(Scheme X). Complex **37** is identified in the crude mixture by ^{1}H NMR spectroscopy, which shows the Ge–H as a quartet and Ge–CH_3 as a doublet, but during isolation it converts into the hydroxy complex **38** which decomposes during attempted isolation. The germoxane complex **39** is obtained by treatment of **33** with water or with sodium methoxide in methanol. Reaction of **33** with $AgBF_4$ does not give a cationic complex, contrary to the previous observation in the phenyl-substituted series.[9]

The formation of siloxane or germoxane complexes is difficult to rationalize. Siloxanes can be obtained from alkoxysilanes, but only by employing vigorous conditions.[49] The presence of water or oxygen is carefully avoided; however, in another set of reactions, Curtis[43] pointed out that the affinity of silicon for oxygen is such that an oxygen atom could be abstracted from the carbonyl ligands.

Conclusion

Siloles and germoles, without phenyl substituents, behave as good η^4-ligands in transition-metal chemistry. They are strongly attached to the metal and are not displaced by phosphines.[42] The absence of aromatic groups avoids the competition between coordination to the diene or to the aromatic system[38] with chromium.

In some cases the silicon atom is probably responsible for new properties, compared to other related η^4-diene complexes, especially the cleavage of the dinuclear cobalt compounds by iodine. In this case, the η^4-silole ring behaves as a pseudo η^5 ligand. This observation is in agreement with studies by photoelectron spectroscopy[29] that show a certain aromatic character of the silole ring in iron tricarbonyl complexes.

The reactivity of the silole ring is rather disappointing, since the only clean reaction is the cleavage with $SnCl_4$. Chlorine can be displaced by several nucleophiles, but in many cases the product is a siloxane complex.

The η^5-silacyclopentadienyl system is not formed, confirming the difficulties in stabilizing sp^2 silicon atoms by coordination to a transition metal.[50]

Acknowledgment. We are grateful to Drs. Guy Dabosi and Monique Martineau for help in the polarographic measurements.

---

(49) Haiduc, I.; Zuckerman, J. J. *Basic Organometallic Chemistry*; De Gruyter: Berlin, 1985; p 130.

(50) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976,** *98,* 7453. Radnia, P.; Mc Kennis, J. S. *J. Am. Chem. Soc.* **1980,** *102,* 6349.

Photochemical Silene Syntheses. 3-Vinylsilacyclobutanes and Their Thermal Reactions

Robert T. Conlin* and Kevin L. Bobbitt

Center for Organometallic Research and Education, Department of Chemistry, North Texas State University, Denton, Texas 76203

Received August 18, 1986

Photolysis of 1,1,2,2-tetramethyl-1,2-divinyl-1,2-disilane at room temperature in a cyclohexane solution of methoxytrimethylsilane yields 1,1-dimethyl-2-((vinyldimethylsilyl)methyl)silene which is trapped in nearly quantitative yield by the methoxysilane. Reaction of the silene with butadiene affords the (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyldimethylsilyl)methyl)-3-vinyl-1-silacyclobutanes in 42 and 29% yields, respectively, along with minor amounts of 1,1-dimethyl-2-((vinyldimethylsilyl)methyl)-1-silacyclohex-3-ene (8%). Low-pressure flow pyrolysis at 450 °C of either the *E* or *Z* isomer provides a relatively mild thermal source of the silene in the gas phase. Two products, 1,1,3,3-tetramethyldisilacyclohex-4-ene and 2,2,5,5-tetramethyl-2,5-disilabicyclo[2.1.1]hexane, are formed from an intramolecular rearrangement of the silene. Other reactions of the 3-vinylsilacyclobutanes include geometric isomerization, ring expansion to the silacyclohex-3-ene, and a homodienyl 1,5-hydrogen shift to 3,3,6,6-tetramethyl-3,6-disiladeca-1,4,8-triene.

Until the recent isolation and convincing spectroscopic characterization of molecules possessing a silicon–carbon π bond by Brook,[1,2] the existence of silenes had been inferred from analogy to the reactivity of alkenes. In the early stages, perhaps the clearest example of an expected similarity was the facility with which silacyclohex-3-enes are formed in the thermal reactions between the silicon–carbon π bond and butadiene.[3] The 2 + 4 cycloaddition thus, with a singular exception, served as a diagnostic for the formation of a silene. That exception was one reported by Jones[4] in which the silene, generated at low temperature by a novel method, produced predominantly 2- and 3-vinyl-substituted silacyclobutanes. This atypical example prompted further investigation of the silene/diene reaction at temperatures where the vinylsilacyclobutane might remain stable.[5]

A clean photochemical source of silenes is 1,2-divinyl-1,1,2,2-tetramethyldisilane (**1**).[6] Ishikawa and co-workers

---

(1) Brook, A. G.; Abdesaken, F.; Gutenkunst, B.; Gutenkunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981,** 191.

(2) For a comprehensive review of new developments in multiply bonded silicon, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985,** *85,* 419–509.

