1 undergoes reversible activation of hydrogen under unusually mild conditions for a cluster complex (i.e., 25 °C, 1 atm of H_2 pressure).[4] We have now found that 1 also undergoes facile addition of unsaturated hydrocarbons which subsequently couple to the alkyne ligand in unusual ways. In this report our preliminary results of these additions are described.

In CH_2Cl_2 solvent at 25 °C compound 1 adds 2 equiv of $PhC{\equiv}CH$ to give a 34% yield of the new compound 2 after 3 h. Compound 2 has been characterized by IR and ^{1}H NMR spectroscopies and by elemental and X-ray diffraction analyses.[6-8] The molecule has been formulated as $Os_4(CO)_{11}[\mu\text{-}C(Ph){=}CH_2][\mu_4\text{-}\eta^3\text{-}SC(Ph){=}C(H)C{\equiv}CO_2Me]$, and an ORTEP drawing of 2 is shown in Figure 1. The cluster consists of a "spiked" triangular arrangment of four metal atoms. The osmium–osmium bonding distances span a considerable range, 2.713 (1)–2.948 (1) Å but do not greatly exceed the distances found in $Os_3(CO)_{12}$, 2.877 (3) Å.[9] The two-carbon group C(24)–C(25) is believed to be a 1-phenylvinyl ligand that is π-bonded to Os(1) and σ-bonded to Os(2).[10] It is believed to have been formed by the addition of one hydrogen atom to the terminal carbon of one of the added PhC_2H ligands. This hydrogen atom is believed to have been derived from the MeO_2CC_2H ligand in 1 (vide infra). The most interesting ligand consists of the four-carbon chain C(13)–C(12)–C(16)–C(17). C(12)–C(13) could be regarded as a carbon–carbon triple bond, 1.37 (2) Å, that is coordinated to the face of the triosmium triangle. C(16)–C(17) is a carbon–carbon double bond, 1.32 (2) Å, that is not coordinated to any metal atoms but is bonded to the sulfur atom, S–C(17) = 1.80 (2) Å. This unusual ligand was apparently formed by the addition of the second PhC_2H molecule to the sulfido and acetylene ligands in 1. The carbon–carbon bond formation was probably preceded by the shift of the hydrogen atom originally bonded to C(12), to the metal atoms, and subsequently to other PhC_2H ligand. The activation of C–H bonds in coordinated terminal acetylenes has been observed previously.[12]

In CH_2Cl_2 solvent at 25 °C, compound 1 adds 2 equiv of allene to give a 46% yield of the new compound 3 after 1.6 h. Compound 3 has been characterized by IR and ^{1}H NMR spectroscopies[13] and by elemental and single-crystal X-ray diffraction analyses. Compound 3 has been formulated as $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}C(H)C(CH_2)_2](\mu_3\text{-}S)$, and an ORTEP drawing of its molecular structure is shown in Figure 2. The molecule consists of an open tetraosmium cluster containing a chain of three metal atoms with the fourth, Os(3), tied to the molecule

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(4) Adams, R. D.; Wang, S. *Organometallics*, preceding paper in this issue.

(5) It should be noted that the structure observed for 1 is in accordance with the bonding requirements of the polyhedral skeletal electron pair theory.

(6) Compound 2 was isolated by TLC on silica gel by eluting with a 1/1, v/v, CH_2Cl_2/hexane solvent mixture. For 2: IR (v(CO) in hexane; cm^{-1}) 2094 (w), 2079 (vs), 2053 (s), 2031 (w), 2019 (m), 2010 (s), 2005 (m), 1990 (w), 1884 (br, vw) 1706 (vw); ^{1}H NMR ($CDCl_3$, δ) 8.44 (s, 1 H), 5.77 (d, 1 H, J_{H-H} = 3.0 Hz), 3.77 (s, 3 H), 3.08 (d, 1 H, J_{H-H} = 3.0 Hz). Satisfactory elemental analyses have been obtained.

(7) Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo K$\bar{\alpha}$ radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAXI computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

