1,2-Bis(trimethylsilyl)-1,2-dimesitylethene. Formation from 1,1-Dimesityl-2-bromoethene

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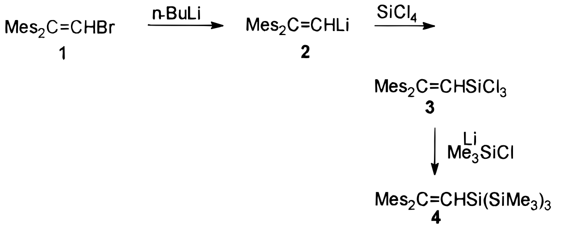
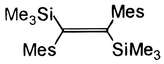
Summary: Treatment of 1,1-dimesityl-2-bromoethene in ether at room temperature with n-butyllithium gave rise to 1,2-dimesitylacetylene, which when treated with lithium and trimethylchlorosilane formed (E)-1,2-bis(trimethylsilyl)-1,2-dimesitylethene in quantitative yield. In contrast, treatment of the bromoethene at −78 °C with n-butyllithium in THF (but not ether) results in halogen-metal exchange: the resulting organolithium reagent was trapped with trimethylchlorosilane.

In the course of another study, a one-pot reaction was carried out starting with 1,1-dimesityl-2-bromoethene, **1**, and *n*-butyllithium as shown in eq 1. After 3 h the solvent was changed from ether to benzene, and the anticipated product **2** was treated with silicon tetrachloride, which should have led to the (trichlorosilyl)ethene **3**. After the mixture was pumped to dryness, addition of excess lithium and trimethylchlorosilane was then expected to lead to 1,1-dimesityl-2-tris(trimethylsilyl)silylethene (**4**).



(1)

On workup, however, an 88% isolated yield of the compound (*E*)-1,2-dimesityl-1,2-bis(trimethylsilyl)ethene (**5**) was obtained, as shown by analytical and NMR data and by an X-ray crystal structure (Figure 1).



5

This unanticipated result was of interest because of the obvious structural rearrangement which had occurred at some stage in the reaction and the question of which reactions had given rise to the observed product **5**: in particular, if **3** had been formed, it was difficult to imagine how reaction with lithium and trimethylchlorosilane would lead to elimination of the trichlorosilyl (or tris(trimethylsilyl)silyl) group present.

It had been established earlier that treatment of **1** in THF with *n*-butyllithium at −78 °C gave the lithium compound **2**, trapped as the corresponding carboxylic acid with CO_2.[1] It is noteworthy that when diethyl ether was used instead of THF as the solvent, no reaction occurred at −78 °C. We have now also captured **2** with trimethylchlorosilane, leading to $Mes_2C{=}CHSiMe_3$ (**7**), characterized by NMR and other methods, as shown in eq 2 and described below.

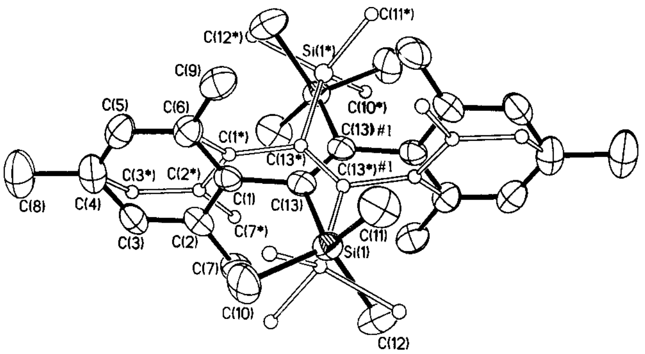
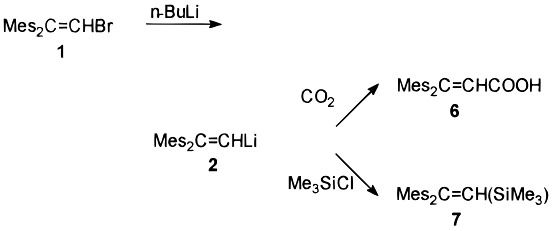


Figure 1. ORTEP diagram for 1,2-bis(trimethylsilyl)-1,2-dimesitylethene (**5**), showing the structures of the molecules disordered in the two sites with occupancy 83:17 (major component has solid bonds).



