Silenes and Silenoids. 7. The Reactions of Alkyllithium Reagents with Vinyldimethylfluorosilane

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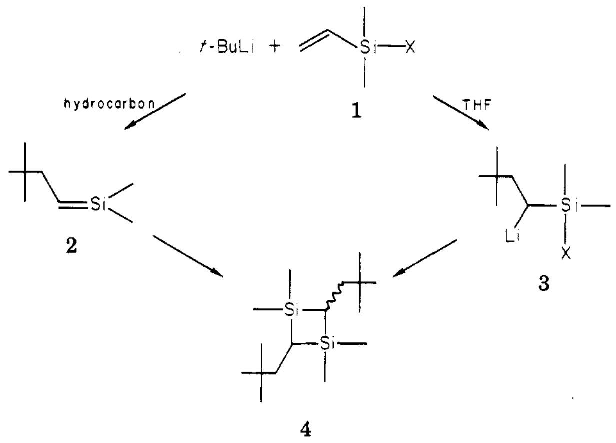
Received August 15, 1983

The reactions of *tert*-butyl-, *sec*-butyl-, and *n*-butyllithium with vinyldimethylfluorosilane include addition to the double bond giving silene and/or silenoid intermediates, fluorine substitution, and an unprecedented vinyl substitution. For the *tert*-butyllithium reaction product stereochemistry and trapping experiments using both cyclopentadiene and methoxytrimethylsilane show that silenes are not formed in tetrahydrofuran and that in hexane about 67% of the 1,3-disilacyclobutanes obtained arise from silene dimerization while 33% are formed by silenoid coupling. In hexane the order of reactivity for addition *t*-Bu > *sec*-Bu > *n*-Bu is opposite that for fluorine substitution. The vinyl substitution reaction is most significant for secondary alkyllithium reagents including the *tert*-butyllithium adduct to vinyldimethylfluorosilane, **3** (X = F), and *sec*-butyllithium. Evidence for the formation of vinyllithium or ethylene in the process could not be obtained.

Introduction

The reaction of *tert*-butyllithium with vinyldimethylchlorosilane, **1** (X = Cl), in hydrocarbon solvents gives rise to 1,1-dimethyl-2-neopentylsilene, **2**, which dimerizes in the absence of trapping reagents to give the corresponding 1,3-disilacyclobutane **4**.[1] The silene can be trapped as its



[4 + 2] cycloadduct with conjugated dienes.[2] In tetrahydrofuran the silene is apparently not formed, and products arising from the α-lithiosilane **3**, a silenoid intermediate, are obtained.[2,3] Typically when the dimers **4** have a silene precursor, their cis/trans ratio is about 1.1 ± 0.1 while the ratio is ca. 3 or 4 when the dimers are formed via the α-lithiosilane **3**.[4,5]

In reactions with **1** (X = Cl), *tert*-butyllithium appears to be unique in producing silene. Both *n*-butyl- and *sec*-butyllithiums give predominantly substitution at silicon to form butyl-substituted silanes.[4] In contrast, the addition reaction of vinyldimethylalkoxysilanes, **1** (X = OMe or OEt), with alkyllithium reagents appears to be quite general for hydrocarbon-soluble organolithiums, giving good yields of monosilacyclobutanes from the α-lithioalkoxysilanes.[6] In an investigation of the effects of leaving groups on silene formation from α-lithiosilanes, Wiberg and coworkers have observed that fluorosilanes are intermediate in reactivity between chlorosilanes and alkoxysilanes with respect to silene product formation.[7] With the objective of increasing the generality of our silene generation method we have undertaken a study of the reactions of alkyllithium reagents with vinyldimethylfluorosilane.

Table I. Comparison of the Effects or Reaction Conditions on the Reaction of *tert*-Butyllithium with Vinyldimethylhalosilanes

expt	1, X =	conditns	1/*t*-BuLi ratio	product yields,[a] % 4	5	6[b]	4 cis/trans
1	F	hexane, −78 °C		24	38	10	62/38
2	Cl[2]	hexane, −78 °C	1	78	0	0	53/47
3	F	hexane, −78 °C	2	21	42	tr	65/35
4	F	hexane, −78 °C	0.5	57	tr	tr	65/35
5	F	hexane, 25 °C	1	50	tr	tr	64/36
6	Cl[2]	hexane, 25 °C	1	46	0	0	54/46
7	F	THF, −78 °C	1	44	1	16	80/20
8	F	THF, −78 °C	2	8	1	56	79/21
9	Cl[8]	THF, −78 °C	0.5	9	0	39[c]	75/25

[a] Determined by GLC using an internal standard calibration. [b] X = Cl or F depending on substrate. [c] A 15% yield of **6** (X = *t*-Bu) was also obtained.

Results

The reaction of *tert*-butyllithium with vinyldimethylfluorosilane[8] in hexane at −78 °C gives only a 24% yield of the anticipated 1,3-disilacyclobutanes **4**. The major product, in 38% yield, is the unexpected 1,1-bis(dimethylfluorosilyl)-3,3-dimethylbutane, **5**. In addition 4-(dimethylfluorosilyl)-3,3,6,6-tetramethyl-3-sila-1-heptene, **6**, is obtained in 10% yield. In an effort to determine the source of **5** we carried out the reaction under a variety of experimental conditions. The results are given in Table I along with data for representative experiments with vinyldimethylchlorosilane.