(8) Orange crystals of 2 were grown from CH_2Cl_2/hexane (10/90, v/v) solvent at −20 °C. The crystals belong to the triclinic system, space group $P\bar{1}$, with a = 12.707 (7) Å, b = 15.616 (3) Å, c = 10.210 (2) Å, α = 90.65 (2)°, β = 111.51 (2)°, γ = 113.42 (2)°, and ρ_{calcd} = 2.71 g/cm^3. The structure was solved by direct methods and refined with 4602 reflections $[F^2 \geq 3.0\sigma(F^2)]$ to final values for the residuals R_F = 0.050 and R_{wF} = 0.057. The phenyl ring attached to C(17) and the methyl carboxylate group were found to exhibit a 50/50 disorder, but this produced no difficulties in the least-squares refinement. Selected interatomic distances (Å) and angles (deg) for 2 are as follows: Os(1)–Os(2) = 2.759 (1), Os(2)–Os(3) = 2.948 (1), Os(2)–Os(4) = 2.826 (1), Os(3)–Os(4) = 2.713 (1), Os(1)–S = 2.400 (4), Os(2)–S = 2.384 (4), Os(2)–C(25) = 2.16 (2), Os(1)–C(24) = 2.29 (2), Os(1)–C(25) = 2.29 (2), Os(2)–C(12) = 2.12 (2), Os(3)–C(13) = 2.09 (2), Os(4)–C(12) = 2.22 (2), Os(4)–C(13) = 2.21 (2), S–C(17) = 1.80 (2), C(12)–C(13) = 1.37 (2), C(16)–C(17) = 1.32 (2), C(24)–C(25) = 1.42 (2); Os(1)–Os(2)–Os(3) = 139.70 (4), Os(1)–Os(2)–Os(4) = 145.91 (3), Os(3)–Os(2)–Os(4) = 56.00 (3), Os(2)–Os(4)–Os(3) = 64.28 (4), Os(2)–Os(3)–Os(4) = 59.72 (3).

(9) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(10) The two hydrogen atoms of atom C(24) were not observed crystallographically but were detected in the ^{1}H NMR spectrum by the resonances at 5.77 and 3.08 ppm which were coupled, J_{H-H} = 3.0 Hz.[6] This coupling value is characteristic of geminal hydrogen atoms in alkenyl groupings.[11]

(11) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1966; p 714.

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(13) Compound 3 was isolated by TLC on silica gel by using a 30/70 v/v, CH_2Cl_2/hexane solvent mixture: IR (v(CO) in hexane, cm^{-1}) 2080 (vs), 2053 (s), 2036 (m), 2014 (2), 1999 (2), 1845 (w), 1703 (w); ^{1}H NMR ($CDCl_3$, δ) 7.17 (1 H), 4.66 (1 H), 4.13 (1 H), 3.94 (1 H), 3.68 (1 H), 3.63 (3 H), 3.47 (1 H), 3.12 (1 H), 2.93 (1 H), 2.68 (1 H). Orange crystals of 3 which contain 0.5 mol of hexane/mol of complex were grown from solutions in a 10/90, v/v, CH_2Cl_2/hexane solvent mixture at −20 °C. The crystals belong to the triclinic crystal system, space group $P\bar{1}$, with a = 15.047 (2) Å, b = 11.472 (2) Å, c = 9.444 (2) Å, α = 103.85 (2)°, β = 89.10 (2)°, γ = 77.20 (1)°, and ρ_{calcd} = 2.73 g/cm^3. The structure was solved by direct methods and refined with 3609 reflections $[F^2 \geq 3.0\sigma(F^2)]$ to final values for the residuals R_F = 0.050 and R_{wF} = 0.057.

by bridging ligands only.[14] The Os(1)–Os(4) bond which contains a bridging carbonyl ligand is significantly shorter than the Os(1)–Os(2) bond, 2.856 (1) Å vs. 2.937 (1) Å. The allene ligand C(19)–C(20)–C(21) is π-bonded to Os(4) and σ-bonded to Os(3) via the central carbon C(20). A similarly coordinated allene ligand was found in the molecule $Os_3(CO)_{11}(\mu_2\text{-}\eta^3\text{-}CH_2CCH_2)$.[15] The second allene molecule has been joined to the other alkyne ligand by the central carbon C(17), C(12)–C(17) = 1.43 (3) Å. This transforms the alkyne into an alkenyl group, C(12)–C(13) = 1.44 (3) Å, that is π-bonded to Os(1) and σ-bonded to Os(3). The allene molecule has become an allyl substituent of this alkenyl group, and it is π-bonded to Os(2). This transformation represents a new example of the coupling of allenes to hydrocarbon ligands.[16]

It is believed that the facile addition of ligands to 1 can be attributed to the "electron-deficient character" of the cluster. The cluster-opening processes can be attributed to the fact that the multiple-ligand additions produce a surfeit of electron donation that ultimately ruptures some of the metal–metal bonds. Efforts to obtain stepwise additions may provide further details about the cluster's transformations and these unusual ligand–ligand coupling processes. These studies are in progress.

Acknowledgment. These studies were supported by the Office of Basic Energy Science of the U.S. Department of Energy. We wish to thank Johnson-Matthey for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, selected interatomic distances and angles, and structure factor amplitudes (70 pages). Ordering information is given on any current masthead page.