(2)

These results appeared to indicate that rearrangement of the mesityl groups did not occur during the first step of the reaction sequence, at least at −78 °C. Treatment of **1** directly with lithium and trimethylchlorosilane gave a complex mixture of products which did not contain any of the final product **5**, on the basis of NMR evidence, indicating that **5** was not formed directly from the reaction of **1** with lithium and trimethylchlorosilane.

The reaction of **1** with *n*-butyllithium was next investigated further. When the reaction was run over 3 h in ether **at room temperature**, the solution almost immediately became orange-red (as distinct from solutions for reactions run at −78 °C, which remained colorless). Quenching of the solution in ethanol after 3 h and workup gave rise in nearly quantitative yield to dimesitylacetylene (**9**), a known compound.[2] This transformation appears to be an example of the Fritsch−Buttenberg−Wiechell rearrangement, investigated also by Curtin and co-workers,[3,4] in which a diarylvinyl halide such as **1** when treated with an alkyllithium reagent has been shown to give rise to a 1,2-diarylacety-

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

[1] Brook, A. G.; Ionkin, A.; Lough, A. J. *Organometallics* **1996**, *15*, 1275.

[2] Fuson, R. C.; Southwick, P. L.; Rowland, S. P. *J. Am. Chem. Soc.* **1944**, *66*, 1109.

[3] Curtin, D. Y.; Crump, J. W. *J. Am. Chem. Soc.* **1958**, *80*, 1922.

[4] Curtin, D. Y.; Flynn, E. W. *J. Am. Chem. Soc.* **1959**, *81*, 4714.

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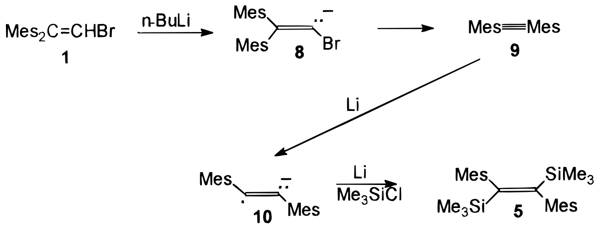
lene such as **9**. The tendency for the sterically congested 1,1-dimesityl compounds to undergo 1,2-mesityl migration under various conditions has frequently been observed[2]. This rearrangement, as shown in eq 3,



(3)

occurs as a result of deprotonation of the vinylic hydrogen by the organolithium reagent, acting as a base, leading to the vinylcarbanion **8,** which then rearranges to the alkyne.[5] Subsequently, when the alkyne **9** was treated with lithium and trimethylchlorosilane under the same conditions as were used in the reaction sequence shown in eq 1, the previously observed product **5** was formed in quantitative yield. Such silylations of an alkyne had been predicted earlier,[6] and numerous results have been reviewed.[7]

The above results explain the chemistry that actually occurred in the sequence shown in eq 1, namely that the original vinyl bromide **1** was converted not to **2** but to **9** because of the temperature employed (room temperature) and **9** of course did not react with the added $SiCl_4$, which ultimately was pumped off. Then on addition of lithium and trimethylchlorosilane, **9** was converted via the anion radical **10** to **5**, as shown in eq 3.

It is now evident that the reaction of $Mes_2C{=}CHBr$ with *n*-butyllithium is very sensitive to temperature and solvent effects. Halogen−metal exchange occurred exclusively at −78 °C in THF (but not ether), as shown by the reactions of the product **2** with carbon dioxide or trimethylchlorosilane. However, at room temperature deprotonation of **1** to **8** followed by rearrangement to dimesitylacetylene **9** occurred exclusively in diethyl ether, and then, as a result of the sequence of steps shown in eq 1, **9** was converted to the alkene **5**. Thus, it is important to be aware of the remarkable temperature and solvent dependence of product formation when carrying out reactions of diarylvinyl halides with organometallic reagents.

Other than the disorder described below, there was nothing unusual about the crystal structure of **5**, whose ORTEP diagram is shown in Figure 1. The molecule is planar about the carbon−carbon double bond, and the length of the central bond (1.344 Å) does not suggest that the molecule is sterically strained.

Experimental Section

All experiments were performed in oven-dried glassware under nitrogen using standard inert-atmosphere and vacuum line techniques. Diethyl ether and THF were dried over sodium benzophenone ketyl and distilled prior to use, and benzene was dried over lithium aluminum hydride prior to distillation.

^1H NMR spectra were obtained on Gemini 200 MHz or Unity 400 MHz instruments, and a Unity 400 instrument was used for ^{13}C NMR and ^{29}Si NMR spectra, which were run in $CDCl_3$ or C_6D_6 as noted. Where necessary, APT or DEPT pulse sequences were employed.

