Hydrolysis and Oxidation of Cp_2M(diene) Complexes. All the complexes were hydrolyzed with 2 N HCl or 2 N DCl in benzene at 5–10 °C. The resulting 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, 2,3-dimethyl-1-butene, or the dideuterated compounds were isolated with a preparative gas chromatograph and were identified by comparison of their MS and ^{1}H NMR spectra with those of authentic samples previously identified.[4,5] 1,4-Diphenyl-1-butene and 1,4-diphenyl-2-butene obtained by hydrolysis of 7 and 8 were identified with reference to the data reported by Bumgardner.[33] The yield of each olefin (Table II) was determined by gas chromatographic analysis within an error of 3%. The purity of the dideuterated olefins was determined to be 96–99% by mass spectroscopy with the use of the corresponding undeuterated olefins as standards. Oxidation was carried out in a closed system; i.e., an excess of dry oxygen (300 mL, dried over P_2O_5) was introduced into the reaction tube containing a toluene solution of a diene complex (3 mmol in 30 mL of toluene) (Schlenk technique). The solution turned colorless after being stirred, for 1–10 min at 25 °C. The formation of 0.93–0.97 molar equiv of the respective conjugated diene was confirmed by GC. Addition of dried air gave the identical result.

(33) C. L. Bumgardner and H. Iwerks, *J. Am. Chem. Soc.*, **88**, 5518 (1966).

Registry No. 1, 75374-50-4; 2, 75361-73-8; 3, 75361-74-9; 4, 80185-89-3; 5, 80161-02-0; 6, 80161-03-1; 7, 75361-76-1; 8, 80161-04-2.

Communications

An Intramolecular Silene Ene Reaction

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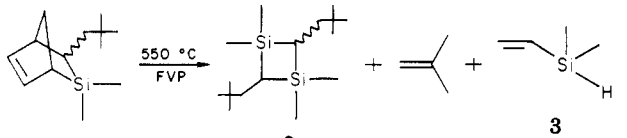
Summary: The flash vacuum pyrolysis of 2,2-dimethyl-3-neopentyl-2-silabicyclo[2.2.1]hept-5-ene (1) gives nearly quantitative yields of cyclopentadiene. In addition to the 1,3-disilacyclobutane dimers of 1,1-dimethyl-2-neopentylsilene (4), two novel silene-derived products, isobutene and dimethylvinylsilane, are produced. Evidence that the latter products are formed in an intramolecular ene-type reaction of the silene, 4, is presented.

To a large extent, the resurgence of interest in the intramolecular ene reactions derives from the facility with which heteroatom π bonds undergo pericyclic processes.[1] With the widespread recognition of the extraordinary reactivity of π bonds between silicon and carbon,[2] it is somewhat surprising that there are no demonstrated examples of ene reactions initiated by a silicon–carbon π bond. In this communication we report a new and mild thermal method for generating silenes in the gas phase as well as an example of an intramolecular ene reaction of a silene.

Flash vacuum pyrolysis[3] of a mixture of the endo and exo isomers of 2,2-dimethyl-3-neopentyl-2-silabicyclo[2.2.1]hept-5-ene (1)[4] at 550 °C leads cleanly to cyclopentadiene in nearly quantitative yield. Four other products are isolated: the cis and trans isomers of 1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutane (2),[5] isobutene, and dimethylvinylsilane (3).[6] These products were all characterized by comparison of their spectral and chromatographic properties with those of authentic samples.



