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New aspects of platinum-catalyzed hydrosilylation of disilylethynes

II. Effects of oxygen and temperature

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Abstract

It has been found that oxygen can markedly influence the outcome of the products from platinum-catalyzed reactions of $Me_3SiC{\equiv}CSiMe_3$ with n-$C_6H_{13}Me_2SiH$ or n-$BuMe_2SiOSiMe_2H$. Under dry air at 130 °C, bis(trimethylsilyl) ethyne and hexyldimethylsilane apparently underwent silyl group exchange reactions to give trimethylsilane, hydrosilylation being a minor reaction. Products derived from oxidation reactions of SiH groups were also detected. With n-$BuMe_2SiOSiMeH$ hydrosilylation was a major reaction. With both hydrides, higher yields of normal adducts were obtained under nitrogen at 130 °C than under dry air, though significant amounts of disilylethynes and isomers of the adducts were still produced. Under nitrogen at low temperature (90 °C), the normal *cis* adducts were obtained in high yields, and these were isolated. Their structures were confirmed by selectively decoupled ^{29}Si NMR.

Introduction

We previously reported that significant amounts of unexpected trisilylethenes and disilylethynes were produced during the platinum-catalyzed hydrosilylation of disilylethynes with high boiling hydrosilanes [1]. The proposed mechanism for the formation of various products involved a combination of elimination of silanes from the primary adducts and subsequent addition of silanes to disilylethynes.

It is known that oxygen is needed for hydrosilylation to take place [2]. The reactions described in the previous report were carried out under an atmosphere of

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nitrogen containing a trace of air. Further investigation showed that the product distributions were affected by the concentration of air in the nitrogen atmosphere over the reaction mixture. We thus decided to examine the outcome of reactions carried out with or without exclusion of air, in order to determine the effect of oxygen.

The effect of reaction temperature has also been investigated, and it is found that normal addition reactions, giving *cis* products, predominated at low temperature (90 ° C). These *cis* products have been isolated, and their structures confirmed by the use of selectively decoupled ^{29}Si NMR data.

Results and discussion

The products mentioned below, with the numbers assigned to them, are shown in Table 1. The *cis–trans* nomenclature (based on the dispositions of the two trimethylsilyl groups) is used for convenience. Unless otherwise stated, the identities of the

Table 1

Compounds mentioned

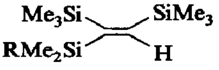
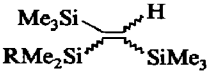
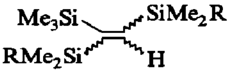
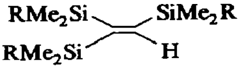
Structure	Compound no.		
	R = Me	R = n-C_6H_{13}	R = n-$C_4H_9Me_2SiO$
$RMe_2SiC{\equiv}CSiMe_3$	**1**	**5**	**14**
RMe_2SiH	**2**	**6**	**15**
 (*cis*)	**3**	**7a**	**16a**
 (*trans*, *gem*)	–	**7b** **7c**	**16b** **16c**
$RMe_2SiC{\equiv}CSiMe_2R$	–	**8**	**17**
 (3 isomers)	–	**9a** **9b** **9c**	**18a** **18b** **18c**
	–	**10**	**19**
$RMe_2SiOSiMe_3$	**4**	**11**	**20**
$RMe_2SiOSiMe_2R$	–	**12**	**21**
	–	**13**	**22**

Table 2

Hydrosilylation of bis(trimethylsilyl)ethyne with hexyldimethylsilane [a]

Run	1	2	3	4
Pt ($\times 10^{-6}$mol) [b]	70	44	44	35
Temp (°C)	90	130	130	130
Time (h)	24	7	7	8
atmosphere	N_2	N_2	air	air
pressure	open	open	open	sealed
Weight loss (%)	n.a. [c]	6.4	17.5	6.8
GC area% [d]				
2	–	2.3	0.7	5.4
1	15.7	13.0	16.1	11.2
6	19.0	10.1	1.7	12.8
3	8.4	4.0	3.8	13.5
5	7.3	17.7	32.7	19.3
7a	49.6	38.6	10.1	19.5
7b	–	1.2	6.9	3.8
7c	–	0.8	0.9	–
8	–	6.6	16.7	7.5
9a	–	–	1.7	1.6
9b	–	1.7	1.1	0.8
9c	–	3.7	1.7	3.3
10	–	–	–	0.4
4	–	–	0.2	–
11	–	–	1.1	–
12	–	–	1.0	–
13	–	–	2.2	–

[a] See Table 1 for structures of compounds. [b] To 1 mol of bis(trimethylsilyl)ethyne. [c] Not measured. [d] Total area = 100.

products are reasonable speculations based on gas chromatography-mass spectrometric (GC-MS) data.

