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Iodochlorination of Silyl- and Germylphenylacetylenes

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ABSTRACT: *Reactions of Si- and Ge-substituted alkynes with $KICl_2$ were investigated. (1-Germatranyl)-phenylacetylenes and (triphenylsilyl)phenylacetylene gave Z-iodochloroalkenes with chlorine and phenyl groups attached to the same carbon atom. Adduct structures were confirmed by X-ray diffraction studies.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:169–174, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20001

INTRODUCTION

Metallatranes, $N(CH_2CHRO)_3M{-}X$, are the most systematically studied compounds of Main group elements with nonclassical coordination number [1]. Those of the group 14 elements have been investigated in detail [2–3]. The main focus is the nature of transannular interaction $M \leftarrow N$ and the influence of apical substituent X on strength of this interaction. Biological activity of these compounds is of great interest as well [2,4]. At the same time the reactivity of metallatranes (M = Si, Ge) has been studied to a very limited extent especially the transformations of apical substituent X. However, it is obvious that the "atrane" moiety possessing specific steric and electronic properties may influence stability, reactivity, and ability to undergo chemical transformations.

Recently we have studied the reactions of element substituted acetylenes with different bromination reagents [5–7]. In general, the treatment of $N(CH_2CHRO)_3GeC{\equiv}CPh$ (R = H, **1**; Me, **2**) with NBS/DMSO led to $N(CH_2CHRO)_3GeC(Br_2)C(O)Ph$. The reactions of **1** and **2** with bromine or TBAT (tetra-*n*-butylammonium tribromide) gave only *Z*-dibromo adducts. The treatment of $Ph_3SiC{\equiv}CPh$ (**3**) with bromine also led to *Z*-isomer. In contrast, Si–C bond in $N(CH_2CH_2O)_3SiC{\equiv}CPh$ (**4**) was broken by Br_2 [7]. The bromination of trialkylsilylacetylenes with bromine led to mixtures of *Z*- and *E*-dibromoadducts, *Z*-isomers were the major products [6,7]. The opposite ratio of *Z*/*E*-isomers were found for reaction of $Alk_3SiC{\equiv}CPh$ with TBAT [7]. In continuation of our studies of triple bond addition reactions here we report the reactions of germatranyl-(**1, 2**) and silatranyl-(**4**) phenylacetylenes as well as their tetracoordinated counterparts, $Ph_3SiC{\equiv}CPh$ (**3**) and $Me_3SiC{\equiv}CPh$ (**5**) with $KICl_2$ leading to iodochloroadducts.

RESULTS AND DISCUSSION

The reactions of germatranes **1** and **2**, as well as (triphenylsilyl)phenylacetylene (**3**) with $KICl_2$ are regio- and stereospecific and lead to corresponding *Z*-isomers **6–8** (Scheme 1). The structures of adducts **6–8** were confirmed by X-ray diffractometry.

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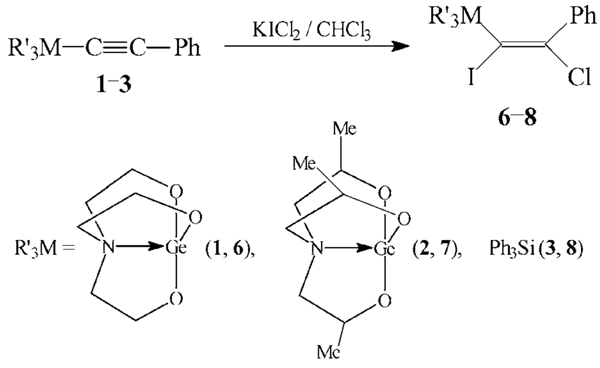


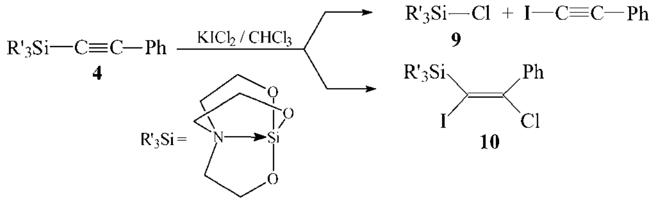
SCHEME 1

On the contrary, treatment of silatranylphenylacetylene **4** with $KICl_2$ gave silatrane **9** as a major product. However, NMR data testify the presence of *Z*-adduct **10** in reaction mixture (Scheme 2).

