drido-bridged species 5 argues in favor of such a notion.

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Note Added in Proof. The structure of $[Rh_2(CO)_3(DPM)_2]$, the Rh analogue of compound 4, has recently been reported (Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285) and is shown to have an unusual structure, but one which is closely related to that proposed by us for compound 4.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and tables of anisotropic temperature factors and calculated hydrogen parameters (10 pages). Ordering information is given on any current masthead page.

Addition of Pseudohalogens to Vinyl- and Allylsilanes. Synthesis of 1-Substituted 2-(Alkylsilyl)- and 2-[(Alkylsilyl)methyl]aziridines Using Phase-Transfer Catalysis

Edmunds Lukevics,* Visvaldis V. Dirnens, Yuri S. Goldberg, Edvards E. Liepinsh, Maris P. Gavars, Ivars Ya. Kalvinsh, and Mariya V. Shymanska

Institute of Organic Synthesis, Latvian SSR Academy of Sciences, 226006, Riga, USSR

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Addition of alkyl dichlorocarbamates to vinylsilanes by either an ionic or a radical mechanism occurs in an anti-Markownikoff orientation to give alkyl chloro[2-chloro-2-(trialkylsilyl)ethyl]carbamates (3). The reduction of 3 with aqueous sodium sulfite affords the corresponding alkyl [2-chloro-2-(trialkylsilyl)-ethyl]carbamates (4). *N*-[2-Chloro-2-(trialkylsilyl)ethyl]-*p*-toluenesulfonamides were obtained by the radical addition of *N*,*N*-dichloro-*p*-toluenesulfonamide (5) to trialkylvinylsilanes with subsequent reduction of the product. Addition of ethyl dichlorocarbamate to trimethylallylsilane (9) yields an equimolar mixture of β- and γ-adducts, while 5 reacts with 9 to give the Markownikoff adduct 7 regardless of the reaction mechanism. Intramolecular alkylation of carbamates 4a–c and sulfonamide 7a under solid–liquid phase-transfer conditions leads to 1-carbalkoxy- and 1-(*p*-tolylsulfonyl)-2-(trialkylsilyl)aziridines. 1-(Ethoxycarbonyl)- and 1-(*p*-tolylsulfonyl)-2-[(trimethylsilyl)methyl]aziridines were synthesized by similar cyclization. The possibility of intramolecular alkylation in a two-phase system under ultrasonic irradiation was demonstrated for carbamate 4c.

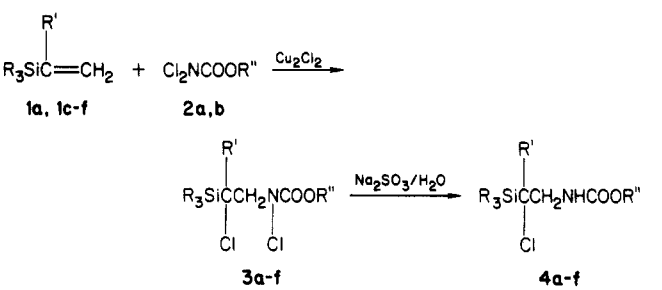
Introduction

In our preliminary communication[1] we proposed a new method for the preparation of silicon-containing aziridines. The addition of methyl dichlorocarbamate to trimethylvinylsilane was found to give methyl chloro[2-chloro-2-(trimethylsilyl)ethyl]carbamate whose reduction with sodium hydrosulfite led to methyl [2-chloro-2-(trimethylsilyl)ethyl]carbamate. The latter was cyclized with sodium hydroxide powder using solid–liquid phase-transfer catalysis to afford 1-(methoxycarbonyl)-2-(trimethylsilyl)-aziridine in good yield. Similarly, 1-(ethoxycarbonyl)-2-[(trimethylsilyl)methyl]aziridine was prepared from trimethylallylsilane and ethyl dichlorocarbamate. The present communication describes the general applicability of the above synthetic scheme for the preparation of N-substituted silicon-containing aziridines.