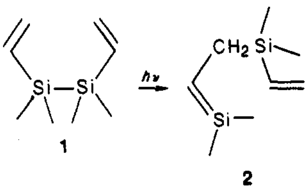
(3) (a) Nametkin, N. S.; Gusel'nikov, L. E.; Ushakova, R. L.; Vdovin, V. M. *Dokl. Akad. Nauk SSSR* **1971,** *201,* 1365. (b) Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981,** *103,* 1843. (c) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1984,** *3,* 918. (d) Frey, H. M.; Kashoulis, A.; Ling, L. M.; Lodge, S. P.; Pidgeon, I. M.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1981,** 915.

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

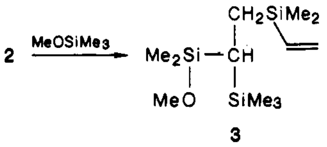
(5) We have learned recently that another silene, generated photochemically from an acylpolysilane, gives predominantly 2 + 2 products with butadiene. In addition, the 2 + 2 pathway with butadiene proceeds in the absence of light with a stable silene. Brook, A. G. XXI Organosilicon Symposium, Tarytown, NY Apr 1986.

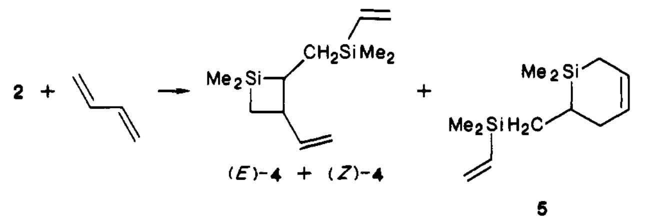
0276-7333/87/2306-1406$01.50/0 © 1987 American Chemical Society

also demonstrated that silenes as **2**, so generated from photolysis of a variety of 1,2-alkenyl-1,2-disilanes, satisfy the hallmarks: dimerization in the absence of a trapping agent and capture by 2,3-dimethylbutadiene to yield the Diels–Alder adduct, a silacyclohex-3-ene.



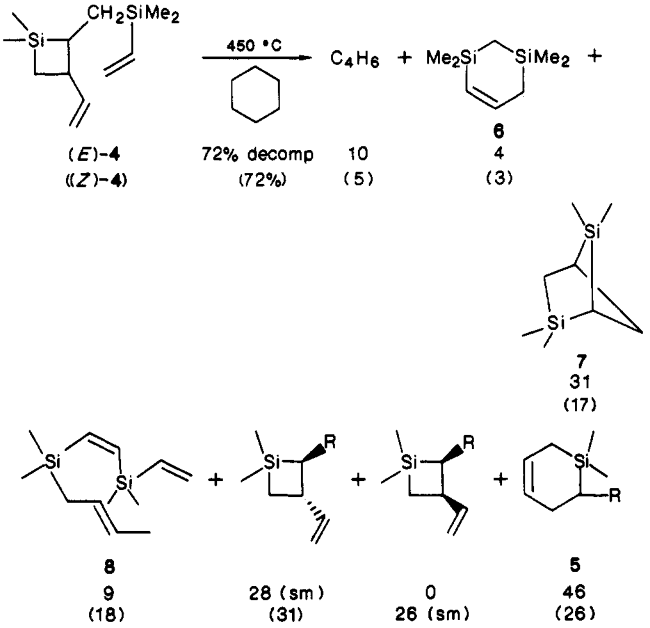
Our preliminary photolyses of **1** with methoxytrimethylsilane as a trapping agent provided the silene adduct 3,3,6,6-tetramethyl-6-methoxy-5-(trimethylsilyl)-3,6-disilaheptene (**3**) in nearly quantitative yield. When the photolysis was carried out in a cyclohexane solution saturated with 1,3-butadiene, three new products were formed: (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyldimethylsilyl)methyl)-3-vinyl-1-silacyclobutane, (*E*)- and (*Z*)-**4** (42 and 29% yields, respectively) and the anticipated 1,1-dimethyl-6-((vinyldimethylsilyl)methyl)-1-silacyclohex-3-ene (**5**) (8%). Overall yields of (*E*)-**4** and (*Z*)-**4** were high, and this method provides a convenient synthesis of the rare 3-vinylsilacyclobutane ring system. When tetrahydrofuran was the solvent in place of cyclohexane, both yields and product distribution were unchanged. The insensitivity of the product ratios to significant changes in solvent polarity is surprising in light of the recent report of the isolation and structure determination of a stable silene/THF adduct.[7] A solvated complex of **2** and THF, if present, displays a reactivity identical with that of unsolvated **2** in the product formation or is in equilibrium as an unreactive partner with the silene.



