Platinum-catalysed Isomerisations of 1,2-Disilylhex-1-enes‡

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(*E*)-2-Butyldimethylsilyl-1-trimethylsilylhex-1-ene **1** and (*E*)-1-butyldimethylsilyl-2-trimethylsilylhex-1-ene **4** undergo platinum-catalysed isomerisation reactions with migrations of carbon–carbon double bonds to form (*E*)- and (*Z*)-1,2-disilylhex-2-enes at elevated temperatures. The reactions proceed under nitrogen but not under dry air. The structures of the products were determined using ^{1}H, ^{29}Si, two-dimensional ^{1}H-^{29}Si, and selectively decoupled ^{29}Si NMR techniques.

Transition-metal-catalysd isomerisation or rearrangement of olefins has previously been extensively investigated.[1] However, there have been no reports on platinum-catalysed isomerisation of 1,2-disilylalkenes.

We have recently reported that trisilylethenes such as (*E*)-1-hexyldimethylsilyl-1,2-bis(trimethylsilyl)ethene undergo platinum-catalysed isomerisation and redistribution reactions at elevated temperatures.[2] The major products were the (*Z*) isomer and bis(hexyldimethylsilyl)trimethylsilylethenes. The isomerisation and redistribution reactions were explained by an elimination–addition sequence of hydrosilanes promoted by platinum. We also reported that the product distributions of the isomerisation–redistribution reactions are affected by the atmosphere (nitrogen *vs.* air) over the reaction mixture.

We have further investigated platinum-catalysed isomerisation reactions of silylolefins and found that 1,2-disilylhex-1-enes undergo isomerisation reactions with migration of carbon–carbon double bonds. These isomerisations took place under nitrogen but not under dry air.

Results and Discussion

Rearrangement Reactions.—(*E*)-2-Butyldimethylsilyl-1-trimethylsilylhex-1-ene **1** underwent isomerisation in the presence of platinum catalysts at elevated temperatures under a nitrogen atmosphere to produce (*Z*)- and (*E*)-2-butyldimethylsilyl-1-trimethylsilylhex-2-ene, **2** and **3**. Similarly (*E*)-1-butyldimethylsilyl-2-trimethylsilylhex-1-ene **4** produced (*Z*)- and (*E*)-1-butyldimethylsilyl-2-trimethylsilylhex-2-ene, **5** and **6**. The catalyst used was tris(tetramethyldivinyldisiloxane)diplatinum(0) or Speier's catalyst ($H_2PtCl_6{\cdot}6H_2O$ in propan-2-ol) (Scheme 1).

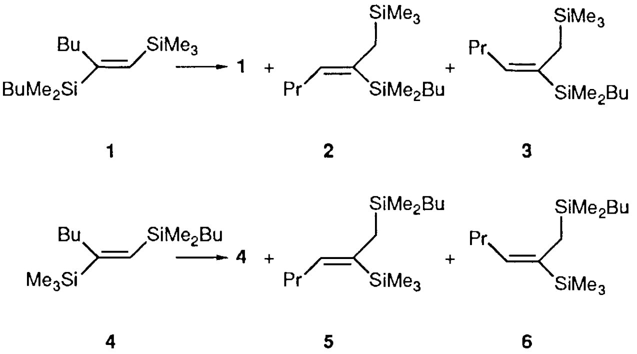
The results are summarised in Table 1 where the figures denote GLC area percentages without calibration. Little weight loss was observed after the reactions indicating that there was no decomposition of the starting compound. The determination of structures of the products is described in the later part of this paper. No detectable reactions took place under dry air or in the absence of platinum catalysts even at 130 °C.

As shown in runs 1–3 in Table 1, disilylhex-2-ene **2** is the major product from **1**. The reaction was faster at 110 than at 85 °C (compare Figs. 1 and 2). Comparison of runs 2 and 3 indicates that there are no significant differences between the disiloxaneplatinum complex and Speier's catalyst, suggesting that the reaction can be catalysed by any homogeneous platinum catalyst.

