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New aspects of platinum-catalyzed hydrosilylation of disilylethynes

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Abstract

The platinum-catalyzed hydrosilylations of bis(trimethylsilyl)ethyne and 1-trimethylsilylethynyl-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane at 130–150 °C were investigated using high molecular weight organosilicon hydrides. In addition to the expected adducts, significant amount of unexpected disilylethynes and trisilylethenes were produced. It is suggested that the reaction sequence involves elimination of silanes from the primary adducts to form disilylethynes and subsequent addition reactions to form various trisilylethenes.

Introduction

The platinum-catalyzed hydrosilylation reactions of mono-silylethynes have previously been extensively investigated [1] but there have been few reports on the hydrosilylation of disilylethynes [2–5]. Bock and Seidl [2] and Sheludyakov, et al. [3] obtained only 3–15% yields of hydrosilylation products from the reaction of bis(trimethylsilyl)ethyne with methylchlorosilanes under reflux. Yarosh, et al. [4] and Schmidbaur and Ebenhoech [5] obtained higher yields from the same reaction under more vigorous conditions in ampoules. In contrast, hydrosilylation of monosilylethynes such as 1-trimethylsilyl-1-hexyne proceeded exothermically at room temperature to give the addition product in high yield [6].

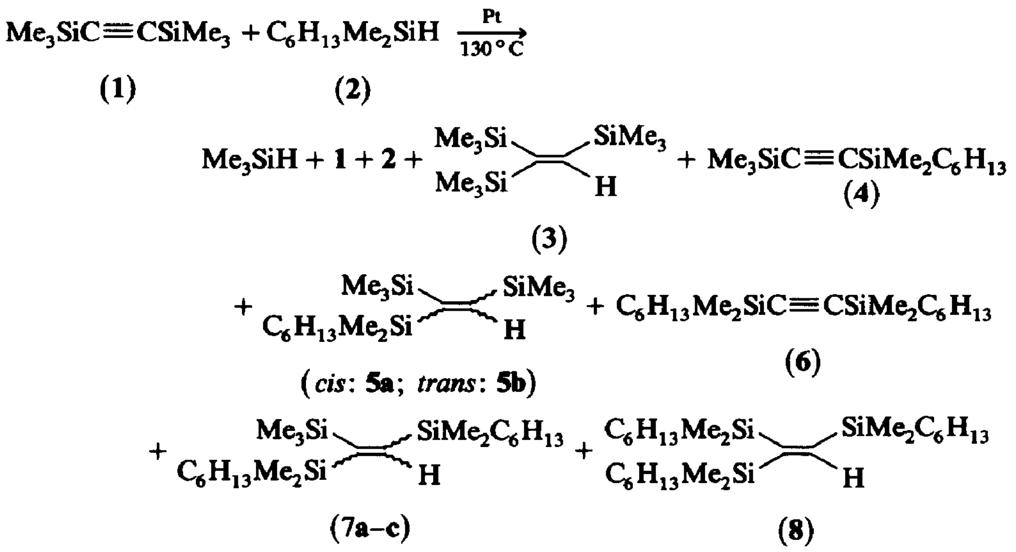
Previous reports on platinum-catalyzed hydrosilylation of mono- or disilylethynes indicated that there is predominantly *syn*-addition to produce disilyl- or trisilylethenes, and there seem to be no reports of formation of by-products from the reactions of disilylethynes.

We have investigated the platinum-catalyzed hydrosilylation of disilylethynes at higher temperatures by using high boiling hydrosilanes, and have found that many unexpected compounds are produced. These are not only isomers of the expected adducts, but also various products derived from elimination and subsequent addition reactions. We describe here these new aspects of the superficially simple platinum-catalyzed hydrosilylation of disilylethynes.

Results and discussion

(1) Hydrosilylation of bis(trimethylsilyl)ethyne (1) with hexyldimethylsilane (2)

The results of the hydrosilylation of **1** with **2** catalyzed by the tetramethyldivinyldisiloxaneplatinum(0) complex [7] (Pt-1 hereafter) at 130 °C are shown in



Scheme 1

Table 1

Hydrosilylation of bis(trimethylsilyl)ethyne with hexyldimethylsilane (130 °C)

Product	Time (h)					
	0	2	4	6	8	23
Me_3SiH	-	0.7	1.3	0.5	0.3	-
1	51.3	35.7	21.0	13.3	8.4	5.7
2	48.7	34.4	18.4	7.9	1.9	0.4
3	-	1.7	3.6	4.3	4.5	5.7
4	-	17.3	24.9	27.4	25.3	25.3
5a	-	12.4	20.2	22.2	21.5	23.8
5b	-	-	0.7	1.4	1.5	3.0
6	-	2.4	7.3	13.9	17.2	21.3
7a	-	-	1.1	1.4	1.5	1.8
7b	-	-	-	-	-	1.8
7c	-	-	2.3	3.7	3.8	5.9
8	-	-	-	-	-	1.8
Total	100.0	104.6	100.8	96.0	85.9	96.5

Each figure shows GC peak area relative to the internal standard (but with the initial total area taken as 100). See Scheme 1 for structures of products.