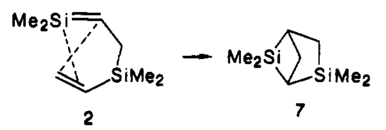


Structural characterization of the photolysis products was straightforward with the aid of ^{13}C and ^{1}H NMR, infrared, and mass spectra (see Experimental Section). We do not observe formation of the 2-vinylsilacyclobutane reported by Jones and co-workers. None of the major products showed a signal for the methylene triplet group, expected to be in the vicinity of δ 30–35 in the ^{13}C NMR spectrum.[8] The configurations of the (*E*)- and (*Z*)-2-((vinyldimethylsilyl)methyl)-3-vinylsilacyclobutanes were determined by the chemical shifts of the hydrogen on the carbon atom β to silicon: δ 1.89 and 2.75, respectively. In the trans isomer, the β-hydrogen is significantly shielded by the cis (vinyldimethylsilyl)methyl substituent while in the cis isomer, shielding of the β-hydrogen by the trans vicinal substituent is almost negligible. Such interactions between a hydrogen and a vicinal cis methyl group in a four-membered ring have been described previously in the assignment of configurations to the isomeric 2,3-dimethyloxetanes.[9]

The possibility that the primary pathway for the silene/butadiene reaction proceeds via a 2 + 2, not a 2 + 4, cycloaddition has not previously received attention. The convenient preparation of (*E*)- and (*Z*)-vinylsilacyclobutanes allows such an investigation. Low-pressure flow pyrolysis of (*E*)-**4** in a cyclohexane carrier at 450 °C produced butadiene (10%),[10] 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene (**6**) (4%), 2,2,5,5-tetramethyl-2,5-disilabicyclo[2.1.1]hexane (**7**) (31%), 3,3,6,6-tetramethyl-3,6-disiladeca-1,4,8-triene (**8**)[11] (9%), **5** (46%), based on percent of reacting starting materials (sm). Overall decomposition was 72% based on 28% recovery of unreacted (*E*)-**4** as indicated by the cyclohexane internal standard. The influence of the vinyl group in the 3-position significantly lowers the temperature required for fragmentation of the four-membered ring. Under the same experimental conditions the saturated 1,1-dimethylsilacyclobutane does not undergo reaction.



The formation of butadiene ensures the gas-phase production of silene **2** from the reverse 2 + 2 cycloaddition of (*E*)-**4**. Product **6**, an isomer of silene **2**, has been reported previously by Barton as a thermal unimolecular product of **2** from the gas-phase pyrolysis of **1** at 620 °C.[12] In that study, formation of the highly strained **7**, most likely arising from an intramolecular silene cycloaddition,



---

[6] Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37.

[7] Wiberg, N.; Wagner, G.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1984**, *271*, 381.

[8] For example, the position of the chemical shift of the β-ring carbon atom in 1,1,2-trimethylsilacyclobutane is δ 27.18. An additional substituent would shift the value of δ further downfield.

[9] Ewing, D. F.; Holbrook, K. A.; Scott, R. A. *Org. Magn. Reson.* **1975**, *7*, 554.

[10] Yields of butadiene were variable since no special measures were taken to quantitatively recover the volatile diene.

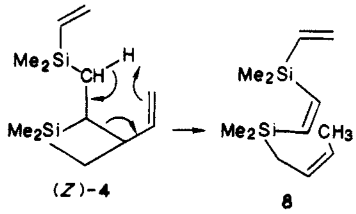
[11] The chemical shift of the methyl carbon of the butenyl group in **8**, δ 17.56, suggests a probable cis substitution. Our analogy is that the alkenyl methyl group of *cis*-propenyltrimethylsilane shows a carbon NMR signal at δ 18.14, whereas the methyl group of the trans isomer resonates at characteristically lower field δ 21.59 (ref 23b). The orientation of silyl groups about the double bond is likely to be cis on mechanistic grounds.

[12] Barton, T. J.; Wulff, W. D. *J. Organomet. Chem.* **1979**, *168*, 23.

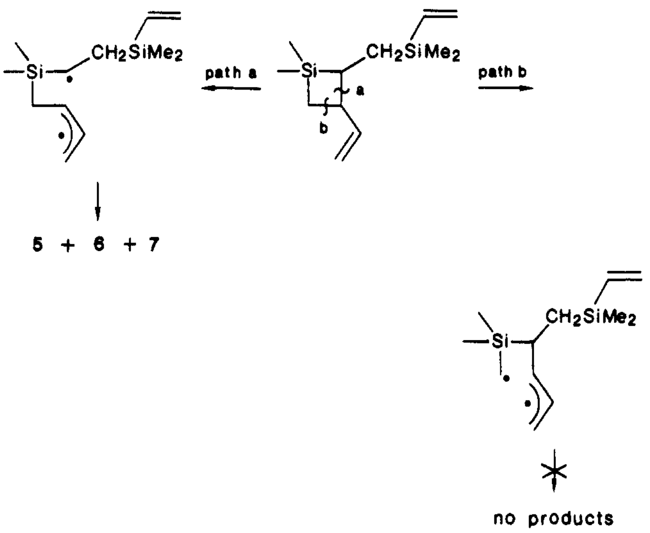
was invoked as the immediate precursor to **6** but not isolated, presumably due to secondary reactions at the higher temperatures. Related examples of the [2.1.1] ring system containing one silicon atom, 1,2,3,3-tetramethyl-3-silabicyclo[2.1.1]hexane[13] and 5,5-difluoro-5-silabicyclo[2.1.0]hex-2-ene,[14] have been described previously. Interestingly, we note that the photochemical formation of **2** from **1** is not thermally reversible in our flow system at 450 °C as no 1,2-divinyldisilane was produced in conditions where it is stable to pyrolysis. Thus, it can be concluded that the rate of the intramolecular 2 + 2 cycloaddition of the silene is faster than the 1,3-vinyldimethylsilyl shift from carbon to silicon. To our knowledge the only other example of a well-characterized intramolecular silene cycloaddition is the isomerization of 1,1-dialkyl-1-silabutadienes to the corresponding silacyclobutanes.[15,16]