Mass spectra were run on a VG-70-250S mass spectrometer operating in the electron impact (EI) mode. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Melting points are uncorrected.

Formation of 1,2-Bis(trimethylsilyl)-1,2-dimesitylethene (5) from 1,1-Dimesityl-2-bromoethene (1). To a solution of 8.0 g (0.023 mol) of 1,1-dimesityl-2-bromoethene[1] in 80 mL of dry diethyl ether was added 9.7 mL of 2.5 M *n*-BuLi in hexane (0.024 mol) at room temperature. The solution turned red almost immediately. After the mixture was stirred overnight, the solvents were removed under reduced pressure and 23 mL of benzene was added, followed by 12.0 g (0.071 mol) of $SiCl_4$. The mixture was stirred overnight, at which time the volatiles were removed under reduced pressure. The resulting solid residue was dissolved in 146 mL of THF, and to the solution was added 25 g (0.23 mol) of trimethylchlorosilane and 1.07 g (0.15 g atom) of finely cut lithium wire. The mixture was stirred for 48 h at room temperature followed by 6 h reflux. Workup followed by recrystallization from methanol gave 8.27 g (88%) of **5**, mp 255−257 °C. Anal. Calcd for $C_{26}H_{40}Si_2$: C, 76.47; H, 9.79. Found: C, 76.45, H, 10.01. ^1H NMR ($CDCl_3$): δ −0.29 (s, 18 H, Me_3Si), 2.27 (s, 18 H, Me of Mes), 6.80 (s, 4 H, CH arom). ^{13}C NMR (C_6D_6): δ 1.11 (Me_3Si), 21.01 (*p*-Me), 22.29 (*o*-Me), 128.66 (*C*H−Ar), 135.39 (*C*−*p*-Me), 135.45 (*C*−*o*-Me), 141.96 (C *ipso*), 160.00 (C=). ^{29}Si NMR (C_6D_6): δ −9.39 (Me_3Si). MS (*m*/*z*): 408 (M^+, 26%), 393 ($M^+ - Me$, 9%), 335 ($M^+ - Me_3Si$, 37%), 177 ($MesSiMe_2{}^+$, 21%), 73 (Me_3Si^+, 100%).

Reaction of $Mes_2C{=}CHBr$ with *n*-BuLi at Room Temperature. To a solution of 0.7 g (0.002 mol) of $Mes_2C{=}CHBr$ in 12.5 mL of dry ether was added 0.95 mL of 2.5 M *n*-BuLi in hexanes (0.0024 mol) at room temperature. The solution turned orange almost immediately, and then red-orange over the next 3 h. The solution was quenched in ethanol and then worked up to give a quantitative yield of 1,2-dimesitylacetylene (**9**), mp 128−129 °C (lit.[2] mp 127.5−128.5 °C). ^1H NMR ($CDCl_3$): δ 2.35 (s, 6 H, *p*-Me), 2.56 (s, 12 H, *o*-Me), 6.96 (s, 4 H, C*H* arom). ^{13}C NMR ($CDCl_3$): δ 21.30 (*p*-Me), 21.48 (*o*-Me), 95.22 (C≡), 127.64 (*C*H arom), 129.35 (*C* ipso), 137.38 (*C*−*p*-Me), 139.81 (*C*−*o*-Me).

Reaction of MesC≡CMes (9) with Li and Me_3SiCl To Yield 5. To a solution of 0.2 g (0.000 76 mol) of dimesitylacetylene (**9**) in 5 mL of dry THF was added 0.82 g (0.0076 mol) of Me_3SiCl and about 0.1 g (0.015 mol) of finely cut Li wire. After the colorless mixture had been stirred for about 5 h at room temperature, during which time the metal surface became black and a white precipitate formed, the reaction mixture turned an intense dark red-brown. After the mixture was stirred overnight at room temperature, quenching in ethanol, followed by workup, led to the isolation of 0.31 g (essentially quantitative) of **5** which had spectroscopic properties identical with those given above.

Attempted Reaction of $Mes_2C{=}CHBr$ with Lithium and Me_3SiCl. A mixture of 0.2 g of **1**, 0.62 g of Me_3SiCl and about 0.06 g of finely cut lithium wire in 4 mL of dry THF was stirred under nitrogen. After about 10 min the reaction mixture turned red and then slowly changed to blue. After the mixture was stirred for 48 h at room temperature and 6 h at reflux, hydrolytic workup gave a complex mixture which did not contain any **5**, based on NMR spectra.