1 2 3

The formation of cyclopentadiene and the 1,3-disilacyclobutanes (2) is consistent with a [2 + 4] cycloreversion of 1, giving cyclopentadiene and 1,1-dimethyl-2-neopentylsilene (4) which undergoes the usual head-to-tail dimerization[2] to form 2. Analogous, possibly concerted, retro Diels–Alder eliminations are known for both the parent hydrocarbon bicyclo[2.2.1]heptene[8] and the related 7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene.[9] It is noteworthy that the ratio of *cis*- and *trans*-disilacyclobutanes formed in the gas phase at 550 °C, 1.15, is the *same ratio* observed when the silene, 4, is generated at low temperature in hydrocarbon solvents by the reaction of *tert*-butyllithium with chlorodimethylvinylsilane.[5] The absence of a temperature effect on this cis/trans ratio is consistent with earlier reports that there is no appreciable energy barrier to silene dimerization[10] and that 4 is produced in the low-temperature reaction.[4,5]

Especially intriguing is the mechanism of formation of isobutene and 3, which are isolated in nearly equal amounts from the reaction mixture.[11] We have established that the disilacyclobutanes, 2, do not give rise to these

(1) (a) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *17*, 476. (b) Hoffmann, H. M. R. *Ibid.* **1969**, *8*, 566.

(2) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(3) Pyrolyses were carried out at 10^{-4}–10^{-5} torr, employing a seasoned hot zone consisting of 10-mm i.d. × 30 cm quartz tube. Residence time in the hot zone was on the order of milliseconds.

(4) Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970.

(5) Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013, **1977**, *99*, 8447.

(6) Recently, Auner and Grobe[7] have reported that 2,2-dimethyl-2-silabicyclo[2.2.1]hept-5-ene, formed as a transient by the addition of 1,1-dimethylsilene to cyclopentadiene, isomerizes through a series of unprecedented steps and eventually leads to benzene as the only isolated product. We have not been able to reproduce their results.

(7) Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *190*, 129.

(8) Herndon, W. C.; Cooper, W. B.; Chambers, M. J. *J. Phys. Chem.* **1964**, *68*, 2016.

(9) Barton, T. J.; Kline, E. *J. Organomet. Chem.* **1972**, *42*, C21.

(10) (a) Gusel'nikov, L. E.; Konobeevski, V. M.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 1086. (b) Basu, S.; Davidson, I. M. T.; Laupert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1282.

(11) In all of our experiments the yield of isobutene appears to be higher than that of 3. This might be due to the difficulty in determining an accurate response factor for the highly volatile isobutene. It is also possible that side reactions provide another source of isobutene or that some of 3 is consumed by subsequent reactions. We have no evidence which resolves this discrepancy at this time.

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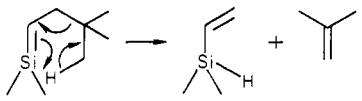
Table I. Results from the Flash Vacuum Pyrolysis of 1 [a] at 550 °C

expt	flow, μL of 1/min	% decompn	% of dimers	2 (cis/trans)	% of isobutene	% of 3	ene/dimer ratio [b]
1	0.7	90	8	1.15	50	40	5.00
2	3.2	76	22	1.15	39	23	1.05
3	30.0	83	48	1.14	19	12	0.25
4 [c]	7.0	36	36	1.15	36	25	0.69

[a] Percent yields determined by VPC using di-*n*-butyl ether as an internal standard. [b] Based on yield of 3/yield of 2. [c] Pyrolysis carried out in the presence of a 6-fold excess of methylene chloride.

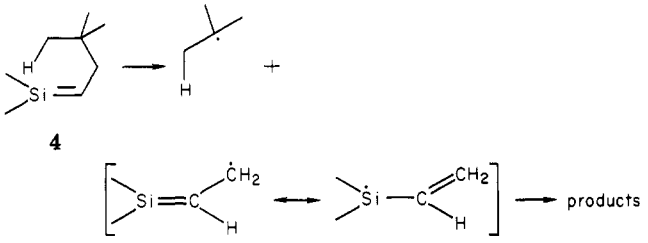
products at 550 °C. Based on the evidence presented below, we propose that these products arise from a unimolecular ene reaction of 4.