Unlike pyrolysis of (*E*)-**4** which produces none of the isomer (*Z*)-**4**, the major product from the pyrolysis of (*Z*)-**4** at the same temperature was that of stereomutation to the trans configurational isomer (*E*)-**4** (31%). Other products included butadiene (5%), **6** (3%), **7** (17%), **8** (18%), and **5** (26%), based on percent of reacting starting material. Overall decomposition was 74% based on 26% recovery of unreacted (*Z*)-**4**, again measured against the cyclohexane internal standard.

The three processes by which substituted 3-vinylsilacyclobutanes rearrange are (1) geometric isomerization, (2) 1,5-sigmatropic shift, and (3) ring expansion. It is surprising that the cis isomer can convert to the probably more stable trans form, but not vice versa, and a simple rationale is complicated by a competing pathway. The cis isomer, unlike the trans, permits the 3-vinyl group to assume the conformation necessary for a homodienyl 1,5-hydrogen shift to form triene **8**. This interpretation is supported by the formation of twice as much **8** from (*Z*)-**4** as from (*E*)-**4**. That some of triene **8**, but not of its probable precursor, (*Z*)-**4** (or the conformationally correct biradical), was isolated in the low-pressure pyrolysis of (*E*)-**4** suggests that vibrationally excited (*Z*)-**4** continued on to the observed triene. Examples of the homodienyl 1,5-hydrogen shift are known for *cis*-2-methylvinylcyclopropane[17] and *cis*-2-ethylvinylcyclobutane[18] and have been suggested for dimethyl-*cis*-1-propenylvinylsilane.[19]



The ring expansion pathway to silacyclohex-3-ene has not been observed previously but has considerable precedent in the all carbon analogues.[20] By analogy to the thermal decomposition of vinylcyclobutane, it is useful to postulate biradicals in a mechanistic sequence leading to products.[21] The only diene fragment, 1,3-butadiene, is consistent with homolysis of the more substituted carbon–carbon bond (path a). The development of allylic resonance in the transition state clearly would favor cleavage of either carbon–carbon bond over the slightly stronger (1–2 kcal/mol) silicon–carbon bonds.[22] Exclusive formation of the unsubstituted diene is indicative of β-stabilization[23] of the more substituted carbon radical by the exocyclic silyl group (path a). Moreover, the products unique to path a, butadiene and **5**, are produced, but no trace of those from path b, cleavage of the less substituted bond, is found.



The relatively facile ring expansion of (*E*)- and (*Z*)-**4** to **5** at 450 °C opens the possibility that silacyclohex-3-enes reported in the previous gas-phase pyrolyses of silene precursors and butadiene at higher temperatures may derive mainly from 3-vinylsilacyclobutanes. The lingering question, not yet addressed, is why the 2 + 2 mode of silene cycloaddition to butadiene is preferred to the usual 2 + 4 pathway.[24] In addition to orbital interactions which frequently control the regioselectivity in the Diels–Alder reaction,[25] conformational forms can affect the cycloaddition. As suggested in Jones' report,[4] the equilibrium ratio, 93:7,[26] of the s-trans to s-cis forms might influence the product distribution. If one assumes that formation of the four-membered ring proceeds from the s-trans conformer and the six-membered ring from s-cis form, the product ratios observed here, 91:9 for **4**:**5**, are remarkably similar to the equilibrium distribution of 1,3-butadiene conformations.

A precise interpretation of the ratio of four- to six-membered ring products from the silene reaction is complex.[27] Four different rate constants, two for the butadiene conformational equilibrium and two for the silene 2 + 2 and 2 + 4 cycloadditions, are necessary for a detailed kinetic analysis. Measures of the activation enthalpy for isomerization of the cis to trans conformers of butadiene

---

(13) Connolly, J. W. *J. Organomet. Chem.* **1974**, *64*, 343.

(14) Lee, W. L.; Shieh, C. F.; Liu, C. S. *J. Organomet. Chem.* **1986**, *302*, 23.

(15) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630.

(16) Burns, G. T.; Barton, T. J. *J. Organomet. Chem.* **1981**, *216*, C5.

(17) Ellis, R. J.; Frey, H. M. *Proc. Chem. Soc.* **1964**, *221*; *J. Chem. Soc.* **1964**, 5578.

