Communications

The First Stable C-Methylated Siloles Having a Si–H Bond

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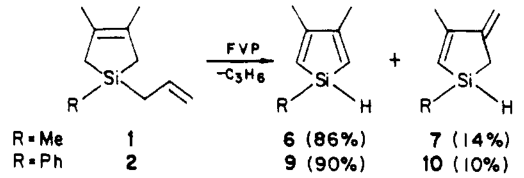
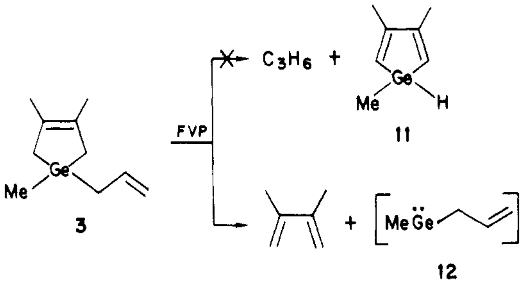
Summary: Flash vacuum pyrolysis of 1-allyl-1,3,4-trimethylsilacyclopent-3-ene (**1**), 1-allyl-1-phenyl-3,4-dimethylsilacyclopent-3-ene (**2**), and 1-allyl-1,3,4-trimethylgermacyclopent-3-ene (**3**) has been studied. Both **1** and **2** decompose by a retro-ene reaction to give 1,3,4-trimethylsilole (**6**) and 1-phenyl-3,4-dimethylsilole (**9**), respectively, together with their transoid isomers; these are the first stable, monomeric, C-methylated siloles which contain a Si–H bond. Thermolysis of **3** produces only 2,3-dimethylbutadiene by a cycloreverse [4 + 2] reaction. Lithium reacts with 1-phenyl-1,3,4-trimethylsilole (**14**) to form the corresponding silacyclopent-3-ene (**15**) rather than the hydrosilole **6** or **9**.

Recently, the chemistry of group 14 metalloles has progressed rapidly owing to the synthesis of C-unsubstituted or C-methylated siloles,[1] germoles,[2,3] and stannoles.[4] Interestingly, 3,4-dimethylsiloles[1d–f] and germoles[3] substituted at the heteroatom[5,6] are much more stable as monomers than 1,1,3-trimethylated[1d,f,3] or 1,1-dimethylated[1b,c,2] derivatives. Regarding group 14 metalloles having M–H bonds, the silole has not yet been fully characterized[7] and 1-methylsilole is not stable enough as a monomer to be isolated.[1a]

Scheme I



Scheme II



Since the double C-methylation of group 14 metalloles causes a stabilization toward the dimerization [4 + 2] reaction, probably by a perturbation of energy levels of frontier orbitals (the LUMO in particularly),[1f] we thought that 3,4-dimethylmetalloles with a Si–H or Ge–H bond would be stable as monomers. To explore this possibility, we have used the novel method of Barton and Burns[1a] to investigate the flash vacuum thermolysis of 1-allyl-1,3,4-trimethylsilacyclopent-3-ene (1).[8,9] The crude product, trapped at −196 °C, consisted of propene and a liquid phase containing only three components: the starting silacyclopentene 1 (50%), 1,3,4-trimethylsilole (**6**, 43%), and its transoid isomer 7 (7%). The yield of **6** and **7** (Scheme I) with respect to consumed 1 was about 80%. As expected, silole **6** does not dimerize, unlike its isomeric 1,1,3-trimethylsilole,[1f] and **6** together with **7** can be distilled under reduced pressure. Compound **6** was identified by spectroscopy and by its maleic anhydride adduct **8**.[10]

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(2) (a) Laporterie, A.; Manuel, G. Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33. (b) Laporterie, A.; Iloughmane, H.; Dubac, J. *Ibid.* **1983**, *244*, C12.

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(4) (a) Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95. (b) Ashe, A. J. III; Drone, F. J. *Organometallics* **1984**, *3*, 495.

(5) We have recently prepared siloles having alkyl, aryl, or alkenyl groups on the silicon atom,[6] using methods described in ref 1f.

(6) (a) Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Phosphorus Sulfur* in press (review). (b) Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. unpublished works.