Table 1 Isomerisations of disilylhex-1-enes **1** and **4** catalysed by platinum[a]

Run	1	2	3	4
Starting compound	**1**	**1**	**1**	**4**
Catalyst	*b*	*b*	Speier's	*b*
Concentration (μmol mol^{-1})	50	50	100	50
T/°C	85	110	110	130
t/h	4	2	2	2
Isomerisation results [GLC area (%)]				
Compound **1** or **4**	46	20	23	42
Compound **2** or **5**	43	54	57	48
Compound **3** or **6**	8	23	17	8

[a] See text for the structure of each compound. [b] Disiloxaneplatinum complex.



Scheme 1

Harrod and Chalk[3] reported double-bond migrations of *n*-olefins catalysed by homogeneous platinum complexes. However, cocatalysts such as ethanol were necessary for migration to take place. Cramer and Lindsey[4] proposed a mechanism with the formation of platinum hydride as an important step for migration. In their reaction schemes, however, cocatalysts such as acids or $SnCl_2 + H_2$ were needed to effect isomerisation. In our case no cocatalysts were added and no proton source was present. It is likely that insertion of platinum into a Si–C bond is a key step of the reaction leading to formation of intermediate **7** or **8** in Scheme 2. The intermediates thus formed undergo hydride transfer from the allyl carbon, assisted by platinum, to give the isomerised products.

To show that the isomerisation is unique to olefins containing silyl groups, dec-1-ene was mixed with the platinum catalyst and

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‡ *Non-SI unit employed:* bar = 10^5 Pa.

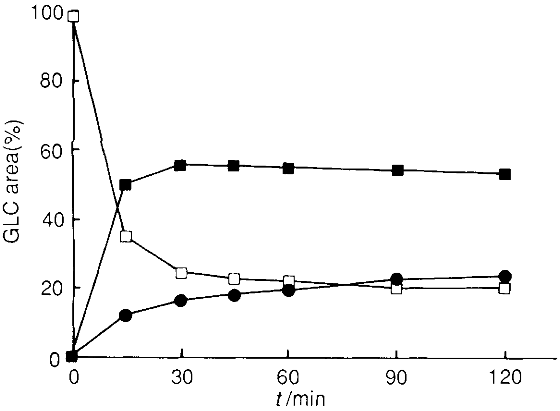


Fig. 1 Platinum-catalysed isomerisation reaction of disilylhex-1-ene **1** at 110 °C. Starting compound: **1** (□), Products: **2** (■) and **3** (●)

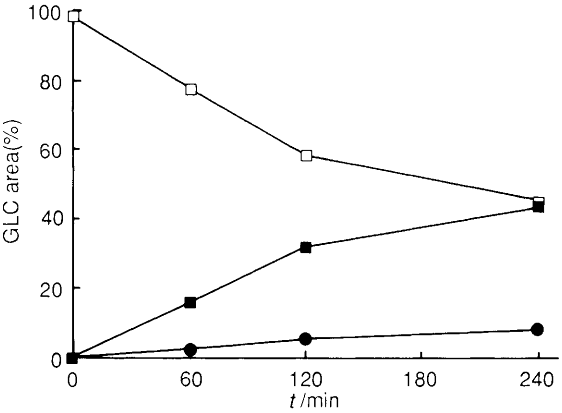


Fig. 2 Platinum-catalysed isomerisation reaction of disilylhex-1-ene **1** at 85 °C. Symbols as in Fig. 1