(18) Jordan, L. Ph.D. Thesis, Yale University, 1971, quoted in Gajewski, J. J., *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981.

(19) Gaspar, P. P.; Lei, D. L. *Organometallics* **1986**, *5*, 1276.

(20) Frey, H. M.; Pottinger, R. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1827.

(21) The ring expansion could equally well be described as a 1,3-sigmatropic shift. Our evidence neither supports nor negates such a description.

(22) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(23) Two experimental measurements of ca. 3 kcal/mol for the stabilization of radicals β to silicon have been reported: (a) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (b) Conlin, R. T.; Kwak, Y.-W. *Organometallics* **1986**, *5*, 1205.

(24) Sustmann, R.; Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(25) For an account of frontier molecular orbital theory, see: Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

(26) Smith, W. B.; Massingill, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 4302.

(27) Swenton, J. S.; Bartlett, P. D. *J. Am. Chem. Soc.* **1968**, *90*, 2056.

range from 4.7 to 5.6 kcal/mol,[28] and thermochemical estimates of the bimolecular silene 2 + 4 cycloaddition are in the same neighborhood, 2–5 kcal/mol.[29] This work suggests that the 2 + 2 cycloaddition to butadiene proceeds with a similar, but lower, energy. With the appropriate diene, temperature/concentration studies could provide a reliable measurement of the activation enthalpy of silene cycloadditions. Such work is currently in progress.[30]

Experimental Section

General Data. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R24B 60-MHz spectrometer using methylene chloride as an internal standard, and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. All chemical shifts are reported in parts per million downfield from external tetramethylsilane.

Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector). Product yields from photolyses and pyrolyses were based on the amount of decomposition of starting material and determined chromatographically with cyclohexane as an internal standard and predetermined response factors for the organosilanes. Infrared spectra of thin films on KBr disks were obtained on a Perkin-Elmer 1330 spectrometer.

Mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph. High-resolution mass spectra were carried out at the MIT facility for mass spectral analysis. Elemental analysis was performed by Galbraith Laboratories, Inc. Photolyses were carried out in a Rayonet Photochemical Reactor (RPR-100) equipped with 254-nm lamps. Flow injection pyrolyses were accomplished by the injection technique as described previously.[3c]

Synthesis of 1,2-divinyl-1,1,2,2-tetramethyldisilane (**1**) followed the literature method[12] from the corresponding dichloride. Previously unreported spectral data: ^{13}C NMR (neat) δ −4.35 (q), 131.17 (d), 138.57 (t); UV (cyclohexane) λ_{max} 225 nm (log ε 3.86). Anhydrous methoxytrimethylsilane was prepared by methanolysis of hexamethyldisilazane (Petrarch) and stored under argon. Butadiene (Phillips) was dried over calcium hydride and distilled before use. Cyclohexane was dried over sodium/potassium alloy and freshly distilled. All samples used in photolyses and pyrolyses experiments were degassed on a Hg-free vacuum line by three freeze/thaw cycles or purged of oxygen by passing argon through the solution.

Photolysis of 1 in Methoxytrimethylsilane. A solution containing 1.0 g (12 mmol) of dry cyclohexane, 0.65 g (6.3 mmol) of methoxytrimethylsilane, and 0.20 g (1.2 mmol) of the disilane was placed in a 5-mm quartz NMR tube and irradiated for 14 h. One new product formed in nearly quantitative yield was isolated by preparative GC ($^1/_4$ in. × 16 ft, 20% OV-17 on Chromobsorb W) as a colorless liquid and identified as 3,3,6,6-tetramethyl-6-methoxy-5-(trimethylsilyl)-3,6-disilaheptene (**3**), the methoxysilane adduct to the silene.

3: ^{1}H NMR (neat) δ 0.20 (9 H, s, Me_3Si), 0.26 (6 H, s, Me_2Si), 0.30 (6 H, s, Me_2Si), 0.82 (2 H, app d, *J* = 2.26 Hz, $SiCH_2$–C), 2.61 (1 H, app t, *J* = 1.27 Hz, Si–CH–Si), 3.50 (3 H, s, MeOSi), 6.00 (3 H, m, CH_2=CH); ^{13}C NMR (neat) δ −3.12 (q), −1.82 (q), −0.57 (q), 6.96 (t), 7.93 (d), 49.42 (q), 130.99 (d), 139.23 (t); MS, *m/e* (relative intensity) 259 (M − 15, 11), 170 (12), 156 (17), 155 (90), 89 (69), 85 (40), 73 (65), 59 (100), 45 (24), 43 (15), 31 (10). Repeated attempts at elemental analysis gave results low in carbon as often observed for alkoxysilanes. Anal. Calcd for $Si_3C_{12}H_{30}O$: C, 52.48; H, 11.77. Found: C, 51.07; H, 11.32. Exact mass measurement, however, did confirm the spectroscopic data: calcd for $Si_3C_{12}H_{30}O$ 274.1604, found 274.1580.