Vinyldimethylfluorosilane is clearly the source of the additional dimethylfluorosilyl group in **5**. However, the use of excess **1** (X = F) (experiment 3) does not increase the yield of **5** significantly. When the reaction is carried

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[1] Jones, P. R.; Lim, T. F. O. *J. Am. Chem. Soc.* **1977**, *99*, 2013–15, 8447–51.

[2] Jones, P. R.; Lim, T. F. O.; Pierce, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4970–3.

[3] Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 2087–98, 3518–32.

[4] Jones, P. R.; White, D. D., unpublished observations.

[5] Conlin, R. T.; Bessellieu, M. P.; Jones, P. R.; Pierce, R. A. *Organometallics* **1982**, *1*, 396–7.

[6] Jones, P. R.; Lim, T. F. O.; McBee, M. L.; Pierce, R. A. *J. Organomet. Chem.* **1978**, *159*, 99–110.

[7] Wiberg, N.; Preiner, G.; Schieda, O.; Fischer, G. *Chem. Ber.* **1981**, *114*, 3505–17.

[8] Svoboda, P.; Vaisarova, V.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2259–64.

[9] Lim, T. F. O. Doctoral Dissertation, North Texas State University, May, 1977.

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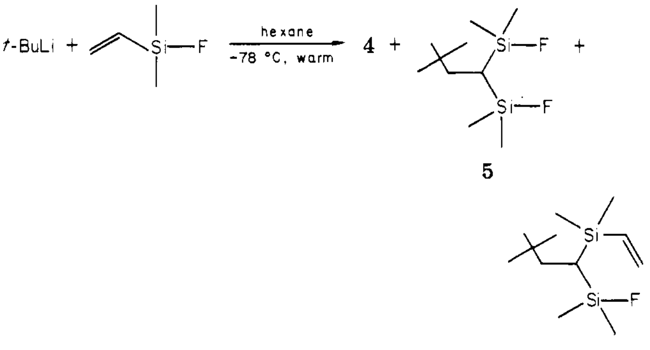


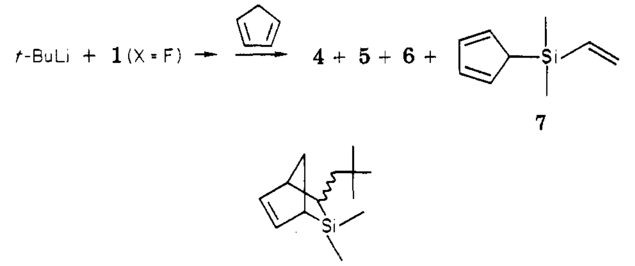
5

6

out by using excess *tert*-butyllithium (experiment 4) or under conditions where silene formation is rapid (experiment 5), the yield of **5** decreases in favor of silene dimer formation. In hydrocarbon solvent no products derived from *tert*-butyl substitution at silicon are obtained.

It should be noted that the vinyldimethylsilyl-substituted product **6** is not obtained in hexane with **1** (X = Cl) (experiment 2 or 6) or with **1** (X = F) in reactions where **5** is not formed. However, **6** is obtained in THF for **1** (X = Cl or F), although only traces of **5** are produced. Compound **6** can arise from the reaction of the silenoid **3** with **1** in THF but may arise from the reaction of **5** with vinyllithium in hexane. In THF the dimer stereochemistry indicates an α-lithiosilane precursor. The high cis/trans ratio of the dimers obtained in THF for **1** (X = F) is comparable with that obtained for **1** (X = Cl) under conditions for which the silenoid intermediate **3** has been shown to be the product precursor.[2,5]

Silene trapping experiments were conducted in this system. With cyclopentadiene as the trap cyclopentadienyldimethylvinylsilane, **7**, and the [4 + 2] silene adducts **8** are obtained. Recently methoxytrimethylsilane has been shown to be a silene trap comparable in efficiency to HCl.[10] In experiments which employed methoxytrimethylsilane as the silene trap, excellent yields of its silene adduct, 2-methoxy-1,5,5-trimethyl-3-(trimethylsilyl)-2-silahexane, **9**, were obtained. The results of the trapping experiments are summarized in Table II.



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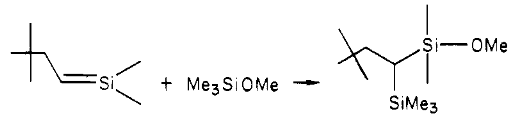