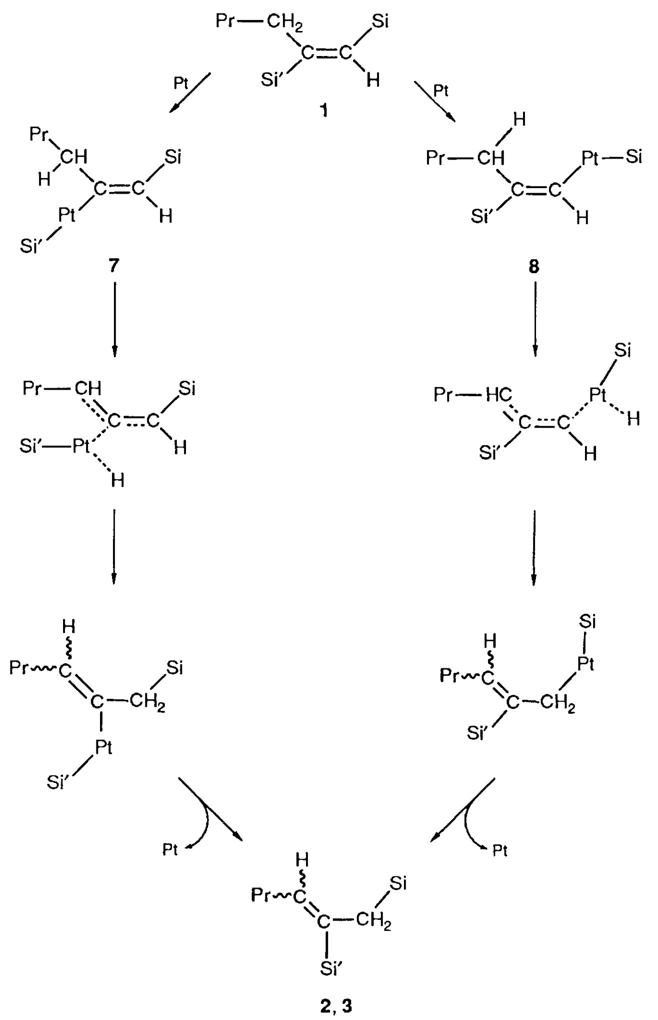
heated at 110 °C for 2 h under nitrogen. No detectable reaction was observed indicating that a simple π-allyl isomerisation mechanism is not operational.

The result of run 4 shows that the isomerisation is not restricted to the specific structure of **1** but is general to disilylolefins.

The reason that isomerisation did not take place under dry air is not clear. Further investigation is needed to elucidate the mechanism of inhibition by oxygen.

Determination of Structures.—The structures of the products were determined using NMR techniques on the product mixtures, because it was difficult to isolate each product due to closeness in boiling points and GLC retention times. As the two products from the reaction using compound **1** had close GLC retention times and similar GLC–MS data to those of **1**, it was reasonably speculated that they were isomers of **1**. It is unlikely that alkyl groups attached to silicon atoms underwent exchange or other alterations under the reaction conditions.

Proton NMR spectra of the starting compound **1** and that of the product mixture are shown in Fig. 3. The two new triplets (δ 5.8 and 5.5, J 7 Hz) indicate that the protons are attached to sp^2 carbons geminal to CH_2 groups. Protons of the geminal CH_2 groups resonate as two quartets (δ 2.0 and 1.9, J 7 Hz) indicating that they are attached to another CH_2 group. The two new singlets (δ 1.62 and 1.51) strongly suggest the presence of two kinds of $SiCH_2C=C$ protons.



Scheme 2

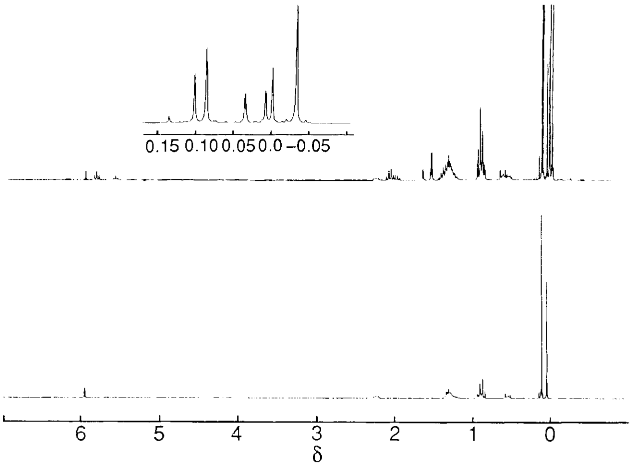


Fig. 3 Proton NMR spectrum of starting compound **1** (lower) and the reaction mixture of run 2 (20% **1**, 54% **2** and 23% **3**) (upper)