Results and Discussion

Addition of Pseudohalogens to Alkenylsilanes. Pseudohalogens, such as alkyl dichlorocarbamates and *N*,*N*-dichloroarenesulfonamides, are known to form adducts readily with alkenes.[2]

Scheme I



a, R = Me, R' = H, R" = Me, b, R = Me, R' = H, R" = Et, c, R = Et, R' = H, R" = Et, d, R = Me, R' = Br, R" = Et, e, R = Et, R' = Br, R" = Et, f, R_3 = Et_2Me, R' = COOMe, R" = Et

Thermal and photochemically induced addition of alkyl dichlorocarbamates follows a free radical mechanism.[2-6] *N*,*N*-Dichloro-*p*-toluenesulfonamide reacts with styrene[7,8] to yield an anti-Markownikoff adduct even when the re-

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Table I. Silicon-Containing Carbamates and Sulfonamides

compd	yield, %	bp, °C (mmHg), or mp, °C	elemental anal. found C	found H	found N	calcd C	calcd H	calcd N
3a	85	93–94 (2)						
3b	80	84–86 (1)						
3c	70	138–144 (1.5)						
3d	80	123–127 (1)						
3e	65	105 (10^{-2})						
3f	6k	90 (0.2)						
4a	80	97–98	40.21	7.68	6.61	40.09	7.63	6.68
4	70	46–48	42.90	8.07	6.30	42.35	8.05	6.26
4c	50	130–135 (1)	49.60	9.08	5.25	49.72	9.04	5.27
4d	80	110–113 (1)	31.84	5.57	4.51	31.75	5.62	4.63
4e	50	100 (10^{-2})	38.76	6.34	4.12	38.33	6.68	4.07
4f	40	85 (0.2)	46.03	8.15	4.47	46.23	8.35	4.49
10 + 11	40[a]	96–98 (1)	45.09	8.14	5.73	45.47	8.42	5.89
7a	53	73	46.93	6.32	4.39	47.14	6.55	4.58
7d	65	128	37.19	4.82	3.57	37.46	4.94	3.64
12	45	67	48.41	6.53	4.21	48.83	6.89	4.38

[a] Total yield of the **10** and **11** mixture.

Table II. ^{1}H NMR Spectra Data for NCl Silicon-Containing Carbamates[a]

compd	δ (J, Hz)
3b	0.16 (9 H, s, $SiMe_3$), 1.29 (3 H, t, OCH_2CH_3), 3.64 and 4.13 (1 H, dd, J_1 = 14.0 J_2 = 3.0, and 1 H, dd, J_1 = 14.0, J_2 = 11.0, CH_2N), 3.66 (1 H, dd, J_1 = 11.0, J_2 = 3.0, CHCl), 4.24 (2 H, q, J = 6.7, OCH_2CH_3)
3c	0.5–1.1 (15 H, m, $SiEt_3$), 1.30 (3 H, t, J = 6.7, OCH_2CH_3), 3.59 and 3.65 (1 H, dd, J_1 = 14.0, J_2 = 2.6, and 1 H, dd, J_1 = 14.0, J_2 = 3.0, CH_2N), 3.89 (1 H, dd, J_1 = 3.0, J_2 = 2.6, CHCl), 4,24 (2 H, q, J = 6.7, OCH_2CH_3)
3d	0.32 (9 H, s, $SiMe_3$), 1.35 (3 H, t, J = 6.4, OCH_2CH_3), 4.26 (2 H, q, J = 6.4, OCH_2CH_3), 4.35 and 4.44 (1 H, and 1 H, AB_q, J = 15.0, CH_2N)
3e	0.6–1.13 (15 H, m, $SiEt_3$), 1.27 (3 H, t, J = 6.7, OCH_2CH_3), 4.27 (2 H, q, J = 6.7, OCH_2CH_3), 4.38 (2 H, s, CH_2N)
3f	0.18 (3 H, s, SiMe), 0.76 and 0.98 (4 H, m, and 6 H, 7, $SiEt_2$), 1.27 (3 H, t, J = 6.7, OCH_2CH_3), 3.78 (3 H, s, OCH_3), 4.13 and 4.55 (1 H and 1 H, AB_q, J = 15.0, CH_2N), 4.20 (2 H, q, J = 6.7, OCH_2CH_3)