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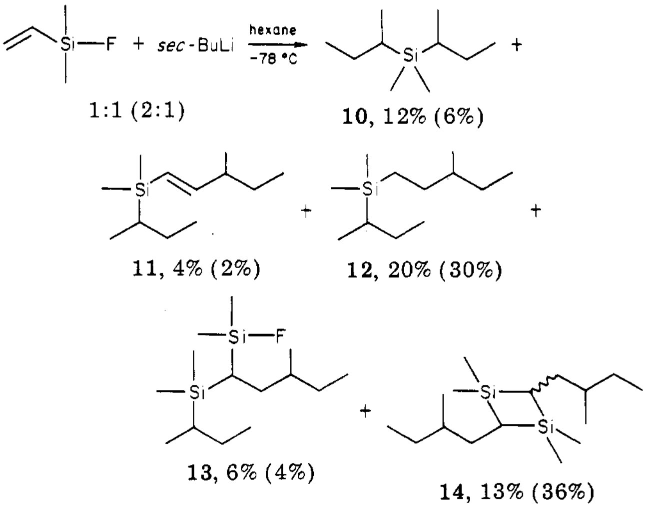
The exo/endo ratio for the silnorbornenes **8** is similar to that obtained when **1** (X = Cl)[2] or thermal sources[5] are used as the silene precursor. In agreement with Davidson's kinetic results[10] methoxytrimethylsilane is much more efficient than cyclopentadiene as a silene trap. Thus in experiments 14 and 15 the silene dimerization pathway is diverted, giving 46% yields of **9** and leaving 26–28% of products **4** and **5** derived from the silenoid **3**. In THF, (experiment 16) no silene is produced. In all experiments using methoxytrimethylsilane as a silene trap the dimer stereochemistry is consistent with the silenoid pathway. On the basis of these results, we can estimate that approximately two-thirds of the 1,3-disilacyclobutanes **4** obtained from the low-temperature reaction of *tert*-butyllithium with **1** (X = F) in hexane arise via silene dimerization with one-third being formed from the α-lithiosilane **3**.[11] If we assume this two-thirds to one-third ratio of the silene and silenoid pathways and that 55/45 and 78/22 represent the cis/trans ratio of **4** for silene and silenoid dimerization, respectively, the calculated cis/trans ratio for **4** in experiments in which both pathways are operative is 63/37, in good agreement with our experimental results.

The results also show that **5** does not have a silene precursor. Overall, the data are only consistent with the production of the bis(dimethylfluorosilyl) compound by the reaction of the α-lithiofluorosilane **3** with vinyldimethylfluorosilane (experiments 1, 3, 4 and 14, 15). This raises the important question of what happens to the vinyl fragment of **1**. While some of it may be giving **6**, we have been unable to determine its fate. In an experiment attempting to intercept vinyllithium using trimethylchlorosilane only a trace of vinyltrimethylsilane was obtained. Similar experiments using acetone or methyl iodide added after the initial addition of *tert*-butyllithium did not give any evidence for vinyllithium. Experiments designed to trap ethylene as its dibromide showed that ethylene is not produced either during the reaction or during hydrolytic workup. There is always some nonvolatile oligomer produced in these reactions. We must assume that part of this oligomer accounts for the missing vinyl group.

The reaction of **1** with *sec*-butyllithium in hexane at −78 °C gives a more complex mixture. Three new products, **10**, **11**, and **12**, for which analogues were not observed in the *tert*-butyl system are formed.



1:1 (2:1)

10, 12% (6%)

11, 4% (2%)

12, 20% (30%)

13, 6% (4%)

14, 13% (36%)

More than half of the products **10**, **11**, **12**, and **13** (42%) arise from substitution of fluorine on silicon by *sec*-butyllithium. Two products, **10** and **13** (18%), are derived from the vinyl substitution reaction discovered with *tert*-butyllithium. Interestingly product **10** must be formed directly by the reaction of *sec*-butyllithium with starting material.[12] Product **12** clearly arises from hydrolysis of

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[10] Davidson, I. M. T.; Wood, I. T. *J. Chem. Soc., Chem. Commun.* **1982**, 550.

[11] It should be noted that Wiberg's studies do not differentiate between the silene and silenoid pathways.[3,7]

Table II. Silene Trapping Experiments in the Reaction of *tert*-Butyllithium with Vinyldimethylfluorosilane, 1 (X = F)

Cyclopentadiene Trap

expt	1/*t*-BuLi ratio	solv	product yield,[a] %					4 cis/trans	8 exo/endo
			4	5	6	7	8		
10	1	hexane	19	1	3	14	4	65/35	52/48
11	2	hexane	17	2	2	7	7	66/34	53/47
12	4	hexane	22	7	2	6	2	66/34	56/44
13	1	THF	12	1	23	tr	0	75/25	

Methoxytrimethylsilane Trap

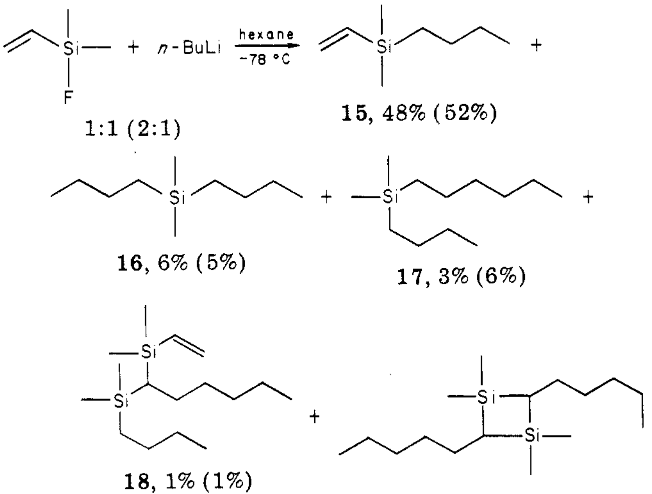
expt	1/*t*-BuLi ratio	solv	product yield, %				4 cis/trans
			4	5	6	9	
14	1	hexane	22	4	0	46	78/22
15	2	hexane	10	18	0	46	78/22
16	1	THF	71	1	3	0	78/22

[a] Yields determined by GLC using an internal standard calibration.

the α-lithio compound **3** (X = *sec*-Bu). Product **11** presumably is formed by the loss of lithium hydride from the same intermediate, a process which we observed previously in the reaction of *tert*-butyllithium with vinyltrimethylsilane.[1] Only a disappointing 13% yield of the silene or silenoid dimer **14** was obtained.