Reaction of $Mes_2C{=}CHBr$ in THF with *n*-BuLi at −78 °C and Then Me_3SiCl To Give $Mes_2C{=}CHSiMe_3$ (7). A 0.7 g (0.0020 mol) sample of **1** in 5 mL of dry THF was cooled to −78 °C and 0.95 mL of 2.5M *n*-BuLi (0.0024 mol) was added

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(5) For a discussion of the mechanism of this rearrangement see: March, J. In *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 978.

(6) See *Organometallic Compounds of Group IV Elements, Vol. 1*; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, p 158 and ref 647.

(7) Calas, R.; Dunoguès, J. *J. Organomet. Chem. Libr.* **1976**, *2*, 354.

Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for $C_{26}H_{40}Si_2$

empirical formula	$C_{26}H_{40}Si_2$
M_r	408.76
cryst size, mm	0.35 × 0.32 × 0.28
cryst class	monoclinic
space group	$P2_1/c$
temp, K	173(2)
a, Å	9.443(2)
b, Å	14.359(3)
c, Å	9.472(6)
β, deg	93.58(1)
V, A^3	1281.8(9)
Z	2
D_{calcd}, g cm^{-3}	1.059
μ(Mo Kα), cm^{-1}	1.47
F(000)	448
ω scan width, deg	0.43
range θ collected, deg	2.58−23.98
no. of rflns collected	2143
no. of indep rfls	2011
R_{int}	0.0179
no. of obsd data ($I > 2\sigma(I)$)	1581
R1 ($I > 2\sigma(I)$)	0.0392
wR2 (all data)	0.1039
goodness of fit	1.031
no. of params refined	219
max peak in final ΔF map, e $Å^{-3}$	0.19

Table 2. Bond Lengths (Å) and Angles (deg) for 5[a]

Si(1)−C(11)	1.861(3)	C(6)−C(1*)	1.42(2)
Si(1)−C(12)	1.867(4)	C(6)−C(9)	1.509(3)
Si(1)−C(10)	1.879(4)	C(13)−C(13)#1	1.344(6)
Si(1)−C(13)	1.914(4)	Si(1*)−C(10*)	1.75(3)
C(1)−C(2)	1.407(4)	Si(1*)−C(11*)	1.84(2)
C(1)−C(6)	1.418(4)	Si(1*)−C(12*)	1.84(2)
C(1)−C(13)	1.515(6)	Si(1*)−C(13*)	1.91(2)
C(2)−C(3)	1.391(5)	C(13*)−C(13*)#1	1.36(3)
C(2)−C(7)	1.506(4)	C(13*)−C(1*)#1	1.51(2)
C(3)−C(4)	1.410(6)	C(1*)−C(2*)	1.41(2)
C(4)−C(3*)	1.21(3)	C(1*)−C(13*)#1	1.51(2)
C(4)−C(5)	1.387(3)	C(2*)−C(3*)	1.43(3)
C(4)−C(8)	1.508(3)	C(2*)−C(7*)	1.54(2)
C(5)−C(6)	1.382(3)		