[a] For ^{1}H NMR spectrum of **3a** see ref 1.

action is run under a nitrogen atmosphere. However, in the presence of $AlCl_3$[7] or atmospheric oxygen[8] the dichlorosulfonamide adds to styrene according to the Markownikoff rule. The observed difference in the adduct formed in the reaction of pseudohalogens and alkenes may be determined by the reaction mechanism (ionic or free radical) which depends on the reaction conditions.[7,8]

We have studied the reaction of trialkylvinylsilanes (**1a**, **1c–f**) and trimethylallylsilane (**9**) with alkyl dichlorocarbamates (**2a,b**) and *N,N*-dichloro-*p*-toluenesulfonamide (**5**). Trimethylvinylsilane (**1a**) reacts with *N,N*-dichlorourethane (**2b**) both in an inert atmosphere and in air. In both cases ethyl chloro[2-chloro-2-(trimethylsilyl)ethyl]carbamate (**3b**), the anti-Markownikoff adduct, is formed. (Scheme I).

When equimolar amounts of **1a** and **2b** were refluxed in an argon atmosphere for 6 h, chlorocarbamate **3c** was obtained (yield 85%). Catalytic amounts of Cu_2Cl_2 initiate the radical addition of pseudohalogens to alkenes.[9] Introduction of Cu_2Cl_2 into the reaction mixture results in a significant enhancement of the process: **3c** is formed in 95% yield during 1 h. Under similar conditions, several

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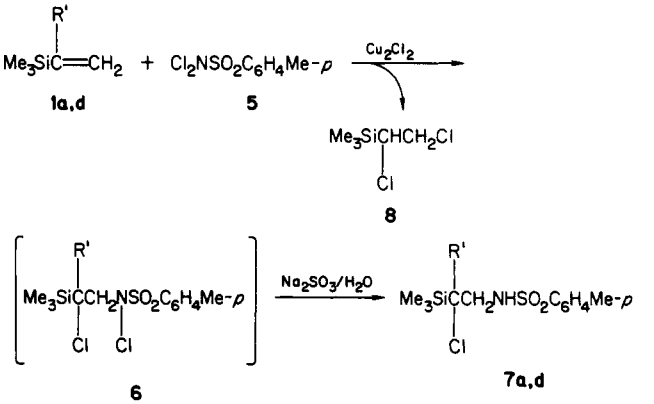
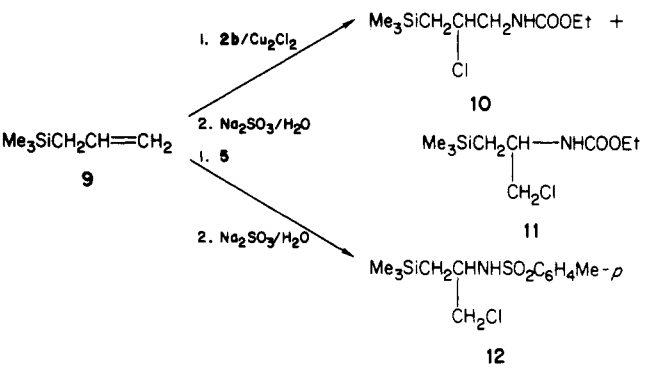
Scheme II

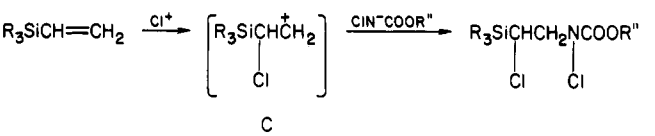


Scheme III



other chlorocarbamates **3** could be obtained in good yield (Tables I and II).