In contrast to the *tert*-butyl system, the use of excess **1** results in an increase in the yield of dimers **14** and a decrease of the vinyl substitution products **10** and **13**. The yield of **12** also increases.

In the reaction of **1** with *n*-butyllithium, the major product is the simple fluorine substitution product **15**.[13] Nearly 60% of the products **15**, **16**, **17**, and **18** involve this process in their formation. Only 6% of the vinyl substitution is obtained; the product **16**[14] resulting from reaction of *n*-butyllithium with the vinylsilane **1**. Only trace amounts of dimers are produced in the reaction. Doubling the ratio of **1** to *n*-butyllithium has little effect on the product distribution.



1:1 (2:1)

15, 48% (52%)

16, 6% (5%)

17, 3% (6%)

18, 1% (1%)

19, tr (2%)

For both the *sec*-butyl- and *n*-butyllithium reactions the products obtained in less than 5% yields were only partially characterized. The characterization of **17** and **19**, based on mass spectral and NMR data, and that of **11** and **18**, based only on mass spectral data, should be regarded as tentative.

Discussion

Vinyldimelthylfluorosilane undergoes at least three different competitive reactions with alkyllithium reagents: addition to the double bond, fluorine substitution, and an unprecedented vinyl substitution. The order of reactivities in hexane for the addition reaction, *tert*-butyl > *sec*-butyl > *n*-butyl, and the fluorine substitution reaction, *n*-butyl > *sec*-butyl >> *tert*-butyl, might naively be attributed to the steric requirements of the lithium reagent. However, for the concentration ranges employed in our studies, ca. 0.4 M, *tert*-butyllithium is tetrameric, *sec*-butyllithium probably exists as an equilibrium mixture of tetramers and hexamers, and *n*-butyllithium is hexameric.[15] We have no idea of how a vinylhalosilane interacts with or modifies these aggregates. There is evidence that unsaturated molecules coordinate with hexameric alkyllithium aggregates, occupying the two vacant faces of the octahedron formed by the lithium atoms.[16] Such a complexation with the *n*-butyllithium hexamer or the hexameric form of *sec*-butyllithium might give the fluorine substitution reaction an entropic advantage over the addition reaction.

The novel vinyl substitution reaction seems to be most important for secondary alkyllithium reagents. Our results indicate a reactivity order of **3** (X = F) > *sec*-butyllithium > the *sec*-butyl analogue of **3** (X = F) > *n*-butyllithium >>> *tert*-butyllithium. The reaction is observed with vinyldimethylfluorosilane, but not with vinyldimethylchlorosilane, and is favored by hydrocarbon solvents. It does not give significant amounts of vinyllithium or ethylene. While intriguing mechanisms involving electron transfer between the alkyllithium reagent and vinyldimethylfluorosilane[17] or processes involving pentacoordiate organofluorosilanes can be written, such speculations seem inappropriate until more is known about the nature of the species that are actually present in these solutions.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen or argon in glassware that was either oven dried and assembled hot or flame dried. Solvents were distilled from lithium aluminum hydride or sodium/potassium alloy immediately prior

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(12) To our knowledge replacement of a vinyl group on a vinyl trialkylsilane by an alkyllithium reagent has never been observed.

(13) Buell, G. R.; Corriu, R.; Guerian, C.; Spialter, L. *J. Am. Chem. Soc.* **1970**, *92*, 7424–8.

(14) Andreev, O. N.; Lavrinovich, L. I. *Zh. Obsch. Khim.* **1968**, *38*, 2743.

(15) Scherr, P. A.; Hogan, R. J.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 6055–59. Lewis, H. L.; Brown, T. L. *J. Am. Chem. Soc.* **1970**, *92*, 4664–70.

(16) Oliver, J. P.; Smart, J. B.; Emerson, M. T. *J. Am. Chem. Soc.* **1966**, *88*, 4101–3. Zerger, R.; Rhine, W.; Stucky, G. *Ibid.* **1974**, *96*, 6048–55.

(17) Sakurai, H.; Tobita, H.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1982**, *104*, 4288–9. Eisch, J. J.; Beuhler, R. J. *J. Org. Chem.* **1963**, *28*, 2876–7.

to use. Solutions of alkyllithium reagents (Aldrich) were standardized by using the method of Gilman and Cartledge.[18] Reagents and solvents were transferred by using standard syringe techniques. GLC analyses of the reaction mixtures were carried out by using a Perkin-Elmer Sigma 3 gas chromatograph equipped with a 25-m SE-54 capillary column, flame ionization detection, and a Hewlett-Packard 3390A reporting integrator, with di-*n*-butyl ether as the internal standard.