Photolysis of 1 in Butadiene. A solution containing 3.0 g (35.7 mmol) of cyclohexane, 0.6 mL of butadiene, and 0.23 g (1.35 mmol) of the disilane was placed in a 25-mm quartz tube and irradiated for 18 h. Three new products were isolated by preparative GC (see above) and identified as (*E*)- and (*Z*)-1,1-dimethyl-2-((vinyldimethylsilyl)methyl)-3-vinyl-1-silacyclobutane ((*E*)-**4** (42%) and (*Z*)-**4** (29%)) and 1,1-dimethyl-6-((vinyldimethylsilyl)methyl)silacyclohex-3-ene (**5**) (8%).

(*E*)-**4**: ^{1}H NMR (neat) δ −0.35 (6 H, s, Me_2Si), −0.16 (3 H, s, Me_3Si), −0.13 (3 H, s, Me_3Si), 0.43 (5 H, m, CH_2Si, CH_3Si, CH–Si), 1.89 (1 H, app pentet, *J* = 8.9 Hz, HCC=), 4.49 (2 H, m, HC=), 5.47 (4 H, m, H_2=C); ^{13}C NMR (neat) δ −5.07 (q), −3.51 (q), −3.25 (q), 1.30 (q), 15.46 (t), 18.08 (t), 31.15 (d), 46.30 (d), 118.35 (d), 131.29 (d), 138.77 (t), 143.71 (t); MS, *m/e* (relative intensity), 209 (M − 15, 1), 156 (17), 155 (100), 112 (17), 97 (33), 96 (11), 85 (63), 73 (23), 59 (94), 58 (11), 55 (10), 45 (13), 43 (29), 31 (16); IR (KBr plates, cm^{-1}) 3060 (m), 3035 (m), 2950 (s), 2895 (m), 2870 (m), 1805 (w), 1622 (m), 1587 (w), 1400 (s), 1240 (s); exact mass calcd for $Si_2C_{12}H_{24}$ 224.1416, found 224.1439. Anal. (obtained on a mixture of (*E*)- and (*Z*)-**4**) Calcd for $Si_2C_{12}H_{24}$: C, 64.20; H, 10.78. Found: C, 63.93; H, 10.97.

(*Z*)-**4**: ^{1}H NMR (neat) δ −0.34 (6 H, s, Me_2Si), −0.13 (3 H, s, MeSi), −0.09 (3 H, s, Me–Si), 0.67 (4 H, m, CH_2–Si), 1.24 (1 H, q, *J* = 7.26 Hz, CH–Si), 2.76 (1 H, pentet, *J* = 7.65 Hz, CHC=), 4.63 (2 H, m, HC=), 5.50 (4 H, m, H_2C=); ^{13}C NMR (neat) δ −3.38 (q), −3.25 (q), −1.37 (q), 0.79 (q), 12.29 (t), 16.52 (t), 27.64 (d), 41.62 (d), 112.95 (d), 131.10 (d), 138.96 (t), 141.70 (t); IR (KBr plates, cm^{-1}) 3063 (m), 3020 (m), 2950 (s), 2895 (m), 1810 (w), 1625 (m), 1585 (w), 1400 (m), 1240 (s); MS, *m/e* (relative intensity) 209 (M − 15, 1), 156 (16), 155 (8), 112 (15), 97 (28), 96 (10), 85 (64), 73 (23), 59 (100), 58 (12), 55 (11), 45 (13), 43 (31), 31 (17). See above for analysis.

5: ^{1}H NMR (neat) δ −0.36 (3 H, s, MeSi), −0.33 (3 H, s, MeSi), −0.27 (6 H, s, Me_2Si), 0.20 (1 H, m, Si–CH), 0.39 (2 H, m, Si–CH_2), 0.85 (2 H, app d, $SiCH_2C$=), 1.66 (2 H, m, =CCH_2C), 5.21 (2 H, app q, HC=CH), 5.40 (1 H, t, *J* = 6.6 Hz, SiCH=C), 5.61 (2 H, d, *J* = 7.0 Hz, SiC=CH_2); ^{13}C NMR (neat) δ −6.12 (q), −3.58 (q), −2.73 (q), 12.87 (t), 15.09 (t), 16.00 (d), 32.51 (t), 125.38 (d), 128.69 (d), 130.97 (d), 139.23 (t); IR (KBr plates, cm^{-1}) 3040 (m), 3000 (s), 2950 (s), 2890 (s), 1900 (w), 1632 (w), 1587 (w), 1400 (s), 1120 (m), 1000 (m); MS, *m/e* (relative intensity) 224 (1), 155 (51), 113 (16), 112 (11), 98 (21), 97 (19), 96 (15), 95 (11), 85 (56), 83 (12), 73 (32), 59 (100), 58 (13), 55 (12), 45 (15), 43 (36), 31 (17); exact mass calcd for $Si_2C_{12}H_{24}$ 224.1416, found 224.1439.

