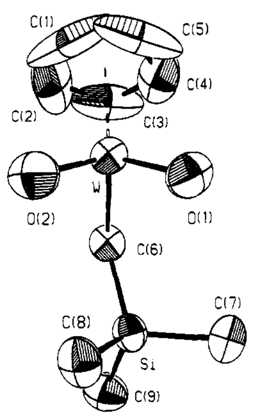

Figure 1. Molecular structure of 1, hydrogen atoms having been omitted for clarity. Selected bond lengths (Å) and angles (deg) are W-O(1) = 1.716 (5), W-O(2) = 1.723 (5), W-C(6) = 2.134 (6), W-C_5H_5(centroid) = 2.107 (6), Si-C(6) = 1.880 (7), Si-C(CH_3, av) = 1.858 (6), O(2)-W-O(1) = 107.8 (3), O(2)-W-C(6) = 99.5 (3), C(6)-W-O(1) = 99.1 (3), W-C(6)-Si = 115.8 (3), and C(6)-Si-C(7) = 109.3 (4).

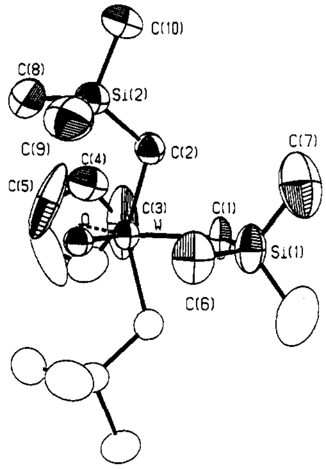

Figure 2. Molecular structure of 2, hydrogen atoms having been omitted for clarity. Selected bond lengths (Å) and angles (deg) are W-O = 1.664 (8), W-C(1) = 2.311 (11), W-C(2) = 2.238 (7), W-C_5H_5(centroid) = 2.131 (6), Si-CH_2(av) = 1.862 (3), Si-CH_3(av) = 1.86 (1), O-W-C(1) = 120.8 (3), O-W-C(2) = 90.2 (2), O-W-C_5H_5(centroid) = 103.0 (4), W-C(1)-Si(1) = 119.0 (6), W-C(2)-Si(2) = 118.9 (3), C(1)-Si(1)-C(7) = 108.5 (5), and C(2)-Si(2)-C(10) = 108.0 (4).

revealed their normal "piano stool" molecular structures with mirror symmetry at the central tungsten atoms (Figures 1 and 2). The most chemically interesting features of both structures involve the tungsten-oxygen linkages whose bond lengths (1.720 (4) Å (av) in 1 and 1.664 (8) Å in 2) are consistent with the existence of W=O double bonds.[5]

Under ambient conditions, complexes 1-3 are diamagnetic solids which are freely soluble in common organic solvents, the solutions of 2 and 3 being moderately air-sensitive. Their spectroscopic properties[11] indicate that their molecular structures in solution are as depicted above. All three compounds are thus best viewed as being 16-electron species, formally containing tungsten in its highest oxidation state of VI. Consistent with this view is the fact that compounds 1-3 appear to be reactive toward both electrophiles and nucleophiles. This reactivity and the mechanisms of reactions 1-3 are currently being investigated.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. We also thank Professor J. Trotter for permitting us the use of his X-ray diffractometer. L.S. acknowledges the Spanish Ministry of Education for the award of a postdoctoral fellowship.

Registry No. 1, 96760-75-7; 2, 96760-76-8; 3, 96791-10-5; (η^5-C_5H_5)W(NO)(CH_2SiMe_3)$_2$, 94620-67-4; [(η^5-C_5H_5)W(NO)I_2]$_2$, 71341-43-0.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^1H and $^{13}C\{^1H\}$ NMR, mass spectral) data for 1, 2, and 3 and tables of fractional coordinates, isotropic and anisotropic thermal parameters, and structure factors for 1 and 2 (35 pages). Ordering information is given on any current masthead page.