Vinylsilanes **1** react with **2** in air in the absence of a catalyst. This suggests an ionic mechanism. The anti-Markownikoff adduct formed in this case may be explained by the ability of the silicon atom to stabilize a positive charge in the β-position of the intermediate carbocation C resulting from the addition of the Cl^+ ion[10] to the vinylsilane.[11]



Hence, the addition of dichlorocarbamates **2** to vinylsilanes **1** proceeds regiospecifically irrespective of the reaction conditions, and both possible mechanisms lead to anti-Markownikoff adducts.

Silicon-containing β-chloro chlorocarbamates **3**[3] are readily reduced by an aqueous solution of sodium bisulfite or sulfite providing the corresponding β-chloro carbamates **4** in good yield (Tables I, III, and IV).

N,N-Dichloroarenesulfonamides add to alkenes similarly to give alkyl dichlorocarbamates.[13,14] The reaction of *N,N*-dichloro-*p*-toluenesulfonamide (**5**) and trimethylvinylsilane (**1a**) in the presence of Cu_2Cl_2 with subsequent treatment of the anti-Markownikoff adduct **6** with aqueous

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Table III. ^{1}H NMR Spectra Data for NH Silicon-Containing Carbamates and Sulfonamides[a]

compd	δ (J, Hz)
4b	0.17 (9 H, s, $SiMe_3$), 1.27 (3 H, t, J = 6.7, OCH_2CH_3), 3.42 and 3.77 (1 H, m, J_1 = 11.0, J_2 = 10.0, J_3 = 4.0, and 1 H, m, J_1 = 11.0, J_2 = 6.0, J_3 = 2.0, CH_2N), 3.44 (1 H, dd, J_1 = 10.0, J_2 = 2.0, CHCl), 4.13 (2 H, q, J = 6.7, OCH_2CH_3), 5.20 (1 H, dd, J_1 = 6.0, J_2 = 4.0, NH)
4c	0.5–1.2 (15 H, m, $SiEt_3$), 1.22 (3 H, t, J = 6.7, OCH_2CH_3), 3.20 and 3.73 (1 H, m, J_1 = 13.0, J_2 = 10.0, J_3 = 4.1 and 1 H, m, J_1 = 13.0, J_2 = 10.0, J_3 = 2.0, CH_2N), 3.53 (1 H, dd, J_1 = 10.0, J_2 = 2.0), 4.11 (2 H, q, J = 6.7, OCH_2CH_3), 5.18 (1 H, dd, J_1 = 10.0, J_2 = 4.1, NH)
4d	0.31 (9 H, s, $SiMe_3$), 1.26 (3 H, t, J = 6.7, OCH_2CH_3), 3.91 (2 H, d, J = 5.2, CH_2N), 4.18 (2 H, q, J = 6.7, OCH_2CH_3), 5.26 (1 H, b s, NH)
4e	0.5–1.2 (15 H, m, $SiEt_3$), 1.27 (3 H, t, J = 6.7, OCH_2CH_3), 3.81 and 3.96 (1 H and 1 H, AB_q, J = 12.9, CH_2N), 4.17 (2 H, q, J = 6.7, OCH_2CH_3), 5.3 (1 H, b s, NH)
4f	0.18 (3 H, s, SiMe), 0.6–1.2 (10 H, m, $SiEt_2$), 1.25 (3 H, t, J = 6.7, OCH_2CH_3), 3.61 and 3.84 (1 H, dd, J_1 = 14.0, J_2 = 7.0, and 1 H, dd, J_1 = 14.0, J_2 = 2.0, CH_2N), 3.76 (3 H, s, OMe), 4.11 (2 H, q, J = 6.7, OCH_2CH_3), 5.1 (1 H, b s, NH)
7a	0.11 (9 H, s, $SiMe_3$), 2.44 (3 H, s, $C_6H_4CH_3$), 3.09 and 3.43 (1 H, m, J_1 = 13.5, J_2 = 10.0, J_3 = 4.0, and 1 H, m, J_1 = 13.5, J_2 = 10.7, J_3 = 2.5, CH_2N), 3.27 dd, J_1 = 10.0, J_2 = 2.5), 4.93 (1 H, dd, J_1 = 10.7, J_2 = 4.0), 7.33 and 7.75 (2 H, d, J = 8.5, and 2 H, d, J = 8.5, p-C_6H_4)
7d	0.51 (9 H, s, $SiMe_3$), 2.46 (3 H, s, $C_6H_4CH_3$), 3.66 (2 H, d, J = 6.3, CH_2N), 5.0 (1 H, t, J = 5.7, NH), 7.33 and 7.75 (2 H, d, J = 8.5, and 2 H, d, J = 8.5, p-C_6H_4)
12	0.00 (9 H, s, $SiMe_3$), 0.82 and 0.98 (1 H, dd, J_1 = 14.5, J_2 = 7.0, and 1 H, dd, J_1 = 14.5, J_2 = 6.8, CH_2N), 2.44 (3 H, s, $C_6H_4CH_3$), 3.44 (2 H, m, CH_2Cl), 3.71 (1 H, m, CHN), 5.02 (1 H, d, J = 8.0, NH), 7.31 and 7.82 (2 H, d, J = 8.5, and 2 H, d, J = 8.5, p-C_6H_4