(7) (a) Hwang, R. J.; Gaspar, P. P. *J. Am. Chem. Soc.* **1978**, *100*, 6626. (b) Siefert, E. E.; Loh, K. L.; Ferrieri, R. A.; Tang, Y. N. *J. Am. Chem. Soc.* **1980**, *102*, 2285. (c) Gaspar, P. P.; Chen, Y.; Helfer, A. P.; Konieczny, S.; Ching-Lin Ma, E.; Mo, S. *J. Am. Chem. Soc.* **1981**, *103*, 7344.

(8) The metallacyclopentene was slowly introduced (with argon as a carrier gas) into a quartz tube (40-cm of length and 9-mm diameter) packed with quartz chips and heated to 600 °C. The exit pressure was 0.05 mmHg. A lower temperature caused lower yields, and a higher temperature increased the quantity of the transoid isomer (**7** or **10**). **1** and **3** were introduced as pure compounds, and **2** was introduced as a pentane solution.

(9) 1 (16.3 g) was prepared as follows:[26] reaction of allylmethyldichlorosilane (31 g, 0.2 mol) with 2,3-dimethylbutadiene (22 g, 0.27 mol) in the presence of Mg, in THF/HMPA (5/1) as solvent; 50% yield; bp 76 °C (15 mmHg); ^{1}H NMr (60 MHz, CCl_4) δ 0.14 (s, 3 H, SiMe), 1.30 (s, 4 H, $SiCH_2$ ring), 1.60 (mask d, $SiCH_2$ all.), 1.66 (s, 6 H, CMe), 4.80 (m, 2 H, $C{=}CH_2$), 5.73 (m, 1 H, CH=C); GC/MS, *m/e* (>5%) 166 (M^+, 4), 126 (12), 125 ($[M - C_3H_5]^+$, 87), *124* ($[M - C_3H_6]^+$, 100%), 123 (42), 110 (9), 109 (21), 97 (13), 95 (8), 85 (20), 83 (18), 81 (5), 69 (13), 67 (11), 59 (79), 55 (16), 53 (10). Anal. Calcd for $C_{10}H_{18}$,Si: C, 72.20; H, 10.90. Found: C, 72.22; H, 10.88. **2** was prepared in the same way from allylphenyldichlorosilane; 30% yield; bp 104 °C (0.2 mmHg); ^{1}H NMR (60 MHz, CCl_4) δ 1.6–1.9 (12 H, $SiCH_2$ + CMe, 1.82, s), 4.83 (m, 2 H, $C{=}CH_2$), 5.73 (m, 1 H, CH=C), 7.3 (m, Ph); GC/MS, *m/e* (>5%) 228 (2), 188 (21), *187* ($[M - C_3H_5]^+$, 100%), 186 ($[M - C_3H_6]^+$, 93), 185 (18), 172 (17), 159 (9), 145 (25), 131 (7), 121 (13), 110 (8), 109 (63), 107 (13), 105 (58), 81 (6), 79 (9), 69 (8), 67 (8), 59 (9), 53 (12). Anal. Calcd for $C_{15}H_{20}Si$: C, 78.87; H, 8.82. Found: 78.92; H, 8.78.

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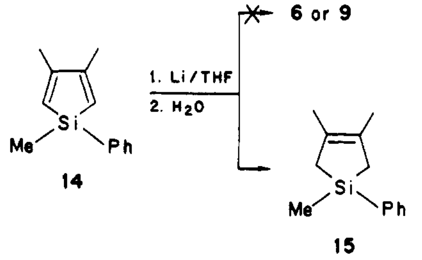
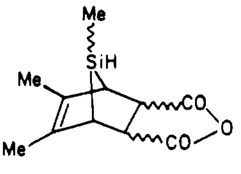
Scheme III



Similarly, the thermolysis of the 1-allyl-1-phenyl-3,4-dimethylsilacyclopent-3-ene (**2**) produced 1-phenyl-3,4-dimethylsilole (**9**) together with its transoid isomer **10**, identified in the same way,[11] but the yield was lower in this case (25%).