Samples for characterization were collected from a thermal conductivity gas chromatograph using a 10% OV-17 on 45/60 mesh Supelcoport stationary phase in a 16 ft by $^3/_8$ in. stainless steel column, programmed at 6 °C/min from 100 to 250 °C. ^{1}H NMR and ^{13}C NMR spectra were obtained on purified samples in capillary tubes inserted in ordinary NMR tubes containing deuteriochloroform or D_2O for the carbon or proton spectra, respectively, using a Perkin-Elmer R24B 60-MHz or JEOL FX-90Q 90-MHz spectrometers. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Finnigan automated 9500 GC/MS system with 70-eV ionizing voltage.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Vinyldimethylfluorosilane, 1 (X = F), was prepared from vinyldimethylchlorosilane[19] using antimony trifluoride with an antimony pentachloride catalyst.[8] The purified starting material showed the following: IR 1400 (C═C), 1258 ($SiCH_3$), 872 cm^{-1} (SiF); ^{1}H NMR 0.04 (d, 6 H, *J*(H–F) = 17.1 Hz), 5.2–6.3 ppm (m, 3 H); ^{13}C NMR –2.0 (*J*(C–F) = 15.9 Hz ($SiCH_3$)), 135.5 and 133.9 ppm (vinyl carbons).

General Method for the Reaction of 1 (X = Cl or F) with Alkyllithium. Solutions of reactants were cooled to the reaction temperature prior to mixing. To a stirred solution of 2.5 mL (22 mmol) of vinyldimethylfluorosilane in 50 mL of solvent was added dropwise a hydrocarbon solution containing the appropriate amount of the alkyllithium reagent. With the exceptions of the reactions carried out at room temperature, experiments 5 and 6, the mixture was held at –78 °C for 3 h by using an acetone/dry ice cooling bath and then was allowed to slowly warm to room temperature overnight with stirring.

When hexane was used as the solvent, a colorless gel formed as a second layer that dissolved when the reaction was quenched with 10 mL of a saturated ammonium chloride solution. The organic layer was separated, combined with three extractions of the aqueous layer with 10-mL portions of ether, and dried over anhydrous sodium sulfate. When THF was used as the solvent, the aqueous layer was saturated with potassium carbonate prior to extraction. After solvents were removed by using a rotary evaporator, GLC analysis was carried out on the residue. Table I summarizes the results of the experiments.

For 1 (X = F), the following new products were isolated by preparative GLC and characterized.

1,1-Bis(dimethylfluorosilyl)-3,3-dimethylbutane, 5: colorless liquid; IR 1256 (SiMe), 869 cm^{-1} (SiF); ^{1}H NMR –0.08 (d, *J*(H–F) = 16.6 Hz, 12 H ($SiMe_2F$)), –0.17 (m, 1 H (methine H)), 0.64 (s, 9 H (*t*-Bu)), 1.20 ppm (d, *J* = 5.2 Hz, 2 H (methylene)); ^{13}C NMR –0.69 (d, *J*(C–F) = 16.1 Hz (SiMe)), 12.16 (t, *J*(C–F) = 11.7 Hz (SiCSi)), 28.94 (*t*-Bu methyls), 31.34 (*t*-Bu *C*), 35.38 ppm (methylene C); MS, *m/e* (relative intensity) 223 (8.2, P – Me), 145 (20.7), 86 (50.8), 77 (80.5), 73 (27.3), 57 (100). Anal. Calcd for $C_{10}H_{24}F_2Si_2$: C, 50.37; H, 10.14. Found: C, 50.58; H, 10.30.

4-(Dimethylfluorosilyl)-3,3,6,6-tetramethyl-3-sila-1-heptene, 6: colorless oil; IR 1400 (C═C), 1250 ($SiCH_3$), 850 cm^{-1} (SiF); –0.18 ^{1}H NMR (s, 6 H ($ViSiMe_2$)), –0.15 (d, *J*(H–F) = 16.2 Hz ($FSiMe_2$)), –0.16 (m, 1 H (methine H)), 0.57 (s, 9 H (*t*-Bu)), 1.21 (d, *J* = 5.1 Hz (methylene H)), 5.2–6.2 ppm (m, 3 H (vinyl H)); ^{13}C NMR –3.1 (d, *J*(C–F) = 8.3 Hz ($FSiCH_3$)), –0.1 and 0.1 (d, *J*(C–F) = 8.2 Hz (vinyl $SiCH_3$)), 9.8 (d, *J*(C–F) = 12.3 Hz (SiCHSi)), 29.6 (*t*-BuMe), 30.1 (*t*-Bu *C*), 37.2 (methylene C), 131.3 and 139.1 ppm (vinyl carbons); MS, *m/e* (relative intensity) 246 (4.1), 231 (15.1), 190 (16.3), 189 (44.8), 149 (21.8), 148 (62.3), 134 (12.5), 133 (77.1), 111 (38.7), 97 (100), 73 (27.2). Anal. Calcd for $C_{12}H_{27}FSi_2$: C, 58.47; H, 11.04. Found: C, 58.64; H, 11.11.

1,1,3,3-Tetramethyl-2,4-dineopentyl-1,3-disilacyclobutanes, 4. The characterization of these compounds has been reported previously.[7] We report here ^{13}C NMR and mass spectral data for them.