I. Hydrosilylation of bis(trimethylsilyl)ethyne with hexyldimethylsilane

The results of the hydrosilylation reactions of bis(trimethylsilyl)ethyne (**1**) with hexyldimethylsilane (**6**) at various temperatures and either under air or nitrogen are listed in Table 2. It can be seen that at 90°C (run 1) under nitrogen the reaction proceeded sluggishly, as shown by the large amount of unchanged **1** and **6** in spite of the longer reaction time and the use of a higher concentration of platinum than in run 2. However, the normal adduct **7a** was obtained as a major product, with little silyl group redistribution.

Runs 2 and 3 show the effects of the presence of oxygen. With dry air passing through the system (run 3), the normal adduct **7a** was no longer a major product. The volatile material, the amount of which is indicated by the weight loss (17.5%), consisted of trimethylsilane (**2**, 99% by GC) and hexamethyldisiloxane (**4**, 1%). The structure of **2** was confirmed by ^{1}H NMR spectroscopy. From the weight loss data it was calculated that about 37% of trimethylsilyl groups were involved in the production of **2**, which evaporated from the reaction vessel. This implies that the molar ratio of trimethylsilyl to hexyldimethylsilyl groups ($Me_3Si/HexMe_2Si$) decreased from 2/1 to 1.26/1 in the reaction mixture. The observed $Me_3Si/HexMe_2Si$

ratio was 1.21/1, based on the assumption that the area of the GC peak for each compound is proportional to its molar concentration.

The formation of **2** was previously [1] considered to involve elimination reaction from initially formed adducts. However, in the present case, this product is much more likely to arise from silyl group exchange [3*]:

$$Me_3SiC{\equiv}CSiMe_3 + RMe_2SiH \xrightarrow{Pt} Me_3SiC{\equiv}CSiMe_2R + Me_3SiH$$

The reason why the exchange reaction becomes predominant in the presence of oxygen is not clear. The product distributions will be determined by the competition between the exchange (substitution), and the addition reactions rather than by the classical Chalk–Harrod mechanism [2]. Steric hindrance, in the case of bis(trimethylsilyl)ethyne, for example, would slow down the addition reaction, allowing the exchange reaction to become more significant. The question of whether oxygen is enhancing the exchange reactions or suppressing the addition reactions cannot be answered at present.

In addition to the ethynes and ethenes, disiloxanes (**11**, **12**) and the disilylethene (**13**) were produced under dry air. The formation of disiloxanes can be attributed to oxidation of SiH to SiOH groups, followed by a dehydrogenation reaction between silanol and SiH groups [4,5]. The formation of the silylethene can be attributed to addition to **5** of the hydrogen produced in this way. Hydrogen addition to **1** would also be expected, since the amount of **1** was comparable with that of **5**, but the relevant addition product, bis(trimethylsilyl)ethane, was not in fact, detected by GC, probably due to overlap with the peak from **1**.

Reaction in a sealed ampoule (run 4) gave a different product distribution from those carried out under atmospheric pressure. Significantly larger amounts of **2** and **3** were obtained than in run 3. The absence of disiloxanes (**11**, **12**) and the disilylethene **13**, even though the reaction was carried out in the presence of oxygen, implies that large partial pressure of oxygen in the atmosphere is needed for the oxidation reaction.

Product **7a** was isolated from run 1 by distillation (overall yield: 47%), and its structure confirmed by elemental analysis and selectively decoupled (decoupled with aliphatic proton and coupled with olefinic proton) ^{29}Si NMR spectroscopy. The data are listed in the experimental section. Coupling constants and chemical shifts are in good agreement with the data given by Schmidbauer and Ebenhoech for tris(trimethylsilyl)ethene [6].