Scheme 1 and Table 1. The reaction temperature was restricted by the boiling point of **1** (136 °C). Each entry in Table 1 shows a GC peak area relative to that for the internal standard with the total peak area for the initial reaction mixture taken as 100. The total area varied from 100 during the reaction partly because the GC response factors for the various products were, as an approximation, assumed to be equal, but the apparent rise in the total peak area in the period from 8 to 23 h reaction can be attributed to some loss of the internal standard. The order of the compounds appearing in Scheme 1 reflects the sequence of the retention times. For products **5** and **7** the presence of geometric isomers was revealed by the GC profile, and the separate peak areas for the isomers are shown.

The structure of each compound was assigned solely on the basis of GC-mass spectrometric (GC-MS) data, and so in principle the products could be isomers of the probable species shown. Identification of the separate isomers (*cis, trans, gem* forms) for compounds **5** and **7** was not possible, although they showed slightly different fragmentation patterns in their mass spectra. The predominant component (**5a**) in the pair of product **5** was assumed to be the expected *cis* isomer.

As shown, various products were obtained in addition to the expected adduct **5a**. Although further investigation is needed to elucidate the mechanism of the reaction overall, the most reasonable route involves elimination of trimethylsilane from **5a** to give **4**, followed by addition of **2** to **4** to give **7**. The formation of **3** can be accounted for in terms of the addition of trimethylsilane to **1**. This proposed scheme is supported by the appearance of large amounts of **4** in the early stages of the reaction. The detection of trimethylsilane (GC-MS and GC-IR, 2110 and 890 cm^{-1}) in the reaction mixture is further evidence for the proposed mechanism.

The appearance of isomer **5b** near the end of the reaction suggested that it was formed from addition of trimethylsilane to compound **4**. The formation of three isomers of **7** indicated that the products must have been formed from both **4** (by addition of **2**) and **6** (by addition of trimethylsilane).

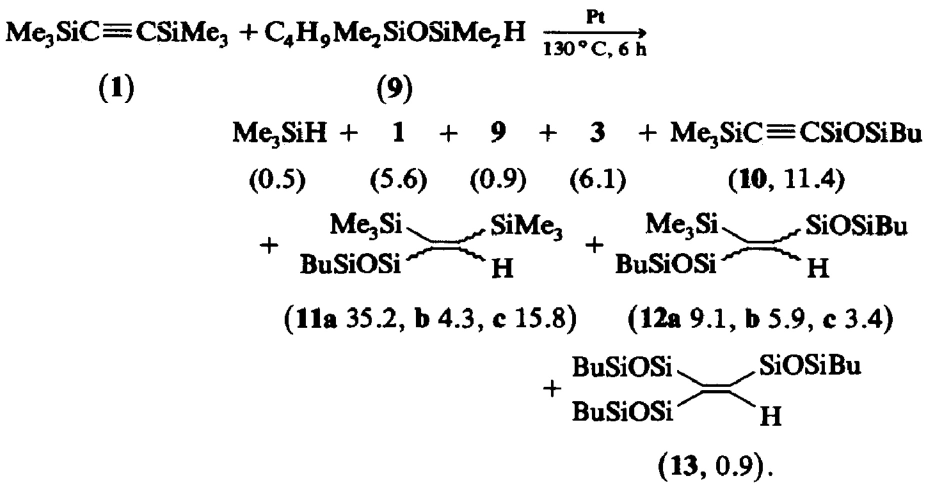
In order to confirm this proposed scheme a mixture of **5a** and **5b** was isolated and heated to 150 °C with the Pt-**1** catalyst. Disilylethynes **1**, **4** and **6** were formed, indicating that elimination reactions had taken place. Further detailed investigations are in progress.