***cis*-4**: ^{13}C NMR –4.8 and 2.5 (SiMe), 12.8 (ring carbons), 29.3 (*t*-BuMe), 31.3 (*t*-Bu *C*), 39.8 ppm (methylene carbons); MS, *m/e* (relative intensity) 284 (15.1), 227 (100), 157 (90.6), 141 (91.9), 131 (43.0), 85 (20.9), 73 (76.2), 59 (71.4), 57 (16.4).

***trans*-4**: ^{13}C NMR –0.71 (SiMe), 12.2 (ring carbons), 29.3 (*t*-BuMe), 31.4 (*t*-Bu *C*), 39.8 ppm (methylene carbons); MS *m/e* (relative intensity) 284 (14.5), 227 (98.3), 157 (94.2), 141 (96.2), 131 (53.2), 99 (28.4), 85 (27.5), 73 (100), 59 (95.2), 57 (62.1), 41 (43.0).

General Method for Trapping Experiments with Cyclopentadiene. A solution prepared as described above of 2.5 mL (22 mmol) of the vinylsilane 1 (X = F or Cl) and 7.7 mL (22 mmol) of *tert*-butyllithium in 50 mL of solvent was stirred at –78 °C for 3 h. After the addition of 2.25 mL (21 mmol) of cyclopentadiene the reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. After hydrolytic workup as described above the residue was analyzed by GLC. The characterization of the products 7 and 8 has been reported.[2] Results of the several trapping experiments are given in Table II, experiments 10–13.

Trapping Experiments with Methoxytrimethylsilane. To a solution of 25 mmol of vinyldimethylfluorosilane in 60 mL of solvent cooled to –78 °C was added dropwise the appropriate amount of a pentane solution of *tert*-butyllithium. After the solution was stirred at –78 °C for 2.5 h, 25 mmol of methoxytrimethylsilane was added and the mixture was allowed to slowly warm to room temperature. Hydrolytic workup was carried out in the usual way. The results are summarized in Table II, experiments 14–16.

2-Methoxy-1,5,5-trimethyl-3-(trimethylsilyl)-2-silahexane, 9, was separated from the reaction mixture and purified by preparative GLC as a colorless liquid: bp 75 °C (3 torr); ^{1}H NMR –0.35 (m, 1 H (methine)), –0.19 (s, 9 H (Me_3Si)), –0.12 (6 H (Me_2Si)), 0.62 (s, 9 H (*t*-Bu)), 1.19 and 1.22 (d, 2 H (diastereotropic CH_2)), 3.11 ppm (s, 3 H (OCH_3)); ^{13}C NMR –1.37 and –0.85 (q (diastereotopic $MeOSi(CH_3)_2$)), 0.19 (q ($Si(CH_3)_3$)), 9.30 (d (SiCHSi)), 29.65 (q ($C(\mathit{C}H_3)_3$)), 31.41 (s ($\mathit{C}(CH_3)_3$)), 37.07 (t, (CH_2)), 49.42 ppm (q (OCH_3)). Anal. Calcd for $C_{12}H_{30}Si_2O$: C, 58.46; H, 12.27. Found: C, 58.64; H, 12.15.

Trapping Experiments with Trimethylchlorosilane, Acetone, and Methyl Iodide. To a solution of 4.8 mL (40 mmol) of 1 (X = F) in 50 mL of hexane, cooled to –78 °C, was added dropwise 7.7 mL (22 mmol) of a *tert*-butyllithium solution in pentane. After the mixture was stirred at –78 ° for 5 h, a solution of 200 mmol of trimethylchlorosilane in 50 mL of THF was added dropwise, and the mixture was allowed to warm to room temperature. Hydrolytic workup gave 1.1% of vinyltrimethylsilane, 49.4% of the dimers **4**, 3.6% of **5**, 9.6% of **6**, and a 9.8% yield of the following:

2-Fluoro-2,5,5-trimethyl-3-(trimethylsilyl)-2-silahexane: colorless liquid; ^{1}H NMR –0.17 (s, 9 H ($SiMe_3$)), –0.03 (d, *J*(H–F) = 17.2 Hz, 6 H ($SiFMe_2$)), –0.19 (m, 1 H (methine H)), 0.63 (s, 9 H (*t*-Bu)), 1.22 ppm (d, *J* = 6.1 Hz, 2 H (methylene H)); ^{13}C NMR –0.39 ($SiMe_3$), 0.68 (d, *J*(C–F) = 10.1 Hz ($SiMe_2F$)), 10.27 (d, *J*(C–F) = 11.2 Hz (SiCSi)), 29.29 (*t*-BuMe), 31.41 (methylene C), 37.00 ppm (methine C). Anal. Calcd for $C_{11}H_{27}FSi_2$: C, 56.34; H, 11.60. Found: C, 56.56; H, 11.55.

Attempts To Trap Ethylene. The reactions described in general procedure were carried out with a setup designed so that the reaction flask was swept with dry nitrogen throughout the experiment. The effluent gas was passed by means of a gas dispersion tube through a trap containing a solution of bromine in carbon tetrachloride. The contents of the trap were analyzed by GLC at the end of the 3-h period at –78 °C, after the reaction had warmed to room temperature and after the reaction mixture had been hydrolyzed. No 1,2-dibromoethane was detected. Analysis of the reaction mixtures gave results identical with those for experiments 1 and 3, Table I.