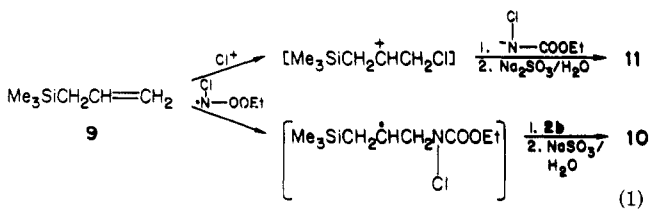
[a] For ^{1}H NMR spectra of **4a**, **10**, and **11** see ref 1.

Na_2SO_3 gives *N*-[2-chloro-2-(trimethylsilyl)ethyl]-*p*-toluenesulfonamide (**7a**) in 20% yield. (1,2-Dichloroethyl)trimethylsilane (**8**)[12] is also formed in 62% yield (Scheme II; Tables I, III, and IV). When the reaction is conducted under an argon atmosphere, the yield of **7a** rises to 53%, while that of **8** drops to 20%.

The reaction of **5** with (α-bromovinyl)silane (**1d**) under conditions similar to those described above for **1a** gives an anti-Markownikoff adduct.

The reaction of trimethylallylsilane (**9**) and pseudohalogens **2** and **5** is not regiospecific (Scheme III; Tables I, III, and IV). The mixture of products obtained from the reaction of **9** and dichlorocarbamate **2c** under inert atmosphere, with Cu_2Cl_2 as a radical initiator, is treated with aqueous sodium sulfite, to give ethyl [2-chloro-3-(trimethylsilyl)-2-propyl]carbamate (**10**) and ethyl [1-chloro-3-(trimethylsilyl)-2-propyl]carbamate (**11**) in a 1:1 ratio (^{1}H NMR data) in 40% yield.

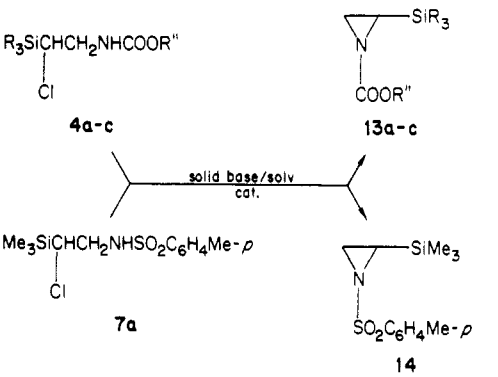
The formation of this product mixture may be due to attack on the allylsilane by both Cl^+ and the ·N(Cl)COOEt radical (eq 1).