(2) Hydrosilylation of bis(trimethylsilyl)ethyne (1) with 1-butyl-1,1,3,3-tetramethyldisiloxane (9)

The results of hydrosilylation of **1** with hydridosiloxane (**9**) catalyzed by Pt-**1** are shown in Scheme 2 (6 h at 130 °C). The figures are the relative GC peak areas (i.e. total area = 100).

The results are somewhat different from those shown in Table 1 and Scheme 1. Bis(disiloxanyl)ethyne was not detected by GC-MS, though a small peak ($< 0.5\%$) between **11** and **12** was detected by GC alone. In addition, three isomers were detected for the adduct **11**, whereas only two isomers were found in the reaction of $C_6H_{13}Me_2SiH$.

When the same reaction was carried out with Speier's catalyst (H_2PtCl_6 in 2-propanol), identical results were obtained, showing that the elimination-addition reactions are not unique to the Pt-**1** catalyst.

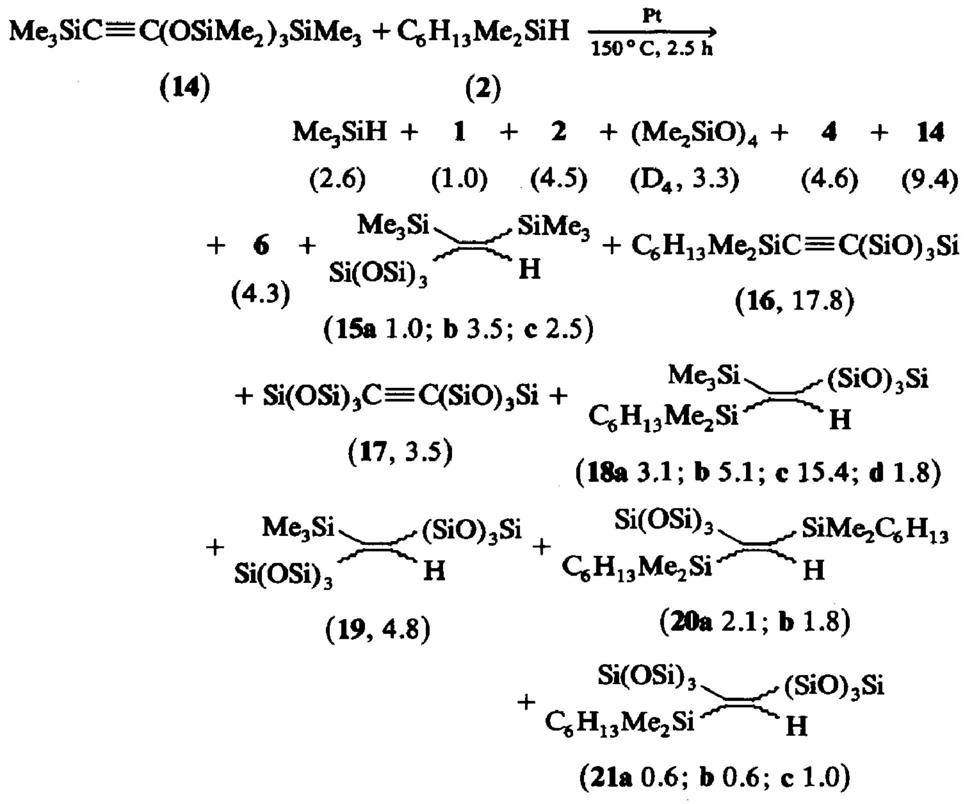


(BuSiOSi = $C_4H_9Me_2SiOMe_2Si$; each figure shows GC peak area %)

Scheme 2

(3) Hydrosilylation of unsymmetrical disilylethyne with hexyldimethylsilane (2)

The reaction between 1-trimethylsilylethynyl-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (14) and hexyldimethylsilane (2) in the presence of Pt-1 catalyst was carried