C(11)−Si(1)−C(12)	106.9(2)	C(5)−C(6)−C(9)	119.9(2)
C(11)−Si(1)−C(10)	107.3(2)	C(1*)−C(6)−C(9)	118.7(7)
C(12)−Si(1)−C(10)	108.0(2)	C(1)−C(6)−C(9)	120.9(2)
C(11)−Si(1)−C(13)	114.23(14)	C(13)#1−C(13)−C(1)	120.6(5)
C(12)−Si(1)−C(13)	113.8(2)	C(13)#1−C(13)−Si(1)	126.1(5)
C(10)−Si(1)−C(13)	106.3(2)	C(1)−C(13)−Si(1)	113.3(2)
C(2)−C(1)−C(6)	119.3(3)	C(10*)−Si(1*)−C(11*)	105.4(12)
C(2)−C(1)−C(13)	120.7(3)	C(10*)−Si(1*)−C(12*)	107.1(11)
C(6)−C(1)−C(13)	119.8(3)	C(11*)−Si(1*)−C(12*)	109.1(11)
C(3)−C(2)−C(1)	120.1(3)	C(10*)−Si(1*)−C(13*)	113.9(10)
C(3)−C(2)−C(7)	118.8(3)	C(11*)−Si(1*)−C(13*)	113.1(8)
C(1)−C(2)−C(7)	121.1(3)	C(12*)−Si(1*)−C(13*)	108.1(10)
C(2)−C(3)−C(4)	120.9(4)	C(13*)#1−C(13*)−C(1*)#1	120(2)
C(3*)−C(4)−C(5)	111.6(11)	C(13*)#1−C(13*)−Si(1*)	125(2)
C(5)−C(4)−C(3)	117.9(3)	C(1*)#1−C(13*)−Si(1*)	114.0(9)
C(3*)−C(4)−C(8)	123.6(12)	C(2*)−C(1*)−C(6)	116.9(12)
C(5)−C(4)−C(8)	121.2(2)	C(2*)−C(1*)−C(13*)#1	118.8(13)
C(3)−C(4)−C(8)	120.6(3)	C(6)−C(1*)−C(13*)#1	124.1(12)
C(6)−C(5)−C(4)	122.8(2)	C(1*)−C(2*)−C(3*)	113(2)
C(5)−C(6)−C(1*)	117.7(7)	C(1*)−C(2*)−C(7*)	123.3(13)
C(5)−C(6)−C(1)	118.9(2)	C(3*)−C(2*)−C(7*)	123(2)
		C(4)−C(3*)−C(2*)	133(2)

[a] Symmetry transformations used to generate equivalent atoms: (#1) −x, −y, −z + 1.

and stirred for 3 h. The colorless solution was quenched with excess Me_3SiCl. Workup of the reaction led to the isolation of 0.6 g (87%) of $Mes_2C{=}CHSiMe_3$, **7**, a colorless viscous liquid, bp approx.125 °C/0.1 mm Hg. Anal. Calcd for $C_{23}H_{32}Si$: C, 82.06; H, 9.59. Found: C, 82.06; H, 9.76. ^1H NMR ($CDCl_3$) δ -0.08 (9 H, s, Me_3Si), 2.19 (9H, br, Me-Ar), 2.27 (9 H, br, Me-Ar), 5.92 (1 H, s, =CH), 6.78 (2 H, s, CH-Ar), 6.82 (2 H, br, CH-Ar); ^{13}C NMR ($CDCl_3$) δ −0.89 (Me_3Si), 20.72, 20.89, 21.12 (each Me-Ar), 21.5−22.2 (very br Me-Ar),[8] 128.46, 129.72 (each *C*H-Ar), 135.81, 135.90, 136.86, 138.85, 140.88 (each *C*-quat Ar), 139.71 (=*C*H), 151.19 (Mes_2*C*=); ^{29}Si NMR ($CDCl_3$) δ −8.54. MS (m/z) 336 (M^+, 10), 321 (M^+ − Me, 84), 263 (M^+ − Me_3Si, 12), 247 (100), 177 (35), 73 (Me_3Si^+, 93).

Attempted Reaction of $Mes_2CH{=}CHBr$ in Et_2O with *n*-BuLi at −78 °C Leading to Starting Material. A 0.1 g sample of **1** in dry ether was cooled to −78 °C, and then 0.26 mL of 2.5 M *n*-BuLi was added. The solution remained colorless when stirred over 3 h and on hydrolytic workup led to a quantitative recovery of **1**.

X-ray Structural Characterization. A summary of selected crystallographic data are given in Table 1. Data were collected on an Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The intensities of 3 standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects but not for absorption.

The structures were solved and refined using the SHELXTL\PC[9] package. Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.35P]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms.

The molecules have a crystallographically imposed inversion symmetry. The structure is disordered over two sites with relative occupancies 83:17 (the minor component is indicated with open bonds in Figure 1). The midpoint of the C=C double bond occupies the same inversion center in both components of disorder. The minor component of disorder corresponds to an approximate mirror image of the major component.

Atomic coordinates are given in the Supporting Information, and bond lengths and angles are given in Table 2. Figure 1 shows the disordered molecule and labeling scheme.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council of Canada.

Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for compound **5** (5 pages). Ordering information is given on any current masthead page.

OM9703696

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[8] Several of the 1,1-dimesityl compounds gave unusual ^1H NMR spectral data (including integrations) due to accidental overlapping and restricted rotation.

[9] Sheldrick, G. M., SHELXTL\PC; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.