Each singlet in the SiMe region (δ 0.10 to −0.03) could be assigned to a $SiMe_3$ or $SiMe_2Bu$ group of each compound in the product mixture by comparison of the integral ratios and GLC areas. The assignments thus made are listed in Table 2. By the use of ^1H-^{29}Si two-dimensional NMR spectroscopy (Fig. 4) it was possible to assign each ^{29}Si peak to each silicon atom (Me_3Si or $BuMe_2Si$) of each species. These assignments are listed in Table 2. Selectively decoupled ^{29}Si NMR spectra, with the decoupler frequency centred on the aliphatic proton, were taken using various decoupling powers. In the resulting spectra all ^{29}Si resonances showed residual coupling constants with the olefinic protons (listed in Table 2) except those at δ 0.54 and 0.83 which did not show any measurable coupling. This indicates that the two silicon atoms are not attached to an sp^2 carbon. Because of the low concentration of the olefinic protons and the high concentration of the aliphatic protons, it was difficult to

Table 2 NMR data for isomerisation products[a]

Compound	Group	δ_H of SiMe	δ_{Si}	J(Si-H)[b]/Hz
1	Me_3Si	0.10	−12.32	5
	$BuMe_2Si$	0.03	−4.30	9
2	Me_3Si	−0.03	0.54	None
	$BuMe_2Si$	0.08	−6.11	12
3	Me_3Si	0.00	0.83	None
	$BuMe_2Si$	0.01	−3.73	8
4	Me_3Si	0.06	−5.54	9
	$BuMe_2Si$	0.09	−10.72	4
5	Me_3Si	0.11	−7.60	11
	$BuMe_2Si$	−0.06	1.60	None
6	Me_3Si	0.03	−4.84	n.a.[c]
	$BuMe_2Si$	−0.03	1.75	n.a.[c]

[a] See text for the structure of each compound. [b] Residual coupling constants to olefinic protons. [c] Not available because of baseline overlapping.

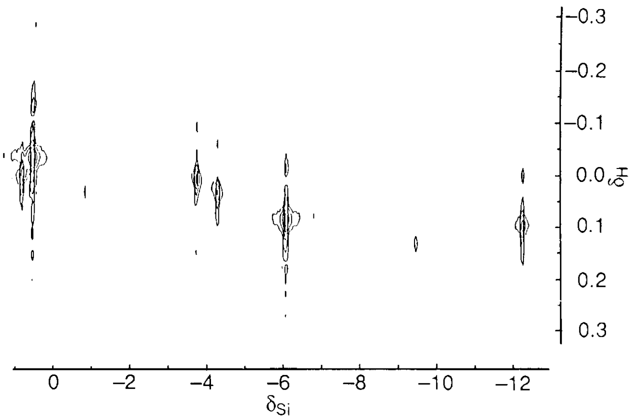


Fig. 4 ^1H–^{29}Si two-dimensional NMR spectrum of the reaction mixture of run 2 (20% **1**, 54% **2** and 23% **3**)

obtain exact values for the coupling constants. The strength of the residual coupling should however be consistent with the known rule, *i.e. trans* > *cis* > geminal.[5] Since it is known that the $BuMe_2Si$ group (J 9 Hz) is *cis* to the olefinic proton,[6] it can be concluded that the $BuMe_2Si$ group resonating at δ −3.73 (J 8 Hz) is also *cis*, whereas the $BuMe_2Si$ group resonating at δ −6.11 (J 12 Hz) is *trans* to the olefinic proton.