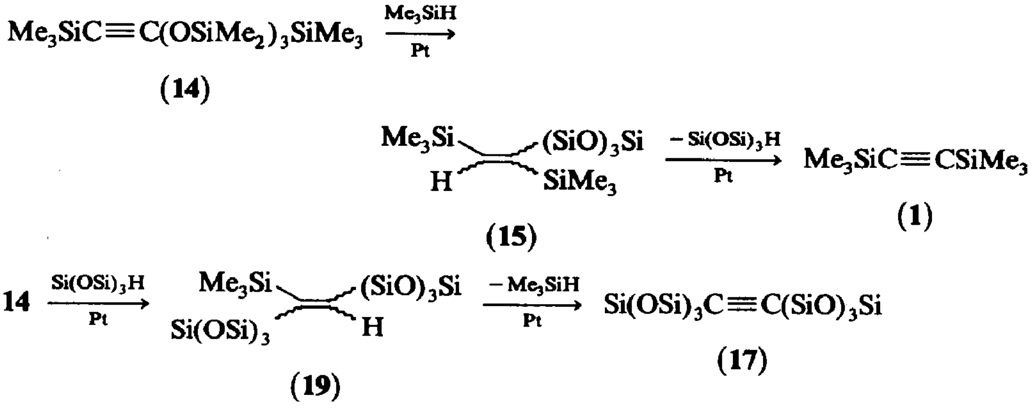
($Si(OSi)_3 = Me_3Si(OSiMe_2)_3$; each figure shows GC peak area %).

Scheme 3

out for 2.5 h at 150 °C. More complicated behaviour was observed because of the asymmetry of the ethyne and the decomposition of the siloxane (to form D_4), and the results are shown in Scheme 3.

It can be seen that almost all possible compounds were produced. When the starting ethyne (**14**) was heated with Pt-1 alone under the same conditions no reaction was detected, ruling out the possibility that silyl group redistribution reactions give rise to the ethynes in Scheme 3.

The formation of **17** can be accounted for in terms of the following reaction sequence:



$(Si(OSi)_3 = Me_3(OSiMe_2)_3)$

Experimental

Measurements

GC analyses were performed with a Hewlett Packard 5890 gas chromatograph equipped with FID and an HP-1 glass capillary column. Peak areas were determined with a Hewlett Packard 3392 integrator. GC-MS data were obtained with a Hewlett Packard 5995 gas chromatograph/mass spectrometer. ^1H and ^{29}Si NMR spectra were recorded on a Bruker AC-P 250 spectrometer. (250 MHz for ^1H; room temperature; solvent: $CDCl_3$; reference: $CHCl_3$ (^1H), Me_4Si (^{29}Si).)

Materials

Bis(trimethylsilyl)ethyne (**1**) (Aldrich) was distilled over CaH_2. Tetramethyldivinyldisiloxaneplatinum(0) complex (Pt-1) was prepared as previously described [8].

Hexamethylcyclotrisiloxane (D_3) (Dow Corning Toray Silicone) was distilled, and its solution in anhydrous tetrahydrofuran (THF) was kept over activated molecular sieves. Chlorosilanes (Dow Corning) were distilled from Mg. Butyllithium in hexane and magnesium (Aldrich) were used as purchased. Other reagents (Aldrich) were freshly distilled before use. THF was distilled from a purple solution of THF/K/benzophenone.

Hexyldimethylsilane (2)

A 1 l flask fitted with a reflux condenser and dropping funnel was charged with THF (300 ml) and magnesium turnings (8.0 g, 0.33 mol). 1-Bromohexane (49.5 g, 0.3

mol) was slowly added with cooling (water bath). When addition was complete, the mixture was set aside at room temperature for 2 h. Dimethylchlorosilane (35 g, 0.37 mol) was added dropwise with cooling (ice bath), and the mixture was then allowed to warm to room temperature and poured into saturated aqueous NH_4Cl (500 ml). The organic layer was washed with saturated NH_4Cl solution three times and dried over Na_2SO_4. The fraction boiling at 149–150 °C was collected. Purity: 99.2% by GC. Yield: 82% based on 1-bromohexane.

^{1}H NMR: δ 0.06 (d, 6H, J 3.6); 0.58 (m, 2H); 0.88 (m, 3H); 1.28–1.33 (m, 8H); 3.86 (m, 1H). ^{29}Si NMR: $\delta - 13.17$. MS: m/e (relative abundance) 144 (1.9) M^+; 143 (5) $M^+ -$ H; 129 (19) $M^+ -$ methyl; 59 (100) $M^+ -$ hexyl.

1-Butyl-1,1,3,3-tetramethyldisiloxane (9)

A cooled (ice bath) 250 ml Schlenk flask, fitted with a dropping funnel, was charged with a THF (30 ml) solution of D_3 (25 g, 0.112 mol). Butyllithium in hexane (2.81 M, 120 ml, 0.336 mol) was added slowly with cooling. When addition was complete the mixture was allowed to warm to room temperature, transferred to a dropping funnel, and added dropwise to dimethylchlorosilane (40 g, 0.423 mol) with ice cooling. The solution was filtered and the disiloxane was isolated by fractional distillation (b.p. 87–90 °C at 88 mmHg). Purity: 99.5%. Yield: 55% based on butyllithium.