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(10) Crystals of 2 are orthorhombic of space group *Cmcm* with *a* = 18.6342 (11) Å, *b* = 9.8767 (6) Å, *c* = 13.1985 (8) Å, and *Z* = 4. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to *R* = 0.028 and R_w = 0.032 for 1562 absorption-corrected reflections with $I \geq 3\sigma(I)$ collected at 22 °C with Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer. The molecule (which possesses exact C_s symmetry) was found to be twofold disordered about a site having crystallographic C_{2v} (*mm*2) symmetry. No satisfactory refinement could be achieved in the noncentrosymmetric space group *Cmc*2_1 as the disorder persisted. Hydrogen atoms were fixed in calculated positions.

(11) Supplementary material.

Extrusion of Dimethylsilylene from 1,1-Dimethyl-1-silacyclopent-3-enes

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Received January 28, 1985

Summary: Dimethylsilylene Me_2Si: has been trapped by addition to 1,3-dienes in the vacuum flow pyrolysis of 1,1-dimethyl-1-silacyclopent-3-ene, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene, and 1,1,2-trimethyl-1-silacyclopent-3-ene. Intramolecular rearrangement products obtained in the pyrolysis of the last compound point to a stepwise extrusion mechanism via alkenylsilirane intermediates.

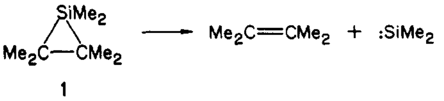
Silylenes differ markedly from carbenes in the ease with which their carbene-like reactions can be reversed. α-Elimination, the inverse of insertion, is a standard route for the generation of silylenes, pioneered by Atwell and Weyenberg.[1,2]

$$\mathrm{XYZSi\text{-}SiXYZ} \xrightarrow{\overset{X}{\delta}} \mathrm{X_2YZSi} + \mathrm{:SiYZ}$$

X = H, halogen alkoxy, alkyl, etc.

Y, Z = H, halogen, alkoxy, alkyl, aryl, etc.

Extrusion of dimethylsilylene from hexamethylsilirane, 1, another α-elimination that is the inverse of π-addition to an olefin, has been developed by Seyferth as a convenient and mild source of Me_2Si:.[3]



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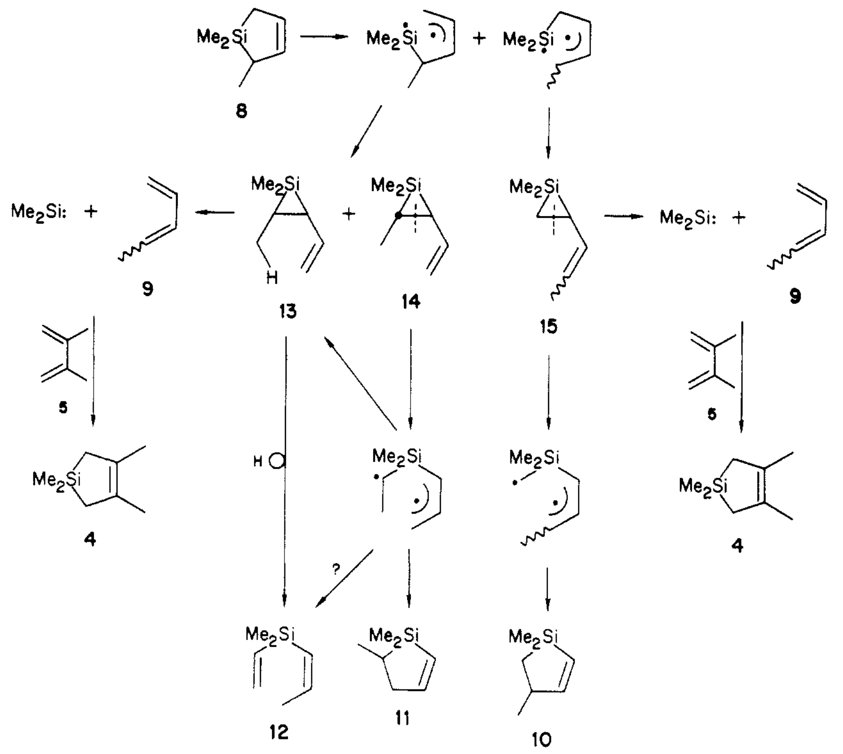
[†] Visiting scholar from the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, China.