For summary of the structure of compound **2**, since there is no Si–H coupling to the olefinic proton in the ^{29}Si NMR spectrum, the Me_3Si group is connected to an sp^2 carbon *via* CH_2. This CH_2 group is not geminal to the olefinic proton as it appears as a singlet in the ^1H NMR spectrum. The $BuMe_2Si$ group is attached to the sp^2 carbon *trans* to the olefinic proton (the largest residual coupling constant), and the olefinic proton is geminal to an alkyl group (triplet in ^1H NMR spectrum). All data including integration of the ^1H NMR spectrum agree well with the structure shown in Scheme 1. The structure of compound **3** can be deduced in a similar manner.

The structures of the products from the reaction using compound **4** were determined using similar techniques. The NMR data and assignments are listed in Table 2. Residual coupling constants of the two silicon atoms to the olefinic protons of compound **6** could not be obtained due to baseline overlapping. Therefore, the actual structure of **6** may be different from that in Scheme 1, though no other structure seems likely.

Experimental

Materials.—Chlorosilanes (Dow Corning or Fluka) were distilled over magnesium. Butyllithium in hexane, methyllithium in diethyl ether and hydrogen hexachloroplatinate(IV) hydrate (Aldrich) were used as purchased. Other reagents (Aldrich) were distilled before use. Tetrahydrofuran (thf) was distilled from a purple solution of thf, potassium and benzophenone. 1-Trimethylsilylhex-1-yne and 1-butyldimethylsilylhex-1-yne were prepared according to the literature procedure[7] (yields 85 and 72%, respectively). Tris(tetramethyldivinyldisiloxane)diplatinum(0) was prepared as reported earlier.[8] Speier's catalyst[9] was prepared by dissolving hydrogen hexachloroplatinate(IV) hydrate in propan-2-ol (0.2 mol dm^{-3}).

Preparation of Compound **1**.—In a Schlenk flask (100 cm^3) with a reflux condenser, 1-trimethylsilylhex-1-yne (10 g, 65 mmol) and chlorodimethylsilane (15 g, 160 mmol) were mixed at room temperature. The disiloxaneplatinum catalyst (2.6 μmol) was added and an exothermic reaction was observed after several minutes. When the exotherm subsided, unreacted chlorodimethylsilane was removed by vacuum. Tetrahydrofuran (50 cm^3) was added to the reaction mixture and the flask was cooled (ice-bath). Butyllithium (23 cm^3 of a 2.8 mol dm^{-3} solution in hexane, 65 mmol) was added dropwise whilst cooling was continued. The reaction mixture was then allowed to stand at room temperature for 1 h and poured into a saturated NH_4Cl aqueous solution. The organic layer was washed with the NH_4Cl solution twice and dried over Na_2SO_4. Compound **1** was obtained by fractional distillation (triphenylphosphine was added to the pot in order to prevent rearrangements catalysed by platinum) with 97.2% purity by GLC [The remaining 2.8% was assumed to be (*E*)-1-butyldimethylsilyl-1-trimethylsilylhex-1-ene because a triplet at δ 6.56 with corresponding integration was observed in the ^1H NMR spectrum. This compound did not react in the course of isomerisations.] Yield: 12.7 g (72%), b.p. 76–77 °C (4 mbar) (Found: C, 66.7; H, 12.4. $C_{15}H_{34}Si_2$ requires C, 66.6; H, 12.7%); δ_H(250.13 MHz, solvent $CDCl_3$) 5.96 (1 H, s, HC=C), 2.24 (2 H, m, CH_2C=C), 1.37–1.21 (8 H, m, 4 CH_2), 0.94–0.84 (6 H, m, 2 CH_3CH_2), 0.59–0.52 (2 H, m, CH_2Si), 0.11 (9 H, s, Me_3Si) and 0.04 (6 H, s, Me_2Si); δ_{Si}(49.54 MHz, $CDCl_3$) −4.30 [$BuMe_2Si$, J(Si–H, olefinic) 8] and −12.32 [Me_3Si, J(Si–H, olefinic) 5 Hz]; m/z 270 (1.5, M^+), 255 (4, M − Me), 214 (37, M − Bu + 1), 213 (19, M − Bu), 140 (88), 139 (100) and 115 (74%, $BuMe_2Si^+$).