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[14] Selected interatomic distances (Å) and angles (deg) for 3 are as follows: Os(1)–Os(2) = 2.937 (1), Os(1)–Os(4) = 2.856 (1), Os(1)···Os(3) = 3.692 (1), Os(3)···Os(4) = 3.551 (1), Os(1)–S = 2.408 (5), Os(3)–S = 2.452 (5), Os(4)–S = 2.442 (5), Os(1)–C(12) = 2.31 (2), Os(1)–C(13) = 2.40 (2), Os(2)–C(16) = 2.26 (2), Os(2)–C(17) = 2.20 (2), Os(2)–C(18) = 2.29 (2), Os(3)–C(13) = 2.17 (2), Os(3)–C(20) = 2.17 (2), Os(4)–C(20) = 2.23 (2), Os(4)–C(19) = 2.37 (2), Os(4)–C(21) = 2.25 (2), Os(2)–Os(1)–Os(4) = 141.22 (4).

[15] Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sankey, S. W. *J. Organomet. Chem.* 1982, *231*, C65.

[16] (a) Chisholm, M. H.; Folting, K.; Heppert, J. A.; Streib, W. E. *J. Chem., Soc., Chem. Commun.* 1985, 1755. (b) Chisholm, M. H.; Johns, W. S. *Inorg. Chem.* 1975, *14*, 1189. (c) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* 1976, *14*, 245.

The Pyrolysis of Dimethyl-*cis*-1-propenylvinylsilane: A New Source of Dimethylsilylene and a New Reaction for the Formation of Carbon–Carbon Double Bonds

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Summary: Pyrolysis of dimethyl-*cis*-1-propenylvinylsilane leads to the extrusion of dimethylsilylene and the formation of a mixture of *cis*- and *trans*-piperylenes. The reaction occurs via a sigmatropic hydrogen shift giving rise to a *cis*-1,1,2-trimethyl-3-vinylsilirane intermediate that releases Me_2Si: by a retro-1,2-cycloaddition. The overall transformation is a new reaction for the formation of carbon–carbon double bonds.

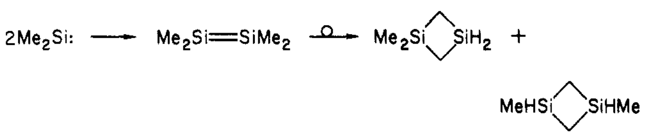
We have recently shown that a 1,5-sigmatropic shift, a homo-retro-ene reaction, is the dominant reaction channel for the silirane intermediate formed by cis addition of dimethylsilylene to *cis,cis*-2,4-hexadiene[1] (Scheme I).

This result encouraged us to examine such a reaction in the backward direction, both to determine whether it is indeed reversible and whether it can be used as a probe for contributions from diradical pathways.

Consider the related all-carbon system. Roth and König found that pyrolysis of *cis*-1,4-hexadiene in the gas phase at 410 °C for 16 h led to a mixture of 23% starting material, 9% of its trans isomer, and 68% 4-methylcyclopentene.[2] For the formation of the methylcyclopentene a pathway was proposed, shown in Scheme II, that is initiated by a step (d) analogous to the reversal of step b of Scheme I. This is followed by cleavage (step e) to a diradical that can cyclize (step f) to the observed product.

We have subjected dimethyl-*cis*-propenylvinylsilane (2),[4] a compound closely analogous to product 1 of Scheme I and of the starting compound in Scheme II, to vacuum flow pyrolysis at 610 °C (0.6 torr) (residence time ca. 5 ms). The results, given in Table I, suggest that both steps a and b of Scheme I are reversible.

As in the hydrocarbon case, the starting material undergoes cis–trans isomerization, and the trans isomer is the most abundant product. The piperylenes are also major products, formed in 36% yield (64% based on unisomerized starting material), and the disilacyclobutanes formed in 19% yield (35% based on unisomerized starting material) are known to be due to isomerization of the tetramethyldisilene dimer of Me_2Si.[3]



When the pyrolysis is carried out in the presence of a 5:1 excess of an efficient trapping agent for silylenes, 2,3-dimethylbutadiene, the adduct of Me_2Si, is formed in 29% yield (50% when corrected for isomerization, 79% based on the piperylenes). It is thus clear that extrusion of dimethylsilylene has occurred. Scheme III is proposed to account for the observed results including the formation in low yields of trimethylsilacyclopentenes 4 and 5.

Here we see a homo-ene reaction, a sigmatropic hydrogen shift, step h, that converts 2 into *cis*-1,1,2-trimethyl-2-vinylsilirane (3) that extrudes Me_2Si:.

That extrusion of Me_2Si does *not* occur directly from 2 is clear from the pyrolysis of its trans isomer reported in Table I. The conversion of trans is much lower than that of cis (by a factor of 3:1), trans to cis isomerization is the major process, and the low yield of piperylenes indicates that only the cis isomer extrudes Me_2Si.

The low yields of trimethylsilacyclopentenes 4 and 5

[†] Visiting scholar from Chengdu Institute of Organic Chemistry of the Chinese Academy of Sciences, Chengdu, China.

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[3] Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* 1976, *98*, 868.

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