Reactions with *sec*-Butyllithium were carried out as described in the general procedure, giving the results shown in the text. The following compounds were isolated by preparative GLC and characterized.

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3,4,4,5-Tetramethyl-4-silaheptane, 10: colorless liquid; ^1H NMR −0.12 (s, 6 H ($SiMe_2$)), 0.6–1.5 ppm (broad envelope, 18 H (*sec*-Bu hydrogens)); ^{13}C NMR −6.57 (q ($Si(CH_3)$)), 13.59 and 13.85 (q (*sec*-Bu methyls)), 20.03 (d (*sec*-Bu methine)), 25.04 ppm (t (*sec*-Bu methylene)); MS, *m/e* (relative intensity) 172 (3), 157 (2), 115 (50), 101 (4), 87 (8), 73 (100), 59 (72). Anal. Calcd for $C_{10}H_{24}Si$: C, 69.67; H, 14.03. Found: C, 69.83; H, 14.26.

3,4,4,7-Tetramethyl-4-sila-5-nonene, 11: MS, *m/e* (relative intensity) 183 (2, P − Me), 141 (100), 127 (8), 113 (20), 99 (31), 85 (43), 73 (40), 59 (52).

3,4,4,7-Tetramethyl-4-silanonane, 12: colorless liquid; ^1H NMR 0.1 (s, 6 H), 0.7–2.6 ppm (br, 22 H); ^{13}C NMR −4.94 (q ($SiCH_3$)), 10.86, 11.44, 13.52, 13.72, 18.56, 21.00, 24.90, 30.63, 37.59 ppm;[20] MS, *m/e* (relative intensity) 185 (2, P − Me), 143 (62), 129 (8), 115 (10), 99 (12), 87 (35), 73 (88), 59 (100). Anal. Calcd for $C_{12}H_{28}Si$: C, 71.90; H, 14.08. Found: C, 71.73; H, 14.09.

5-(Dimethylfluorosilyl)-3,4,4,7-tetramethyl-4-silanonane, 13: colorless oil; ^1H NMR 0.08 (s, 6 H), 0.25 (d, 6 H, $J(H-F)$ = 13 Hz), 0.6–2.7 ppm (br, 21 H); ^{13}C NMR −4.75 and −4.29 (diastereotopic $Si(CH_3)_2$), −0.52 (d, $J(C-F)$ = 17.6 Hz) and 0.81 (d, $J(C-F)$ = 16.1 Hz (diastereotopic $SiF(CH_3)_2$)), 10.66, 11.15, 13.26, 18.40, 19.25, 20.54, 20.68, 24.64, 28.48, 30.24, 31.99, 36.48 ppm;[20] MS, *m/e* (relative intensity) 261 (2, P − Me), 219 (35), 205 (5), 141 (100), 127 (15), 113 (14), 99 (22), 85 (36), 77 (12), 73 (42), 59 (46). Anal. Calcd for $C_{14}H_{33}Si_2F$: C, 60.80; H, 12.03. Found: C, 60.92; H, 12.09.

2,4-Bis(2-methylbutyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane, 14: colorless liquid; ^1H NMR 0.15 (br, 12 H), 0.76–2.6 ppm (br, 24 H); ^{13}C NMR mixture of 68% *cis*-**14** and 32% *trans*-**14** estimated from spectrum, −5.14 and 2.79 (q ($Si\text{-}Ch_3$ is cis isomer)), −0.98 (q ($SiCH_3$ in trans isomer)), 11.44 (CH_3CH_2 of *sec*-Bu)), 14.76 (d (ring C in trans isomer)), 15.41 (d (ring C in cis isomer)), 18.99 (t (CH_3 of *sec*-Bu)), 29.26 (t (methylene of *sec*-Bu)), 32.12 (t (methylene on ring in cis isomer)), 32.84 (t (methylene on ring in trans isomer)), 37.98 ppm (d, (methine of *sec*-Bu)); MS, *m/e* (relative intensity) 284 (4), 269 (1), 227 (30), 157 (42), 141 (80), 131 (90), 113 (16), 99 (28), 85 (100), 73 (85), 59 (88). Anal. Calcd for $C_{16}H_{36}Si_2$: C, 67.52; H, 12.75. Found: C, 67.63; H, 12.82.

From the reactions with *n*-butyllithium the following compounds were isolated.

3,3-Dimethyl-3-sila-1-heptene, 15:[13] ^1H NMR −0.15 (s, 6 H), 0.2–1.3 (br, 9 H), 5.0–6.2 ppm (m, 3 H); ^{13}C NMR −3.97 (q ($SiCH_3$)), 13.13, 26.08, and 25.75 (t (CH_2's of *n*-Bu)), 14.48 (q (CH_3 of *n*-Bu)), 130.51 (d) and 138.51 ppm (t) (vinyl carbons); MS, *m/e* (relative intensity) 142 (1), 127 (6), 114 (8), 99 (4), 85 (100), 71 (38), 59 (70).