II. Hydrosilylation of bis(trimethylsilyl)ethyne and 1-n-butyl-1,1,3,3-tetramethyldisiloxane

The results of hydrosilylation of **1** with the hydrodisiloxane **15** are listed in Table 3.

Under nitrogen, more than an 80% yield of the normal adduct **16a** was obtained when the reaction was carried out at 90 °C (run 5), compared with the 50% yield of normal adduct obtained from **6** under similar conditions in run 1. It is known that electron withdrawing groups attached to hydrosilane increase the ease of hydrosilylation [7].

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[*] Reference number with asterisk indicates a note in the list of references.

Table 3

Hydrosilylation of bis(trimethylsilyl)ethyne with 1-n-butyl-1,1,3,3-tetramethyldisiloxane [a]

Run	5	6	7	8
Pt ($\times 10^{-6}$mol) [b]	70	44	44	35
Temp (°C)	90	130	130	30
Time (h)	21	7	7	8
atmosphere	N_2	N_2	air	air
pressure	open	open	open	sealed
Weight loss (%)	n.a. [c]	4.2	7.2	< 0.4
GC area % [d]				
2	–	1.1	–	0.6
1	1.9	6.5	12.1	2.0
15	–	0.5	–	0.3
3	6.8	7.7	4.6	14.0
14	–	10.3	15.0	2.8
16a	83.7	46.5	22.1	39.4
16b	2.0	4.6	2.1	9.0
16c	–	5.5	17.2	8.5
17	–	–	0.5	–
18a	4.5	9.3	4.0	9.9
18b	–	4.8	3.4	6.3
18c	–	1.5	3.4	3.8
19	–	0.7	1.2	0.9
4	–	–	0.6	–
20	–	–	2.0	–
21	–	–	3.3	–
22	–	–	4.5	–

[a] See Table 1 for structures of compounds. [b] To 1 mol of bis(trimethylsilyl)ethyne. [c] Not measured. [d] Total area = 100.

The differences in product distributions between runs 6 and 7 are not as great as those between runs 2 and 3. Ethyne species were more abundant under air atmosphere but the difference was not large. The large amount of **16c** under air can be taken as an indication of initial formation of a large amount of **14** (which subsequently undergoes addition of **2**).

In run 7, the calculated ratio $Me_3Si/BuMe_2SiOMe_2Si$ from the weight loss was 1.65/1 and the observed one was 1.67/1.

With the reaction performed in a sealed ampoule (run 8), only a very small amount of **2** was detected by GC. Weight loss from the reaction mixture was less than 0.4%. These observations can be regarded as indications of the ease of trimethylsilane addition to **14**, which is reflected in the amount of the isomers (**16b**, c), of the adduct. The amount of **3** (14.0%) is very close to that found in run 4 (13.5%), and so addition to **1** is not important in this case. It can be concluded that the presence of the siloxy group induces facile addition reactions when it is attached to either the silylethynyl groups or the SiH groups. The absence, or presence of only very small amounts of **17** in runs 5–8 also supports the suggestion about the ease of addition.

Cis compound **16a** was isolated by distillation from the reaction mixture from run 5 (overall yield: 77%) and its structure confirmed by elemental analysis and selectively decoupled ^{29}Si NMR. Data are listed in the experimental section.

Experimental

Measurements

GC analyses were performed with a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and an HP-1 glass capillary column (25m). Peak areas were determined with a Hewlett Packard 3392 integrator. GC-MS data were obtained using a Hewlett Packard 5995 gas chromatograph/mass spectrometer. ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AC-P 250 spectrometer. [250.13 MHz for ^{1}H; room temperature; solvent: $CDCl_3$; reference: $CHCl_3$ (^{1}H), Me_4Si (^{29}Si)]

Materials

Bis(trimethylsilyl)ethyne (**1**) (Aldrich) was distilled over CaH_2. Platinum(0)-tetramethyldivinyldisiloxane complex (Pt-**1**) was prepared as described previously [8], as were hexyldimethylsilane (**6**) and 1-n-butyl-1,1,3,3-tetramethyldisiloxane (**15**) [1].