Low-Pressure Flow Pyrolysis. A solution of 30 μL of (*E*)-**4** was diluted with 270 μL of dry cyclohexane and injected through a serum cap, in 10-μL portions, at 4-min intervals, into the pyrolysis chamber held at 450 °C. Pressure, measured at the exit of the hot zone, was <0.1 torr, and the total time for the injection pyrolysis was 2 h. Decomposition of (*E*)-**4** was 72% and provided four new silicon containing products: 1,1,3,3-tetramethyl-1,3-disilacyclohex-4-ene (**6**) (4%), 2,2,5,5-tetramethyl-2,5-disilabicyclo[2.1.1]hexane (**7**) (31%), 3,3,6,6-tetramethyl-3,6-disiladeca-1,4,8-triene (**8**) (9%), and (**5**) (46%) along with butadiene (10%) and unreacted (*E*)-**4**. The low mass balance of approximately 65% was due in part to incomplete recovery of butadiene. Product yields were based on the amount of (*E*)-**4** that reacted as indicated by the inert internal standard, cyclohexane.

6: ^{13}C NMR (neat) δ 144.82 (d), 129.28 (d), 18.53 (t), 0.52 (q), −0.65 (q), −1.24 (t); ^{1}H NMR, IR, and mass spectra agreed with previously reported values.[12]

7: ^{1}H NMR (neat) δ −0.05 (3 H, s, MeSi), −0.9 (3 H, s, MeSi), −0.12 (3 H, s, MeSi), 0.40 (3 H, s, MeSi), 0.49 (1 H, m, Si–CH–Si), 0.62 (2 H, m, Si–CH_2), 1.44 (2 H, m, C–CH_2–C)), 1.84 (1 H, m, Si–CH); ^{13}C NMR (neat) δ −5.86 (q), −1.17 (q), −0.91 (q), −0.07 (q), 13.78 (t), 19.31 (d), 28.16 (d), 31.67 (t); IR (KBr plates, cm^{-1}) 2946 (s), 2916 (m), 2836 (s), 1426 (w), 1256 (s), 942 (s), 841 (s); MS, *m/e* (relative intensity) 170 (4), 155 (14), 130 (15), 129 (100), 97 (14), 96 (47), 95 (14), 85 (13), 73 (34), 59 (48), 55 (11), 45 (17), 43 (44), 31 (13); exact mass calcd for $Ci_2C_8H_{18}$ 170.0947, found 170.0940.

8: ^{1}H NMR (neat) δ −0.38 (6 H, s, Me_2), −0.30 (6 H, s, Me_2Si), 1.02 (2 H, m, CH_2Si), 1.51 (3 H, m, CH_3C=); ^{13}C NMR (neat) δ −4.03 (q), −3.58 (q), 17.56 (q), 21.00 (t), 122.97 (d), 126.09 (d),

---

[28] (a) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (b) Carreira, L. A. *J. Chem. Phys.* **1975**, *62*, 3851.

[29] (a) Walsh, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1415. (b) Davidson, I. M. T.; Ijadi, I.-M.; Barton, T. J.; Tillman, N. *J. Chem. Soc., Chem. Commun.* **1984**, 478.

[30] In contrast to the results described herein and in ref 4 and 5 for the low-ambient temperature silene/butadiene reaction, an exclusive and quantitative 2 + 4 cycloaddition of 1,1-dimethyl-2-(trimethylsilyl)-2-(di-*tert*-butylmethylsilyl)silene to butadiene has been reported: Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467.

131.62 (t), 137.62 (d), 148.92 (d), 150.28 (d); IR (KBr plates, cm^{-1}) 3057 (w), 3017 (w), 2970 (s), 1600 (w), 1417 (m), 1255 (s), 1187 (m), 1018 (m), 843 (s); MS, *m/e* (relative intensity) 209 (M − 15, 1), 169 (31), 141 (14), 86 (10), 85 (100), 83 (9), 73 (32), 59 (78), 58 (11), 55 (14), 43 (25), 31 (11); exact mass calcd for $Si_2C_{12}H_{24}$ 224.1416, found 224.1410.

Product distribution from pyrolysis of (*Z*)-**4** under the same conditions was butadiene (5%), **6** (3%), **7** (17%), **8** (18%), (*E*)-**4** (3%), **5** (26%), and unreacted (*Z*)-**4** (26%). Decomposition of (*Z*)-**4** was 74%, and mass balance was approximately 70%.

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for financial support of this work. We thank the Mass Spectrometry Facility at the Massachusetts Institute of Technology for obtaining high resolution mass spectra and Prof. A. G. Brook for communicating results prior to publication.

Registry No. **1**, 1450-29-9; **2**, 108367-02-8; **3**, 108367-03-9; (*E*)-**4**, 108367-04-0; (*Z*)-**4**, 108367-05-1; **5**, 108394-64-5; **6**, 27549-17-3; **7**, 108367-06-2; **8**, 108394-65-6; methoxytrimethylsilane, 1825-61-2.