^{1}H NMR: δ 0.06 (s, 6H); 0.16 (d, 6H, J 2.7); 0.51–0.58 (m, 2H); 0.89 (t, 3H, J 6.9); 1.27–1.36 (m, 4H); 4.70 (sept, 1H, J 2.7). ^{29}Si NMR: $\delta - 7.0$; 9.9. MS: 190 (1.4) M^+; 189 (1.0) M^+-H; 175 (15) M^+-methyl; 133 (100) $M^+ -$ butyl.

1-Trimethylsilylethynyl-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (14)

The preparation of this siloxane will be described elsewhere [9]. purity: 98.5%.

^{29}Si NMR: $\delta - 21.1$; -20.8; -19.9; -18.8; 7.3. MS: 377 (81) $M^+ -$ methyl; 155 (21) $Me_3SiC{\equiv}CSiMe_2{}^+$.

Hydrosilylation

Hydrosilylation reactions were carried out as follows. Equimolar proportions of the disilylethyne and the silicon hydride, along with the platinum complex [7] (20–60 ppm by weight of platinum) and tetradecane (internal standard) were placed in a 10 ml, pear-shaped flask. The flask was not purged with nitrogen prior to its connection to a gas manifold in which a constant nitrogen flow was maintained. The flask was immersed in an oil bath held at the chosen temperature, and the progress of the reaction was monitored by GC. Each product was identified by GC-MS (and in one case by GC-IR).

GC-MS data for products

m/e (relative abundance, %).

3: 244 (33) M^+; 229 (17)$M^+ -$ methyl; 171 (19) $M^+ -$ trimethylsilyl; 156 (100). **4**: 240 (0.3) M^+; 225 (13) $M^+ -$ methyl; 155 (97) $M^+ -$ hexyl; 156 (86) $M^+ + 1 -$ hexyl; 73 (100). **5**: 299 (3) $M^+ -$ methyl; 229 (0.7) $M^+ -$ hexyl; 230 (65) $M^+ + 1 -$ hexyl; 59 (100). **6**: 295 (0.2) $M^+ -$ methyl; 225 (17) $M^+ -$ hexyl; 143 (34) hexyldimethylsilyl$^+$; 141 (67); 73 (100). **7**: 369 (0.5) $M^+ -$ methyl; 300 (5) $M^+ + 1 -$ hexyl; 143 (17) hexyldimethylsilyl$^+$; 73 (61); 59 (100). **8**: 370 (2) $M^+ + 1 -$ hexyl; 143 (9) hexyldimethylsilyl$^+$; 73 (26); 59 (100) **10**: 271 (4) $M^+ -$ methyl; 229 (100) $M^+ -$

butyl; 215 (90). **11**: 360 (5) M^+; 345 (5) M^+-methyl; 303 (2) M^+-butyl; 156 (100); 73 (88). **12**: 476 (2) M^+; 461 (3) M^+- methyl; 419 (2) M^+- butyl; 133 (100); 73 (77). **13**: 592 (2) M^+; 577 (2) M^+-methyl; 535 (2) M^+-butyl; 133 (100); 73 (75). **15**: 451 (1) M^+-methyl; 295 (60) $Me_3Si(OMe_2Si)_3{}^+$; 156 (36); 73 (100). **16**: 447 (31) M^+-methyl; 377 (5) M^+-hexyl; 363 (81); 207 (95); 73 (100). **17**: 599 (2) M^+-methyl; 295 (77) $Me_3Si(OMe_2Si)_3{}^+$; 207 (100); 73 (34). **18**: 521 (3) M^+-methyl; 451 (6) M^+-hexyl; 452 (10) $M^+ + 1 -$ hexyl; 221 (88); 207 (100). **19** 673 (2) M^+-methyl; 295 (70) $Me_3Si(OMe_2Si)_3{}^+$; 207 (100). **20**: 591 (1) M^+-methyl; 521 (4) M^+-hexyl; 295 (13) $Me_3Si(OMe_2Si)_3{}^+$; 207 (43); 59 (100). **21**: 743 (0.5) M^+-methyl; 673 (1) M^+-hexyl; 295 (7) $Me_3Si(OMe_2Si)_3{}^+$; 207 (25); 73 (100). Trimethylsilane: 74 (3) M^+; 73 (46) M^+-H; 59 (100) M^+-methyl. D_4: 281 (8) M^+-methyl; 207 (62); 73 (100).

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