Iodochlorination of (trimethylsilyl)phenylacetylene **5** led to iodochloroalkene **11** (*Z*/*E* = 6/1) (Scheme 3). The *Z*/*E* signal assignment and ratio has been determined by comparison of ^1H NMR and ^{13}C NMR spectroscopy data for compound **11** with those previously found for corresponding dibromoalkene [7].

Iodochloroalkenes synthesized may serve as useful intermediates for further organic transformations mainly due to the presence of reactive carbon-iodine bond in the molecules.

The exclusive formation of *Z*-dihaloalkenes **6–8** in iodochlorination reactions of acetylenes **1–3** might be attributed to the possible steric hindrances derived from the presence of bulky groups at triple bond. Similar *cis*-stereospecific addition of bromine to triple bond was previously found for *tert*-BuC≡CPh [8]. Steric crowding is probably less in the case of silane **5** when *E*-adduct also formed together with *Z*-iodochloride. Silatrane **4** should be noted apart, since the main course of its reaction with $KICl_2$ is the cleavage of the Si—C bond. It may occur either as a result of the halogen attack on Si—C bond or owing to addition of halogen to triple bond followed by β-elimination.



SCHEME 2

$$\underset{\mathbf{5}}{Me_3Si{-}C{\equiv}C{-}Ph} \xrightarrow{KICl_2/CHCl_3}$$

$$\rightarrow \underset{\mathbf{11}}{Z,E\text{-}Me_3Si{-}C(I){=}C(Cl){-}Ph}$$

SCHEME 3

The structures of iodochloroalkenes were confirmed by elemental analyses, ^1H and ^{13}C NMR spectroscopy, mass-spectrometry as well as X-ray crystallography (for **6–8**). To the best of our knowledge, the only one crystal structure of iodochloroalkene, (*cis*-$C_6H_5SO_2C(I){=}C(Cl)H$), was reported [9]. The molecular structures of **6, 7**, and **8** are shown in Figs. 1–3. Carbon-carbon double bond lengths in **6–8** (1.312(7)–1.34(1) Å) are close to those previously found in corresponding dibromides (1.27(1)–1.31(1) Å) [5,7]. The coordination polyhedron of the germanium atom in germatranes *Z*–**6** and *Z*–**7** represents a distorted trigonal bipyramid with N and C atoms in the apical positions and the three oxygen atoms in equatorial sites. The germanium atom is displaced by 0.23–0.24 Å towards the phenylethenyl substituent from the equatorial plane defined by the three oxygen atoms. The N—Ge—C fragment is almost linear (176.9(2)° and 177.4(3)°) in both molecules. The N—Ge distances in compound **6** and **7** lie within the typical range for germatranes (2.160(2)–2.32(1) Å) [10,11] and clearly verify the existence of N—Ge transannular bond in these compounds. No short intermolecular contacts were observed in the structures of **6–8**.

EXPERIMENTAL

General Comments

1–5 were prepared as described earlier [7]. All solvents were dried by standard procedures and distilled before use. NMR spectra were recorded at 25°C on Bruker AC 300 and Varian VXR 400 spectrometers; $CDCl_3$ was used as the solvent and for internal deuterium lock. The chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm relative to internal TMS. The IR spectra were recorded on Zeiss UR-20. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectra (EIMS) were obtained on a VARIAN CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes.