Quaternary Onium Hexachloroplatinates: Novel Hydrosilylation Catalysts

Irina G. Iovel, Yuri Sh. Goldberg, Mariya V. Shymanska, and Edmunds Lukevics*

Institute of Organic Synthesis, Latvian SSR, Academy of Sciences, 226006 Riga, USSR

Received July 21, 1986

A number of quaternary ammonium, phosphonium, and arsonium hexachloroplatinates have been synthesized and used as hydrosilylation catalysts. The highest activity was observed for the quaternary hexachloroplatinates with highly lipophilic cations. Phase-transfer agents (onium salt, crown ether) were found to activate K_2PtCl_6 during hydrosilylation by solubilizing the $PtCl_6^{2-}$ ion. It has been shown that polymer-bound quaternary phosphonium hexachloroplatinate is also an effective hydrosilylation catalyst that can be used repeatedly without appreciable loss of activity.

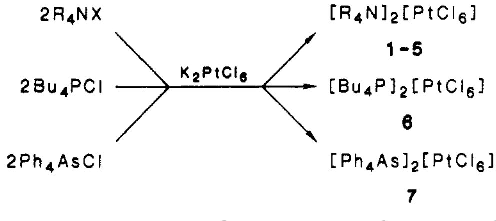
Introduction

Catalytic hydrosilylation most commonly involves the use of Speier's catalyst (hexachloroplatinic acid dissolved in isopropyl alcohol) whose activity is deemed to be due to the $PtCl_6^{2-}$ ion.[1-3] However, there have been no reports so far on how the nature of the counterion might affect the activity of the hexachloroplatinate anion.

Herein we describe the preparation of some quaternary ammonium, phosphonium, and arsonium hexachloroplatinates and their activity as catalysts for hydrosilylation.

Results and Discussion

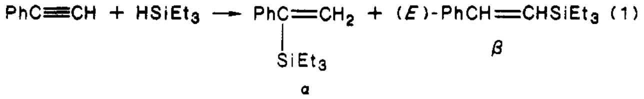
The quaternary bis(onium)hexachloroplatinates **1–7** have been prepared by ion exchange using stoichiometric amounts of K_2PtCl_6 dissolved in water and the corresponding onium halides dissolved in dichloromethane or water.



1, R = Me; **2**, R = Bu; **3**, R = *n*-C_8H_{17}; **4**, R = *n*-$C_{18}H_{37}$; **5**, R_4 = $Et_3(PhCH_2)$; X = Cl, Br, HSO_4

The hexachloroplatinates **1–7** were obtained in 75–95% yield as crystals varying in color from beige to red (Table I). The ^{1}H NMR spectra of the synthesized platinates (Table II) were essentially the same as those of the starting quaternary onium halides.

The catalytic properties of the onium hexachloroplatinates obtained were examined in the hydrosilylation of phenylacetylene by triethylsilane. In the presence of platinates **1–7**, a mixture of two isomers, the α- and β-cis-addition products, are invariably formed (eq 1). Their



$$\mathrm{PhC{\equiv}CH + HSiEt_3 \longrightarrow \underset{\alpha}{\underset{SiEt_3}{PhC}}{=}CH_2 + \underset{\beta}{(\mathit{E})\text{-}PhCH{=}CHSiEt_3}} \quad (1)$$

formation was confirmed by GC, ^{1}H NMR, and GC–mass spectrometry studies. The ^{1}H NMR parameters were consistent with the literature data;[4] the GC–mass spectra showed molecular ion peaks with *m/z* 218. The tetraalkylammonium hexachloroplatinates **2**, **3**, and **4** with bulky lipophilic[5] cations were the most active among the compounds examined. Phosphonium (**6**) and arsonium (**7**) platinates as well as the catalysts **1** and **5** containing a less lipophilic tetraalkylammonium cations[5] were the least reactive (Table III). β-Addition is predominant in all cases, the ratio of the α- and β-isomers depending on the catalyst cation. The relative content of the α-isomer in the products increases with decreasing net rate of the hydrosilylation (Table III).

Reaction 1 was also carried out in the presence of hexachloroplatinic acid and potassium hexachloroplatinate. The latter practically failes to catalyze the process; the activity of $H_2PtCl_6{\cdot}6H_2O$ is equal to that of the most active tetraalkylammonium hexachloroplatinates (Table III). The hygroscopicity of $H_2PtCl_6{\cdot}6H_2O$ causes some difficulties in its handling, but the nonhygroscopic quaternary onium platinates are easy to store and handle.

The hydrosilylation of phenylacetylene in the presence of one of the most active platinum catalysts, $[Bu_4N]_2[PtCl_6]$, was performed by various silanes. Table IV sum-

---

[1] Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* **1977**, *5*, 1.

[2] Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

[3] Marciñiec, B., Ed. *Hydrosililowanie*; Pañstwowe Wydawnictwo naukowe: Warszawa, 1981.

[4] Pukhnarevich, V. B.; Sushchinskaya, S. P.; Pestunovich, V. A.; Voronkov, M. G. *Zh. Obshch. Khim.* **1973**, *43*, 1283.

[5] Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 493.