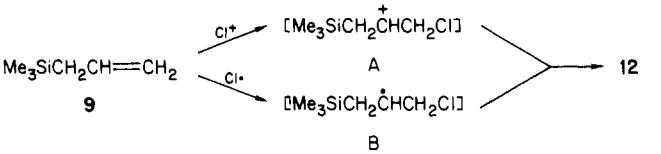


(1)

Ionic or free radical addition of **5** to **9** gives a Markownikoff adduct. After reduction, the only product isolated from the reaction mixture was *N*-[1-chloro-3-(trimethylsilyl)-2-propyl]-*p*-toluenesulfonamide (**12**). Apparently, in this case the reaction proceeds via allyl carbocation A or allyl radical B, respectively.

Scheme IV





Synthesis of N-Substituted 2-(Trialkylsilyl)aziridines. Reports on silicon-containing aziridines with a Si–C bond are very scarce.[15–20] The reactions of pseudohalogen addition to alkenylsilanes presented here result in β-chloro carbamates. Compounds of this type are known to undergo intramolecular cyclization to aziridines.[21]

We have studied the possibility of intramolecular alkylation of carbamates **4**, **7**, **10**, and **12** to yield the corresponding 1-substituted 2-(trialkylsilyl)aziridines using solid bases in a two-phase catalytic system.[20–23]

Methyl (2-chloro-2-trimethylsilyl)ethylcarbamate (4a) under solid-liquid phase transfer conditions in the presence of catalyst (tetraoctylammonium bromide) at room temperature was transformed in good yield to 1-ethoxycarbonyl-2-trimethylsilylaziridine (13a) (Scheme IV, Table V–VII). Likewise, intramolecular alkylation of carbamates 4b and 4c leads to the corresponding 2-(trialkylsilyl)aziridines (13b and 13c). Arenesulphonamide **7a** under similar conditions is converted to 1-(*p*-tolylsulphonyl)-2-(trimethylsilyl)aziridine (**14**).

In similar fashion, cyclization of reduced pseudohalogen and allylsilane adducts (**10** + **11**, **12**) yielded the first aziridines with the silicon atom separated from the heterocycle by a methylene group. The mixture of carbamates **10** and **11** gives 1-carbethoxy-2-[(trimethylsilyl)methyl]-aziridine (**15**), while sulfonamide **12** results in 1-(*p*-tolylsulfonyl)-2-[(trimethylsilyl)methyl]aziridine (**16**) (Tables V–VII).

The control experiment conducted with **4b** revealed that the formation of aziridine **13b** also occurs, but very slowly, without catalyst. This prompted us to examine the possibility of intramolecular alkylation of **4** to **13** using ul-

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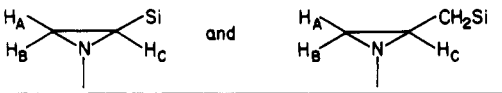
Table V. Synthesis of 1-Substituted 2-(Trialkylsilyl)- and 2-[(Trialkylsilyl)methyl]aziridines under Phase-Transfer Conditions

carbamate or sufonamide	reactn conditns[a]				product	yield, %	elemental anal. found			elemental anal. calcd		
	solv	base	time, h	temp, °C			C	H	N	C	H	N
4a	hexane	NaOH	4	25	**13a**	75[b]	48.47	8.52	8.17	48.56	8.67	8.09
4b	MeCN	NaOH	3.5	25	**13b**	72[b]	51.14	8.92	7.36	51.34	9.09	7.49
4c	hexane	NaOH	6.5	25	**13c**	90[c]	57.39	10.11	6.03	57.64	10.04	6.11
7a	hexane–MeCN (3:1)	K_2CO_3	5	25	**14**	60[c]	53.86	7.21	5.07	53.53	7.06	5.20
10 + 11	hexane	NaOH	1 (3)[d]	25	**15**	20[b]	53.42	9.38	6.85	53.73	9.45	6.9
12	hexane	NaOH	2	25	**16**	50[b]	55.97	7.64	5.16	55.12	7.42	4.35

[a] Catalyst $(C_8H_{17})_4N^+Br^-$ (10 mol %). [b] Preparative yield. [c] Determined by GLC using absolute calibration. [d] Catalyst $Et_3N^+CH_2PhCl^-$ (10 mol %).