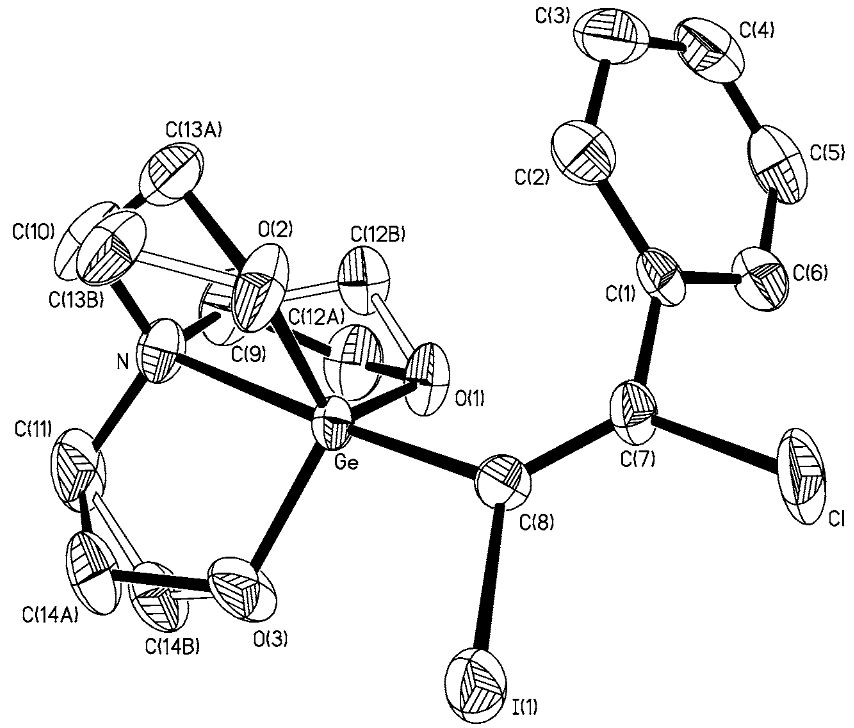


FIGURE 1 Molecular structure of **6**. Minor components of disordered groups are shown using open lines. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N–Ge 2.213(5), Ge–C(8) 1.960(5), C(7)–C(8) 1.325(7), C(8)–I(1) 2.075(5), C(7)–Cl 1.753(6), N–Ge–C(8) 176.9(2), Ge–C(8)–I(1) 115.2(3), Ge–C(8)–C(7) 126.0(4), I(1)–C(8)–C(7) 118.7(4), C(8)–C(7)–Cl 123.1(5), C(1)–C(7)–C(8) 125.2(5).

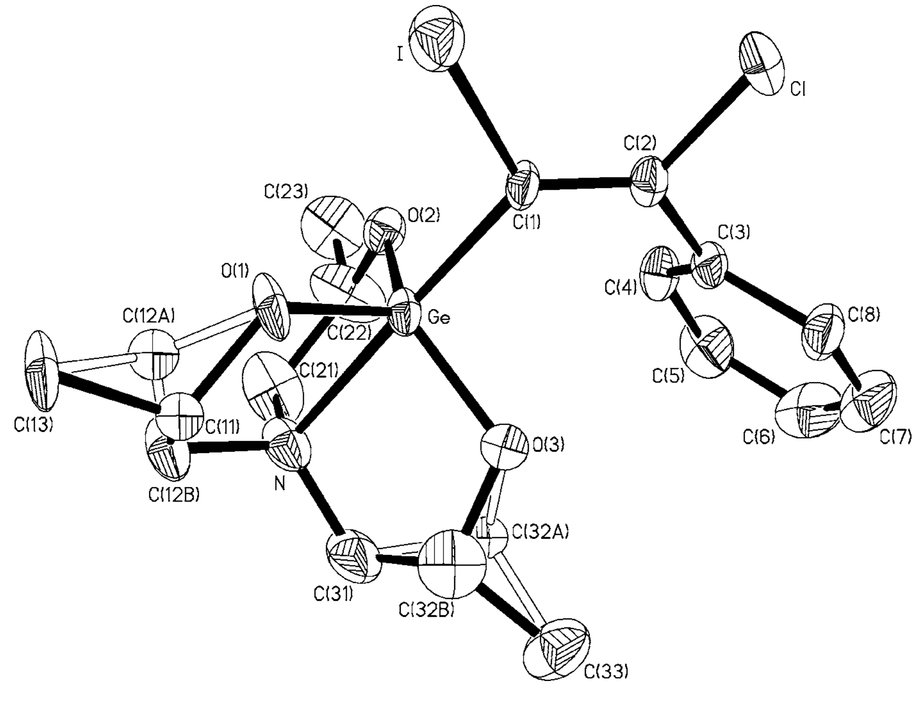


FIGURE 2 Molecular structure of **7**. Minor components of disordered groups are shown using open lines. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N–Ge 2.216(8), Ge–C(1) 1.980(9), C(1)–C(2) 1.34(1), C(1)–I 2.047(9), C(2)–Cl 1.76(1), N–Ge–C(1) 177.4(3), Ge–C(1)–I 115.5(4), Ge–C(1)–C(2) 124.4(7), I–C(1)–C(2) 120.1(7), C(1)–C(2)–Cl 122.0(8), C(1)–C(2)–(3)C 125.5(9).