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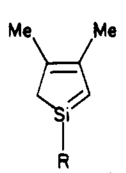

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In contrast, the flash thermolysis of the germanium analogue of **1**, 1-allyl-1,3,4-trimethylgermacyclopent-3-ene (**3**),[12] did not give the germole **11** but only 2,3-dimethylbutadiene (DMB) as the sole identifiable product[13] (Scheme II).

Thermolysis of group 14 metallacyclopent-3-enes should occur by two cycloreverse reactions: one of the retro-ene type, which is characteristic of allylsilanes,[14] and the other of the reverse [4 + 2] type, which is the more frequently observed reaction, as in silacyclopent-3-enes[15] and germacyclopent-3-enes.[16] Compound **3** also undergoes the latter reaction.

The intramolecular retro-ene reaction of an allysilane, which causes elimination of propene and the formation of silaethene (Si=C),[14] should, in the case of 1-allylsilacyclopent-3-enes, lead to 1-silacyclopenta-1,3-diene (**13**), an intermediate[1a] which rearranges ([1,5]-H) to 1-silacyclopenta-2,4-diene (**6** or **9**) or its transoid isomer (**7** or **10**).[17]

There is a striking analogy between flash thermolysis and mass spectral fragmentation[9,12] of metallacyclopentenes **1**–**3**. Both experiments involve the elimination of propene (from **1** or **2**) or DMB (from **3**) as the main process.

In an attempt to prepare siloles **6** and **9** by a condensed-phase reaction, we tried to cleave an exocyclic bond of 1-phenyl-1,3,4-trimethylsilole (**14**).[19] Although 1-substituted phospholes react with alkali metals at the exocyclic bond[20] and the Si–Me exocyclic bonds of 1,1,3,4-tetramethylsilole are cleaved by organolithium reagents with retention of the dienic ring,[21] we found that lithium attacked the dienic system of silole **14** causing 1,4 addition. Thus, after hydrolysis of the reaction mixture, we isolated 1-phenyl-1,3,4-trimethylsilacyclopent-3-ene (**15**)[22] exclusively (Scheme III) Considering the behavior of C-unsubstituted or C-methylated metalloles as ligands in coordination chemistry,[2b,3,23–25] we think that anions or silacyclopentadienyl species which might be derived from hydrosiloles **6** or **9** will also be excellent ligands. This work is in progress.

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Registry No. **1**, 102725-46-2; **2**, 102725-47-3; **3**, 102725-48-4; **4**, 102725-54-2; **5**, 102725-55-3; **6**, 102725-49-5; **7**, 102725-50-8; **8**, 102725-51-9; **9**, 102725-52-0; **10**, 102725-53-1; **14**, 98749-91-8; **15**, 54797-05-6; DMB, 513-81-5; $CH_2=CHCH_2MgBr$, 1730-25-2; MeMgI, 917-64-6; allylmethyldichlorosilane, 1873-92-3; allylphenyldichlorosilane, 7719-03-1; 1,1-diodo-3,4-dimethylgermacyclopent-3-ene, 5764-63-6; maleic anhydride, 108-31-6.

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(10) **6**: bp 60–63 °C (45 mmHg); ^{1}H NMR (60 MHz, C_6D_6) δ 0.13 (d, *J* = 4 Hz, SiMe), 1.70 (m, $SiCH_2$, **7**), 1.83 (s, CMe), 4.57 (m, SiH), 5.77 (br s, C=CH, **6**, 85%), 5.13 and 5.92 (m, $C=CH_2$ and C=CH, **7**, 15%); IR 2120 (SiH), 1520 (C=C siloles[1f]); GC/MS, *m/e* (>5%): 124 (M^+, 41), 123 (20), 110 (12), *109* ($[M - Me]^+$, 100%), 107 (6), 97 (6), 95 (12), 84 (7), 83 (36), 82 (6), 81 (23), 69 (26), 68 (7), 67 (28), 66 (11), 59 (7), 58 (8), 55 (13), 53 (18). Anal. Calcd for $C_7H_{12}Si$: C, 67.66; H, 9.73. Found: C, 67.69; H, 9.68. **8**: viscous oil; two isomers appear in the ^{1}H NMR spectrum (60 MHz, C_6D_6) δ –0.26 (d, *J* = 3 Hz, SiMe, isomer **a**), –0.20 (d, *J* = 3 Hz, SiMe, isomer **b**), 1.50 (s, CMe, **b**), 1.57 (s, CMe, **a**), 3.00 (m, SiCH), 2.93 (m, O=CCH, **a**), 3.13 (m, O=CCH, **b**), 3.60 (m, SiH, **a**), 4.30 (m, SiH, **b**), SiMe {SiH, **a**} –0.26 (s), SiMe{SiH, **b**} –0.20 (s); **a**/**b** = 55/45. Anal. Calcd for $C_{11}H_{14}O_3Si$: C, 59.42; H, 6.34. Found: C, 59.35; H, 6.40.