4 3

If dimerization is second order in silene while the ene reaction is first order in silene, one would predict the dimerization to be favored over the ene reaction with increasing silene concentration. The results in Table I support this hypothesis. With increasing flow rates and therefore increasing silene concentration, the ratio of disilacyclobutanes to dimethylvinylsilane increases 20-fold. At low flow, 3 is obtained in 5 times greater yield than the dimers 2; at high flow, the situation is reversed, with dimers being produced in yields 4 times greater than the ene product. Thus, dimethylvinylsilane production is clearly of lower kinetic order than the case for silene dimerization and is most probably first order.

In addition to the ene pathway for the formation of 3, a radical mechanism, involving a rate-determining homolysis of the carbon–carbon bond β to silicon in the silane, 4, followed by hydrogen abstraction could account for the



ene products. In order to assess the importance of such a pathway, we carried out the pyrolysis of 1 in the presence of a large excess of methylene chloride. If silyl radicals are produced in the pyrolysis, rapid chlorine abstraction should surpress the hydrogen abstraction[12] and chlorodimethylvinylsilane should appear as the main silicon-containing product of the ene pathway.

We have tested this method for detecting silyl radicals by carrying out the copyrolysis of methylene chloride with allyltrimethylsilane, a known source of silyl radicals.[13] The trimethylsilyl radicals are scavenged in nearly quantitative yield to give trimethylchlorosilane. None of the secondary products usually associated with silyl radicals are produced in the presence of methylene chloride.[14]

When the flash vacuum pyrolysis of 1 is carried out in the presence of an excess of methylene chloride, the product distribution is not affected (experiment 4). Because of the increased pressure differential across the reaction zone, the residence time of 1 is decreased, resulting in a correspondingly lower percent decomposition. The relative amounts of isobutene and 3 remain nearly constant (cf. experiment 2), and the ene/dimer ratio is consistent with the flow rate. No chlorodimethylvinylsilane is detected in the reaction mixture. Silyl radicals are thus eliminated as precursors to the isobutene and 3, products of the silene 4. In light of these results, the most reasonable alternative is an intramolecular ene reaction of 1,1-dimethyl-2-neopentylsilene.

In a large number of bimolecular reactions between silenes and organic systems such as propene,[15] isoprene,[16] and acetone,[17] acyclic products containing the exchanged fragments of both reaction partners are found. For the most part, these reactions have been described in terms of the sequence: cycloaddition and ring opening to biradicals, followed by hydrogen atom migration. However, it is conceivable that these reactions proceed by an *intermolecular* concerted pericyclic process. Experiments to explore this possibility are currently in progress in our laboratories.

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Registry No. *endo*-1, 74107-88-3; *exo*-1, 74107-87-2; *cis*-2, 62518-77-8; *trans*-2, 62518-76-7; 3, 18243-27-1; 4, 79991-59-6; isobutene, 115-11-7; cyclopentadiene, 542-92-7.

(12) (a) Sakurai, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2, pp 741–808. (b) Cadman, P.; Tilsley, G. M.; Trotman Dickenson, A. F. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 914.
(13) Davidson, I. M. T.; Wood, I. T. *J. Organomet. Chem.* **1980**, *202*, C65.
(14) Namavari, M.; Conlin, R. T., unpublished results.
(15) Nametkin, N. S.; Gusel'nikov, L. E.; Ushakova, R. L.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1740.
(16) Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.
(17) (a) Golino, C. M.; Bush, R. D.; Roark, D. N.; Sommer, L. H. *J. Organomet. Chem.* **1974**, *66*, 129. (b) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18.

Condensation of Propiolic Esters with Olefins Catalyzed by the $C_5H_5Fe(CO)_2$ Cation

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Summary: Methyl propiolate or tetrolate condense with a number of olefins in a reaction catalyzed by either η^5-$C_5H_5Fe(CO)_2$(isobutylene)BF_4 or η^5-$C_5H_5Fe(CO)_2$(THF)-BF_4 to give 1,3-dienes, cyclobutenes, and 5,6-dihydro-2-pyrones.

The $C_5H_5Fe(CO)_2$ cation (Fp^+) is known to activate olefins in $Fp(\eta^2\text{-olefin})^+$ x^- complexes toward addition by

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