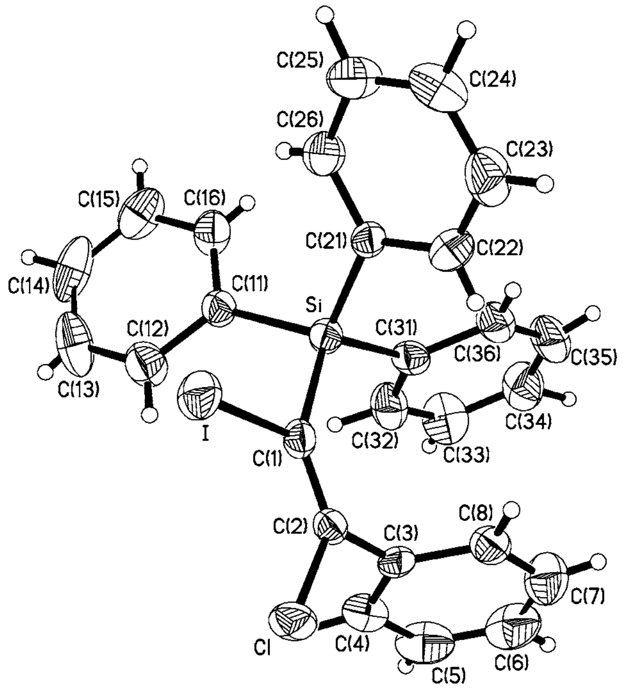


FIGURE 3 Molecular structure of **8**. Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): Si–C(1) 1.896(5), C(1)–C(2) 1.312(7), C(2)–C(3) 1.473(7), C(1)–I 2.106(5), C(2)–Cl 1.782(5), Si–C(1)–I 109.2(2), Si–C(1)–C(2) 130.9(4), I–C(1)–C(2) 119.9(4), C(1)–C(2)–Cl 122.5(4), C(1)–C(2)–C(3) 126.5(4), Cl–C(2)–C(3) 111.0(4).

Reactions of Studied Phenylacetylenes with $KICl_2$

Phenylacetylene (**1–5**) (3.1 mmol) was added to a solution of $KICl_2$ (6.2 mmol) in 50 ml of $CHCl_3$. The reaction mixture was stirred for 24 h at room temperature then washed with 5% aqueous $Na_2S_2O_3$ (3 x 30 ml) and water (20 ml). Organic layer was dried over sodium sulfate, and the solvent was removed in vacuo.

1: Recrystallization of solid residue from $CHCl_3$/*n*-hexane yielded *Z*-2-chloro-1-(1-germatranyl)-1-iodo-2-phenylethene (**6**) (76%), m.p. 176–178°C (decomp.). Calcd. for $C_{14}H_{17}ClGeINO_3$ (482.150): C, 34.88; H, 3.55; N, 2.91. Found: C, 35.14; H, 3.71; N, 2.93. IR (Nujol): ν(C=C) 1572 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.69$ (t, 6H, NCH_2); 3.52 (t, 6H, OCH_2); 7.24–7.30, 7.48–7.52 (2m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 52.50$ (NCH_2); 56.95 (OCH_2); 99.96 (IC=); 127.16, 128.26, 128.82, 141.51 (C_6H_5); 146.89 (ClC=). EI MS (70 eV): $m/z = 483$ (M^+, 4%), 356 (M^+ – I, 72%), 220 ($M^+ - C_8H_5ClI$, 100%), 190 ($M^+ - C_8H_5ClI - CH_2O$, 36%), 160 ($M^+ - C_8H_5ClI - 2CH_2O$, 47%), 146 ($M^+ - C_8H_5ClI - CH_2O - CH_2CH_2O$, 41%), 130 ($M^+ - C_8H_5ClI - 3CH_2O$, 7%).