Hydrosilylation under nitrogen

In a pear-shaped flask equipped with a reflux condenser, **1** (10 g, 59 mmol for runs 1 or 5, 1 g, 5.9 mmol for runs 2 and 6), was placed with the hydrosilane (equimolar), and the Pt-**1** catalyst (amount shown in Tables 2 and 3). The flask was evacuated to 0.1 mmHg with cooling (liquid N_2), then high-purity grade nitrogen was admitted, and the flask was warmed to 30 ° C. This procedure was repeated 4 times. The flask was then kept in an oil bath at the desired temperature for a specific period (shown in Tables 2 and 3). Weight loss was measured after the mixture had been cooled to room temperature, and the mixture was then analyzed by GC.

Hydrosilylation under dry air

The reaction mixture was made up as described above (1 g scale). The flask, immersed in the oil bath, was fitted with a reflux condenser leading to a cold trap (−78 ° C). Air was supplied very slowly through a $CaCl_2$ drying tube so that fresh air flowed continuously over the reaction mixture. The outcome was investigated by the procedure described above.

Hydrosilylation in sealed ampoules

The reaction mixture was made up as before (2 g scale) and placed in a 10 ml ampoule. The air in the ampoule was allowed to remain and the ampoule was sealed, and then immersed in the oil bath for 8 h. Weight loss was measured after 24 hours at room temperature, and the mixture analyzed by GC.

Isolation of cis compounds

Compounds **7a** and **16a** were isolated by distillation and the ^{29}Si NMR spectra with coupling to the olefinic proton and decoupling to the aliphatic proton were recorded. Distillations were carried out after addition of 1,2-bis(diphenylphosphino)ethane to prevent redistribution reactions catalyzed by platinum.

7a: b.p. 88–89 ° C/0.04 mmHg. Found: C, 60.95; H, 12.56. $C_{16}H_{38}Si_3$ calcd.: C, 61.06; H, 12.17%. **16a**: b.p. 87–89 ° C/0.02 mmHg. Found: C, 53.32; H, 11.56. calcd.: C, 53.26; H, 11.17%.

^{29}Si NMR data:

		Me$_3$*Si* *trans* to H	Me$_3$*Si* *gem* to H	RMe$_2$*Si* *cis* to H
7a	δ (ppm)	−8.69	−11.62	0.18
	J (Hz)	20.38	4.51	15.52
16a	δ (ppm)	−9.26	−11.10	−2.22
	J (Hz)	20.14	4.84	16.53
3 (lit. data [6])				
	δ (ppm)	−8.32	−11.29	−0.95
	J (Hz)	22.01	4.89	16.63

NMR data for other compounds

Hexyldimethylsilyl-trimethylsilylethyne (**5**) and 1-n-butyl-3-(trimethylsilylethynyl)-1,1,3,3-tetramethyldisiloxane (**14**) were obtained as mixtures with tris(trimethylsilyl)ethene (**3**). ^{29}Si{^{1}H} NMR spectra of **5** and **14** were obtained by subtracting signals due to **3**. **5**: δ −17.17 (HexMe$_2$*Si*); −19.23 (Me$_3$*Si*). **14**: δ 10.56 BuMe$_2$*Si*); −18.82 (Me$_3$*Si*); −20.70 (OMe$_2$*Si*C≡C).

GC-MS data of products

Data for compounds **1–3**, **5–10** and **13–16** were given previously [1]. *m/e* (relative abundance): **4**: 147 (100) M^+ − methyl; 73 (30). **11**: 217 (20) M^+ − methyl; 147 (11) M^+ − hexyl; 148 (58) M^+ − hexyl + 1, 73 (100). **12**: 287 (4) M^+ − methyl; 217 (23) M^+ − hexyl; 133 (100). **13**: 242 (0.7) M^+; 227 (1) M^+ − methyl; 157 (100) M^+ − hexyl; 158 (28) M^+ − hexyl + 1. **17**: 345 (3) M^+ − butyl; 290 (90); 144 (100). **20**: 263 (8) M^+ − methyl; 221 (30) M^+ − butyl; 73 (100). **21**: 379 (2) M^+ − methyl; 337 (18) M^+ − butyl; 115 (32); 73 (100). **22**: 273 (13) M^+ − methyl; 231 (10) M^+ − butyl; 133 (43); 73 (100).

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