5,5-Dimethyl-5-silanonane, 16:[14] ^1H NMR −0.30 (s, 6 H), 0–1.2 ppm (br, 18 H); ^{13}C NMR −3.77 (q ($SiCH_3$)), 13.33, 26.40, 26.08, (t (CH_2's of *n*-Bu)), 14.89 ppm (q (CH_3 of *n*-Bu)); MS, *m/e* (relative intensity) 172 (1), 157 (6), 115 (78), 101 (12), 73 (74), 59 (100).

5,5-Dimethyl-5-silaundecane, 17: ^1H NMR 0.08 (s, 6 H), 0.6–2.6 ppm (br, 22 H); ^{13}C NMR −3.84 (q ($SiCH_3$)), 14.89 (q (CH_3 of *n*-Bu)), 13.66 (CH_3 of *n*-hexyl)), 22.56, 23.86, 26.14, 26.46, 31.60, 32.90, 33.23, 33.49 ppm (CH_2 groups); MS, *m/e* (relative intensity) 185 (4, P − Me), 143 (52), 129 (10), 115 (35), 101 (10), 87 (16), 173 (70), 59 (100).

4-*n*-Pentyl-3,3,5,5-tetramethyl-3,5-disila-1-nonene, 18: MS, *m/e* (relative intensity) 231 (6, P − Me), 219 (1), 189 (2), 176 (6), 153 (15), 141 (40), 127 (42), 114 (55), 99 (44), 85 (100), 77 (15), 73 (22), 59 (73).

2,4-Di-*n*-pentyl-1,1,3,3-tetramethyl-1,3-disilacyclobutane, 19: colorless liquid; ^1H NMR 0.15 (s, 6 H), 0.17 (s, 6 H), 0.6–2.6 ppm (br, 24 H); −3.71 and −3.51 (q ($SiCH_3$)), 13.66 and 14.63 (q (CH_3 or *n*-Bu)), 13.98 and 14.89 (d (CH in ring)), 22.63, 23.47, 24.40, 26.60, 28.22, 28.74, 29.07, 32.38 ppm (t (CH_2 groups)); MS, *m/e* (relative intensity) 227 (18, P − Bu), 213 (3), 199 (2), 171 (4), 153 (18), 141 (48), 131 (88), 115 (14), 99 (12), 85 (55), 73 (52), 59 (100).

Acknowledgment. We thank the Robert A Welch Foundation, the National Science Foundation, and the North Texas State University Organized Research Fund for support of this work. Helpful discussions with Professors J. P. Oliver and R. West and the assistance of Dr. Francis Huang in obtaining the mass spectral results is gratefully acknowledged.

Registry No. 1, X = F, 38755-76-9; 1, X = Cl, 1719-58-0; *cis*-**4**, 62518-77-8; *trans*-**4**, 62518-76-7; **5**, 87656-63-1; **6**, 87656-64-2; **9**, 87656-65-3; **10**, 87656-66-4; 11, 87681-17-2; **12**, 87656-67-5; **13**, 87656-68-6; *cis*-**14**, 87656-69-7; *trans*-**14**, 87656-72-2; **15**, 24343-24-6; **16**, 996-06-5; **17**, 80054-50-8; **18**, 87656-70-0; **19**, 87656-71-1; 2-fluoro-2,5,5-trimethyl-3-(trimethylsilyl)-2-silahexane, 87681-18-3; *tert*-butyllithium, 594-19-4; *sec*-butyllithium, 598-30-1; *n*-butyllithium, 109-72-8; antimony trifluoride, 7783-56-4; antimony pentachloride, 7647-18-9; cyclopentadiene, 542-92-7; methoxytrimethylsilane, 1825-61-2; trimethylchlorosilane, 75-77-4; acetone, 67-64-1; methyl iodide, 74-88-4.

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(20) Because of the large number of diastereotopic protons in the molecule, the off-resonance proton-decoupled spectrum was extremely complex and all of the carbon resonances were not assigned.

Efficient Syntheses of New Fulvalene-Bridged Carbonyl Complexes of Cobalt, Ruthenium, Chromium, Molybdenum, and Tungsten

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Received July 29, 1983

A variety of new dimetallafulvalene carbonyl complexes have been prepared by slow addition of cold purified dihydrofulvalene in heptane to boiling solutions of metal carbonyls. Reaction of $Co_2(CO)_8$ with dihydrofulvalene allows efficient preparation of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_4Co_2$. $Ru_3(CO)_{12}$, $Cr(NCEt)_3(CO)_3$, $Mo(CO)_6$, and $W(NCEt)_3(CO)_3$ react to form the intramolecularly metal–metal bonded complexes $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_4Ru_2$ and $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_6M_2$ (M = Cr, Mo, and W). Attempts to generate the analogous iron complexes were unsuccessful. Reaction of a mixture of $Ru_3(CO)_{12}$ and $Mo(CO)_6$ with dihydrofulvalene affords a better than statistical yield of the mixed metal-metal bonded complex $(\eta^5{:}\eta^5\text{-}C_{10}H_8)(CO)_5MoRu$.

Introduction

Cyclopentadienylmetal carbonyl dimers and their derivatives are among the most extensively studied classes of organometallic compounds. Dinuclear metal complexes are often postulated as simple models with which to study the interactions of molecules with metal surfaces.[1] Cy-

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