2: Recrystallization of solid residue from $CHCl_3$/*n*-hexane yielded *Z*-2-chloro-1-[1-(3,7,10-trimethyl)germatranyl]-1-iodo-2-phenylethene **(7)** (69%). Calcd. for $C_{17}H_{23}ClGeINO_3$ (524.230): C, 38.95; H, 4.42; N, 2.67. Found (%): C, 38.78; H, 4.29; N, 2.88. IR (Nujol): ν(C=C) 1575 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 0.92$–3.92 (18H, $ABXM_3$ system of NCH$_2$CHMeO group protons); 7.19–7.23, 7.49–7.53 (2m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 19.98$, 20.17, 20.45, 22.79 (CH_3); 59.64, 62.19, 62.54, 62.81, 63.65, 64.06, 65.61, 65.68 (NCH_2CHO); 101.81 (IC=); 128.36, 128.39, 129.28, 140.39 (C_6H_5); 145.94 (ClC=) (other six signals of double bond and aromatic carbons were not found due to the small concentration); two diastereomers.

3: Recrystallization of solid residue from toluene yielded *Z*-2-chloro-1-iodo-2-phenyl-1-(triphenylsilyl)ethene (**8**) (86%), m.p. 135.0–135.5°C. Calcd. for $C_{26}H_{20}ClISi$ (522.89): C, 59.72; H, 3.86; Si, 5.37. Found (%): C, 59.60; H, 3.77; Si, 5.49. IR (Nujol): ν(C=C) 1576 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 6.70$–6.74, 6.83–6.87, 7.00–7.02, 7.20–7.23, 7.27–7.31, 7.48–7.50 (6m, 20H, $4C_6H_5$). ^{13}C NMR ($CDCl_3$) $\delta = 103.38$ (IC=); 127.58, 127.68, 136.03, 147.67 (SiC_6H_5); 128.66, 129.45, 133.58, 138.22 (C_6H_5C); 151.28 (ClC=). EI MS (70 eV): $m/z = 522$ (M^+, 2%), 445 (M^+ – Ph, 1%), 395 (M^+ – I, 28%), 359 (M^+ – I – Cl, 17%), 317 (M^+ – I – Ph, 95%), 259 ($SiPh_3^+$, 92%), 241 (M^+ – I – 2Ph, 14%), 217 (Ph_2SiCl^+, 100%).

4: ^1H NMR spectrum of solid residue washed with *n*-hexane has shown the presence of starting material **4**, 1-chlorosilatrane (**9**), and Z-adduct **10** (ratio 1:10:1). Recrystallization of solid residue from $CHCl_3$/*n*-hexane yielded precipitate with *Z*-2-chloro-1-iodo-2-phenyl-1-(1-silatranyl)ethene (**10**) as major component. ^1H NMR ($CDCl_3$) $\delta = 2.70$ (t, 6H, NCH_2); 3.54 (t, 6H, OCH_2); 7.19–7.26, 7.40–7.43 (2m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 51.60$ (NCH_2); 57.59 (OCH_2); 101.65 (IC=); 128.49, 128.56, 129.40, 139.57 (C_6H_5); 146.97 (ClC=). The ^{13}C NMR spectrum of filtrate indicated the presence of $IC{\equiv}CC_6H_5$: ^{13}C NMR ($CDCl_3$) $\delta = 6.05$ (IC≡); 94.11 ($\equiv CC_6H_5$); 123.37, 128.21, 128.77, 132.30 (C_6H_5).

5: Fractionation of the liquid residue gave *Z*,*E*-2-chloro-1-iodo-2-phenyl-1-(trimethylsilyl)ethene (**11**) (90%), b.p. 170–176°C (4 Torr). Calcd. for $C_{11}H_{14}ClISi$ (336.67): C, 39.24; H, 4.19; Si, 8.34. Found (%): C, 39.87; H, 4.25; Si, 8.49. IR (Nujol): ν(C=C) 1576 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = -0.06$ (s, 9H, $SiMe_3$, *Z*-isomer); 0.39 (s, 9H, $SiMe_3$, *E*-isomer); 7.29–7.38 (m, 5H, C_6H_5). *Z*/*E* ratio = 18/1. ^{13}C NMR ($CDCl_3$) $\delta = -0.04$ ($SiMe_3$, *Z*-isomer), 0.91 ($SiMe_3$, *E*-isomer); 109.38 (IC=); 128.24, 128.28, 128.63, 139.68 (C_6H_5, *Z*-isomer); 129.22, 129.36, 129.42, 138.57 (C_6H_5, *E*-isomer); 145.76 (ClC=); signals of double bond