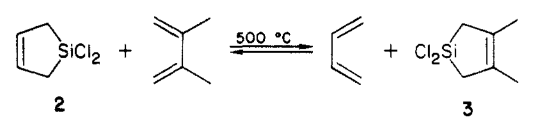
(1) Atwell, W. H.; Weyenberg, D. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 469 and references contained therein.

(2) Gaspar, P. P. *React. Intermed.* (*Wiley*) **1978**, *1*, 229; **1981**, *2*, 335; **1985**, *3*, 333.

Scheme I

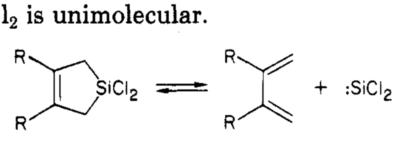


Extrusion of silylenes from 1-silacyclopent-3-enes is a much more recently observed phenomenon[4] and is of interest because it is the inverse of a process that is virtually unknown in carbene chemistry, formal 1,4-addition to a 1,3-diene.[5] Chernyshev and co-workers have reported the transfer of dichlorosilylene from 1,1-dichloro-1-silacyclopent-3-ene (2) to 2,3-dimethylbutadiene in 80% yield.[4]



2 3

The reversibility of this reaction and the formation of no products other than 1-silacyclopent-3-enes 2 and 3 was interpreted in terms of a *concerted* extrusion of dichlorosilylene, and this suggestion received further support from the demonstration that the product yields were independent of the concentration of trapping agent; i.e., the loss of $SiCl_2$ is unimolecular.



2, R=H
3, R=Me

Chernyshev further concluded that, since the extrusion of :$SiCl_2$ from 1,1-dichloro-1-silacyclopent-3-enes 2 and 3 was regarded as a concerted process, its inverse, the addition of :$SiCl_2$ to 1,3-dienes, is also concerted. This is of course in accord with the principle of microscopic reversibility.[6]

In contrast, we have presented evidence for stepwise reactions in our investigation of the addition of dimethylsilylene :$SiMe_2$ to 1,3-dienes equipped at one or both termini of the π-electron system with methyl groups that could serve as stereochemical markers.[7-9]

Given this apparent difference in addition mechanisms, it seemed important to examine the pyrolysis of 1,1-dimethyl-1-silacyclopent-3-enes to determine whether silylene extrusion would occur and, if so, by what mechanism. We were mindful of the report of the activation parameters for the pyrolysis of 1,1-dimethyl-1-silacyclopent-3-ene by Davidson, Barton, and co-workers, who did not indicate what products were formed.[10] In embarking on these experiments we were also aware that while dichlorogermylene, :$GeCl_2$, was trapped in the pyrolysis of the germanium analogue of 2, no dimethylgermylene, :$GeMe_2$, was captured in the pyrolysis of 1,1-dimethyl-1-germacyclopent-3-ene.[11]

We have found that extrusion of dimethylsilylene is an efficient process. When 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (4) is subjected to vacuum flow pyrolysis at 700 °C at a pressure of $^1/_2$ torr and residence time ca. 5 ms, 54% decomposition occurred and 2,3-dimethylbutadiene (5) was obtained in 89% yield. When 4 was pyrolyzed in the presence of excess butadiene (C_4H_6:4 = 10) at slightly higher pressure and longer residence time, products from the addition of dimethylsilylene to butadiene were found in a combined yield of 65% based on the amount of 4 consumed (70% decomposition).

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[3] Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 7162; *J. Organomet. Chem.* **1976**, *117*, C51. Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288 and other references contained therein.

[4] Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *J. Organomet. Chem.* **1984**, *271*, 129 and references contained therein.

[5] Moss, R. A.; Jones, M., Jr. *React. Intermed. (Wiley)* **1978**, *1*, 69; **1981**, *2*, 59; **1985**, *3*, 45.

[6] Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions", Wiley: New York, 1963; pp 73–4.

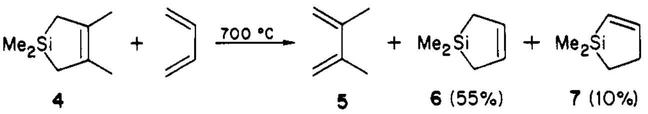
[7] Gaspar, P. P.; Hwang, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 6198.