(11) **9** and **10** were separated from the crude product by preparative GLC. **9**: **1H** NMR (60 MHz, C_6D_6) δ 1.83 (s, CMe), 4.77 (m, SiH), 5.73 (br s, C=CH, **9**, 90%), 5 and 5.86 (m, $C=CH_2$ and C=CH, **10**, 10%), 7.13 and 7.47 (m, Ph); IR 2130 (SiH), 1520 cm^{-1} (C=C siloles[1f]); GC/MS, *m/e* (>5%) 187 (18), *186* (M^+, 100), 185 (14), 172 (10), 171 (66), 146 (6), 145 (23), 143 (9), 142 (7), 141 (6), 131 (13), 108 (22), 107 (23), 106 (8), 105 (51), 79 (11), 67 (13), 53 (18). Anal. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57. Found: C, 77.45; H, 7.50.

(12) **3** was obtained by the following reactions. (i) $CH_2=CHCH_2MgBr$ with 1,1-diiodo-3,4-dimethylgermacyclopent-3-ene:[27] 1,1-diallyl-3,4-dimethylgermacyclopent-3-ene (**4**), 60% yield. (ii) HCl, acetone[28] with **4**: 1-allyl-1-chloro-3,4-dimethylgermacyclopent-3-ene (**5**), 85% yield. (iii) MeMgI with **5**: 1-allyl-1,3,4-trimethylgermacyclopent-3-ene (**3**), 70% yield; bp 118 °C (24 mmHg); ^{1}H NMR (60 MHz, CCl_4) δ 0.28 (s, 3 H, GeMe), 1.45 (s, 4 H, $GeCH_2$ ring), 1.63 (s, 6 H, CMe), 1.73 (mask d, $GeCH_2$ all.), 4.76 (m, 2 H, $C=CH_2$), 5.66 (m, 1 H, CH=C); GC/MS (^{74}Ge), *m/e* (>5%) 212 (M^+, 1), 171 ($[M - C_3H_5]^+$, 61), 129 (13), 115 ($[M - Me - C_6H_{10}]^+$, 24), *89* ($[M - C_3H_5 - C_6H_{10}]^+$, 100); see ref 18. Anal. Calcd for $C_{10}H_{18}Ge$: C, 56.96; H, 8.60. Found: C, 56.93; H, 8.57.

(13) The copyrolysis of **3** with butadiene did not result in trapping of the germylene **12** to form 1-allyl-1-methylgermacycylopent-3-ene, but instead a metallic mirror of germanium was observed in the quartz tube, indicating that germylene **12** must be much less stable than dimethylgermylene which can be trapped by 1,3-dienes.[16] The thermolysis of **3** at a lower temperature (500 °C) caused lower yields but not a retro-ene reaction.

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(17) The thermal isomerization of siloles **6** and **9** into **7** and **10** is also possible.[1d,f]

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(19) For the synthesis of **14** in three steps from 1-phenyl-1,3,4-trimethylsilacyclopent-3-ene (**15**) see ref 6a.

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(21) Dubac, J.; Iloughmane, H.; Laporterie, A.; Roques, C. *Tetrahedron Lett.* **1985**, *26*, 1315.

(22) **15**: bp 82 °C (0.7 mmHg); ^{1}H NMR (60 MHz, CCl_4) δ 0.43 (s, 3 H, SiMe), 1.57 (br s, 4 H, $SiCH_2$), 1.75 (s, 6 H, CMe), 7.4 (m, Ph); identified by comparison with an authentical sample prepared by reaction of phenylmethyldichlorosilane with DMB in the presence of Mg.[6]

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