TABLE 1 Crystal Data, Data Collection and Refinement Parameters for Compounds **6, 7**, and **8**

	6	**7**	**8**
Empirical formula	$C_{14}H_{17}ClGeINO_3$	$C_{17}H_{23}ClGeINO_3$	$C_{26}H_{20}ClISi$
Formula weight	482.23	524.30	522.86
Colour, habit	yellow block	yellow block	pink block
Crystal size (mm)	0.2 × 0.2 × 0.2	0.5 × 0.2 × 0.1	0.3 × 0.2 × 0.1
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
Unit cell dimensions:			
a/Å	9.371(3)	8.318(4)	10.433(2)
b/Å	10.096(2)	14.414(8)	10.551(3)
c/Å	17.220(5)	16.783(5)	10.739(3)
$\alpha/^\circ$	90	90	88.59(2)
$\beta/^\circ$	95.93(2)	93.02(3)	83.53(2)
$\gamma/^\circ$	90	90	74.73(2)
Volume (Å^3)	1620.5(8)	2009(2)	1133.1(5)
Z	4	4	2
D_{calc} (g cm^{-3})	1.977	1.733	1.532
μ (mm^{-1})	3.968	3.208	1.594
F(000)	936	1032	520
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature (K)	293	293	293
Radiation (λ/Å)	graphite monochromatized MoKα (0.71073)	graphite monochromatized MoKα (0.71073)	graphite monochromatized MoKα (0.71073)
θ range (°)	2.34–25.48	2.43–24.98	2.00–24.97
Index ranges	$-11 \leq h \leq 11$ $0 \leq k \leq 12$ $0 \leq l \leq 20$	$-9 \leq h \leq 9$ $-17 \leq k \leq 3$ $-4 \leq l \leq 19$	$-12 \leq h \leq 8$ $-12 \leq k \leq 12$ $0 \leq l \leq 12$
Reflections collected	3113	5845	3811
Independent reflections	3011 [$R_{int} = 0.0494$]	3527 [$R_{int} = 0.0564$]	3630 [$R_{int} = 0.0176$]
Data/restraints/params	3011/0/218	3085/0/216	3312/0/342
Goodness-of-fit on F^2	1.371	1.036	1.059
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1100$	$R_1 = 0.0597$, $wR_2 = 0.1482$	$R_1 = 0.0381$, $wR_2 = 0.0890$
R indices (all data)	$R_1 = 0.0542$, $wR_2 = 0.1133$	$R_1 = 0.1327$, $wR_2 = 0.1831$	$R_1 = 0.0745$, $wR_2 = 0.1019$
Extinction coefficient	0.0277(10)	–	–
Largest diff. peak/hole (e Å^{-3})	0.894/−0.924	0.909/−1.388	0.807/−0.345

carbons were not found due to the small concentration of ***E*-11**. EI MS (70 eV): $m/z = 336$ (M^+, 4%), 321 ($M^+ - Me$, 4), 209 ($M^+ - I$, 1), 193 ($M^+ - I - Me$, 3), 159 ($M^+ - I - Cl - Me$, 12%), 136 ($M^+ - I - SiMe_3$, 7%), 93 (Me_2SiCl^+, 100%), 73 ($SiMe_3{}^+$, 29%).

X-Ray Crystallography Study of **6–8**

Table 1 summarizes the crystal data as well as details of data collection and structure determination. The structures were solved by direct methods (SHELX-86 [12]) and refined by full-matrix least squares on F^2 (SHELXL-97 [13]) with anisotropic displacement parameters for all non-hydrogen atoms. In the structures **6** and **7** β-carbon atoms of atrane fragments were found to be disordered over two positions with approximately equal occupancies. In the structures **6** and **7** all hydrogen atoms were placed in calculated positions and refined using a riding model. As for the structure **8**, all hydrogen atoms were located from difference Fourier synthesis and refined isotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-223441 for **6**, 223442 for **7**, and 223443 for **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: C44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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