[8] Lei, D.; Hwang, R. J.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1.

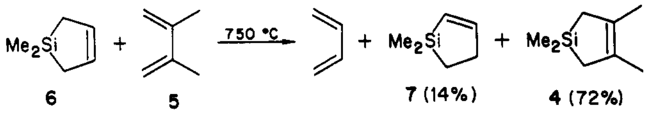
[9] Lei, D.; Gaspar, P. P. "Addition of Dimethylsilylene to *cis,cis*-2,4-Hexadiene: Evidence for a Concerted Vinylsilacyclopropane Rearrangement", *J. Chem. Soc., Chem. Commun.*, in press.

[10] Davidson, I. M. T.; Fenton, A.; Ijadi-Maghsoodi, S.; Scampton, R. J.; Auner, N.; Grobe, J.; Tillman, N.; Barton, T. J. *Organometallics* **1984**, *3*, 1593.

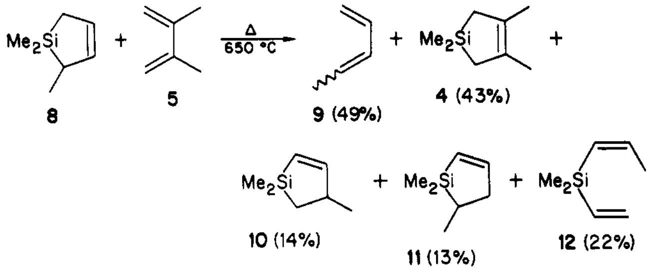
[11] Kolesnikov, S. P.; Rogozhin, I. S.; Safarov, M. G.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *6*, 1423; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* **1981**, p 1143.



The formation of 1,1-dimethyl-1-silacyclopent-2-ene (**7**) in addition to the formal 1,4-adduct **6** is probably due to isomerization of **6** to **7** under the reaction conditions. When pure **6** is subjected to pyrolysis at 750 °C (1 torr), a 16% yield of **7** was obtained in addition to 53% butadiene (69% decomposition of **6**). In the presence of excess dimethylbutadiene **5** (**5**:**6** = 5), the expected product of dimethylsilylene-transfer was obtained, and the conversion of starting material (70% decomposition of **6**) was the same as in the absence of trapping agent.



From these results it appears that the loss of the Me$_2$Si unit from silacyclopent-3-enes **4** and **6** is reversible and unimolecular, and thus it is fair to conclude that extrusion of dimethylsilylene occurs. There is in addition clear evidence for nonconcerted extrusion[12] in the pyrolysis of 1,1,2-trimethyl-1-silacyclopent-3-ene (**8**), synthesized by the elegant method of Conlin,[13] in the presence of 2,3-dimethylbutadiene (**5**).



We see that in addition to the product of silylene transfer **4**, there is an equal yield of intramolecular rearrangement products **10**, **11**, and **12**. These latter products have also been obtained in the addition of Me$_2$Si: to the piperylenes **9**,[8] but in the present experiment the large excess of **5** over **9** ensures that the extruded silylene is captured by **5**. The formation of **10**, **11**, and **12** is most easily rationalized in terms of carbon–carbon bond cleavage in the alkenylsilirane intermediates **13**, **14**, and **15** shown in Scheme I.

Since products **10**, **11**, and **12** are formed, together with **8**, in the addition of Me$_2$Si to *cis-* and *trans*-piperylene **9**,[8,14] loss of dimethylsilylene from 1,1,2-trimethyl-1-silacyclopent-3-ene (**8**) appears to be the inverse of the silylene addition. It is therefore hardly surprising that the same alkenylsilirane intermediates **13**, **14**, and **15** are proposed for the extrusion pictured above as for the previously studied silylene addition. Once the addition has been shown to be reversible, the extrusion must follow the same mechanism.

We thus conclude that extrusion of dimethylsilylene from trimethylsilacyclopentene (**8**) is a nonconcerted process whose ultimate step is the loss of Me$_2$Si: from alkenylsilirane intermediates. The mechanism of dimethylsilylene extrusion from 1,1-dimethyl-1-silacyclopent-3-ene (**6**) and other related processes including the extrusion of dichlorosilylene from 1,1-dichloro-1-silacyclopent-3-enes[4] must be regarded as remaining an open question until tests for the concertedness are applied.