Preparation of Compound **4**.—Compound **4** was prepared by a similar procedure to that used for **1**. 1-Butyldimethylsilylhex-1-yne was hydrosilylated by chlorodimethylsilane, followed by addition of methyllithium to afford **4**, b.p. 66–68 °C (0.3 mbar), purity 93.6% by GLC (plus 6.2% isomer) (Found: C, 66.6; H, 12.9. $C_{15}H_{34}Si_2$ requires C, 66.6; H, 12.7%); δ_H(250.13 MHz; solvent $CDCl_3$) 5.95 (1 H, s, HC=C), 2.24 (2 H, m, CH_2C=C), 1.37–1.21 (8 H, m, 4 CH_2), 0.93–0.84 (6 H, m, 2 CH_3CH_2), 0.61–0.55 (2 H, m, CH_2Si), 0.09 (6 H, s, Me_2Si) and 0.06 (9 H, s, Me_3Si); δ_{Si}(49.54 MHz, $CDCl_3$) −5.54 [Me_3Si, J(Si–H, olefinic) 9] and −10.72 [$BuMe_2Si$, J(Si–H, olefinic) 4 Hz]; m/z 270 (0.7, M^+), 255 (1.6, M − Me), 214 (17, M − Bu + 1), 213 (9, M − Bu), 140 (49), 139 (13) and 115 (100%, $BuMe_2Si^+$).

Isomerisation Reactions.—Compound **1** or **4** (1.0 g, 3.7 mmol) was mixed with the platinum catalyst (amount shown in Table 1) and the mixture was divided into two parts, each of which was then placed in a pear-shaped flask (5 cm^3) fitted with a reflux condenser. To one flask vacuum was applied down to 0.15 mbar at room temperature, then it was filled with nitrogen (Air Products, high-purity grade). The procedure was repeated three times and finally the top of the reflux condenser was connected to a manifold with a constant nitrogen flow. The other flask (for experiment under air) was connected, through the reflux condenser, to a $CaCl_2$ drying tube (30 cm) with its other end open to air. The prepared flasks were put in an oil-bath set at the desired temperature. The reaction mixture was analysed by GLC periodically. GC–MS data for products [m/z (relative abundance, %)]: **2** 270 (6, M^+), 214 (17, M − Bu + 1), 140 (43), 139 (13), 115 (100, $BuMe_2Si^+$) and 73 (58, Me_3Si^+); **3** 270 (7, M^+), 214 (24, $M - Bu + 1$), 140 (41), 139 (10), 115 (100, $BuMe_2Si^+$) and 73 (99, Me_3Si^+); **5** 270 (6, M^+), 255 (0.6, $M - Me$), 214 (22, $M - Bu + 1$), 140 (63), 139 (13), 115 (30, $BuMe_2Si^+$), 73 (67, Me_3Si^+) and 59 (100); **6** 270 (6, M^+), 255 (0.4, $M - Me$), 214 (19, $M - Bu + 1$), 213 (3, $M - Bu$), 140 (36), 139 (13), 115 (100, $BuMe_2Si^+$) and 73 (10, Me_3Si^+).

Measurements.—The GLC analyses were performed with a Hewlett-Packard 5890 gas chromatograph with a flame ionisation detector and an HP-1 glass capillary column (25 m). Peak areas were determined with a Hewlett-Packard 3392 integrator. The GC–MS data were obtained using a Hewlett-Packard 5995 gas chromatograph/mass spectrometer (70 eV, *ca.* 1.12×10^{-17} J). Proton or ^{29}Si NMR spectra were recorded using either a Bruker AC-P 250 (250.13 MHz for ^1H) or AMX 500 (500.13 MHz) spectrometer (solvent, $CDCl_3$; reference, $CHCl_3$ for ^1H, $SiMe_4$ for ^{29}Si).

Acknowledgements

The NMR spectra were recorded by Mr. C. M. Dadswell.

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Received 6*th August* 1990; *Paper* 0/03556D