Acknowledgment. This work has been carried out with financial support from the United States Department of Energy. This is DOE technical report DOE/ER/01713-137.

Registry No. 4, 16109-39-0; 5, 513-81-5; 6, 16054-12-9; 7, 18187-50-3; 8, 3528-14-1; 9, 504-60-9; 10, 93297-71-3; 11, 93297-70-2; 12, 93297-72-4; butadiene, 106-99-0.

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[12] A small contribution from concerted extrusion is not precluded by these data.

[13] Conlin, R. T.; Peterson, L. L. *J. Organomet. Chem.* **1982,** *232,* C71.

[14] Differences in temperature account for *differences* between the product ratios reported here from the pyrolysis of the silacyclopentene and those reported in ref 8 for the addition of Me$_2$Si: to the piperylenes.

Selective Reductions of Carbonyl Compounds with Group 6 Metal Carbonyl Hydrides

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Summary: Aldehydes were selectively reduced to alcohols in the presence of ketones by Et$_4$N[μ-HMo$_2$(CO)$_{10}$] and HOAc in refluxing THF; α,β-unsaturated esters or ketones were reduced at the carbon–carbon double bond only. After prolonged reaction with excess reducing agent, an unhindered cyclohexanone was partially reduced with high stereoselectivity.

Since reductions of carbonyl groups represent one of the most fundamental transformations in organic chemistry, new reagents which can function as selective reducing agents are always being sought. Although a number of reagents will discriminate fairly well between an aldehyde and a methyl ketone, one of the most difficult tests for a chemoselective reducing agent is the discrimination between aldehydes and unhindered cyclohexanones. All of the reagents previously reported to demonstrate this type of selectivity are stoichiometric rather than catalytic agents and most are main-group hydride derivatives;[1] typically, the selectivity results from diminished activity and steric bulk. Although the reagents are effective in performing selective reductions, some shortcomings can be identified for each of them. In general, the adverse features are their relatively great expense (magnified by their stoichiometric nature) and/or their moisture sensitivity.

In contrast to main-group metal hydrides, transition-metal hydrides have been studied very little as reducing agents for organic compounds. The one most studied is the hydridotetracarbonylferrate, [HFe(CO)$_4$]$^-$, which is effective in reducing a variety of functional groups but is difficult to handle.[2] The related binuclear anion [HFe$_2$(CO)$_8$]$^-$, reduces carbon–carbon double bonds in activated compounds but does not reduce carbonyl groups.[3] Organic

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[1] (a) Posner, G. H.; Runquist, A. W.; Chapdelaine, M. J. *J. Org. Chem.* **1977,** *42,* 1201. (b) Fung, N. Y. M.; de Mayo, P.; Schauble, J. H.; Weedon, A. C. *J. Org. Chem.* **1978,** *20,* 3977. (c) Krishnamurthy, S. *J. Org. Chem.* **1981,** *46,* 4629. (d) Brown, H. C.; Kulkarni, S. U. *J. Org. Chem.* **1977,** *42,* 4169. (e) Midland, M. M.; Tramontano, A. *J. Org. Chem.* **1978,** *43,* 1470. (f) Yamaguchi, S.; Kabuto, K.; Yasuhara, F. *Chem. Lett.* **1981,** 461. (g) Nutaitis, C. F.; Gribble, G. W. *Tetrahedron Lett.* **1983,** *24,* 4287. (h) Sorrell, T. N.; Pearlman, P. S. *Tetrahedron Lett.* **1980,** *21,* 3963.

[2] See, for example: (a) Cole, T. E.; Pettit, R. *Tetrahedron Lett.* **1977,** 781. (b) Watanabe, Y.; Mitsudo, T.; Yamashita, M.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1975,** *48,* 1478. (c) Alper, H. *J. Org. Chem.* **1976,** *38,* 2694. (d) Cainelli, G.; Panunzio, M.; Umani-Ronchi, A. *J. Chem. Soc. Perkin Trans.* **1975,** *1,* 1273.

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