Table VI. ^1H NMR Spectra Data for 1-Substituted Silicon-Containing Aziridines[a]



compd	δ (J, Hz)
13b	−0.08 (9 H, s, $SiMe_3$e, 1.11 (3 H, t, J = 7.4, OCH_2CH_3), 1.50 (1 H, dd, J_1 = 8.0, J_2 = 5.7, H_C), 1.90 (1 H, dd, J_1 = 5.7, J_2 = 1.3, H_A), 2.22 (1 H, dd, J_1 = 8.0, J_2 = 1.3, H_B), 3.98 (2 H, q, J = 7.4, OCH_2CH_3)
13c	0.4–1.04 (15 H, m, $SiEt_3$), 1.24 (3 H, t, J = 6.7, OCH_2CH_3), 1.59 (1 H, dd, J_1 = 7.8, J_2 = 5.2, H_C), 2.1 (1 H, dd, J_1 = 5.2, J_2 = 1.1, H_A), 2.4 (1 H, dd, J_1 = 7.8, J_2 = 1.1, H_B), 4.13 (2 H, q, J = 6.7, OCH_2CH_3)
14	−0.09 (9 H, s, $SiMe_3$), 1.91 (1 H, dd, J_1 = 8.4, J_2 = 5.8, H_C), 2.08 (1 H, dd, J_1 = 5.8, J_2 = 1.0, H_A), 2.69 (1 H, dd, J_1 = 8.4, J_2 = 1.0, H_B), 2.45 (3 H, s, $C_6H_4CH_3$), 7.31 and 7.80 (2 H, d, J = 8.4, and 2 H, d, J = 8.4, p-C_6H_4)
16	0.04 (9 H, s, $SiMe_3$), 0.64 and 1.04 (1 H, dd, J_1 = 14.6, J_2 = 8.0, and 1 H, dd, J_1 = 14.6, J_2 = 5.2, $SiCH_2$), 1.94 (1 H, d, J = 4.0, H_A), 2.6 (1 H, d, J = 6.4, H_B), 2.82 (1 H, m, H_C), 2.44 (3 H, s, $C_6H_4CH_3$), 7.33 and 7.82 (2 H, d, J = 8.4, and 2 H, d, J = 8.4, p-C_6H_4)

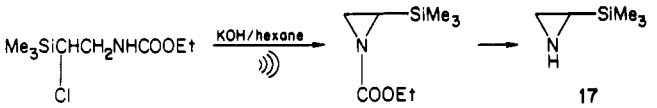
[a] For ^1H NMR of aziridines **13a** and **15** see ref 1.

Table VIII. Conversions of [2-Chloro-2-bromo-2-(trialkylsilyl)ethyl]carbamates under Phase-Transfer Conditions

carbamate	solv	reactn conditns base (molar equiv)	cat.[a]	time, h	temp, °C	yield[b] of 18, %
4d	light petroleum	KOH (1.5)	$(C_8H_{17})_4N^+Br^-$	2	25	39
4d	benzene	NaOH (2.0)	$(C_8H_{17})_4N^+Br^-$	7	25	37
4d	benzene	K_2CO_3 (2.0)	$Et_3N^+CH_2PhCl^-$	42	25	60
4d	benzene	K_2CO_3 (2.0)		42	25	48
4d	benzene	Et_3N (2.0)		8	80	0
4e	hexane	NaOH (1.0)	$(C_8H_{17})_4N^+Br^-$	2	25	50

[a] 10 mol %. [b] Determined by GLC using absolute calibration.

trasonic irradiation.[24,25] Indeed, ultrasonication (100 W, 55 KHz) of the two-phase system **4b** in hexane/solid KOH gives **13b**, the yield reaching 45% after 0.5 h (GLC data). Further treatment, however, decreases **13b** content and leads to the appearance of 2-(trimethylsilyl)aziridine (**17**).[19]

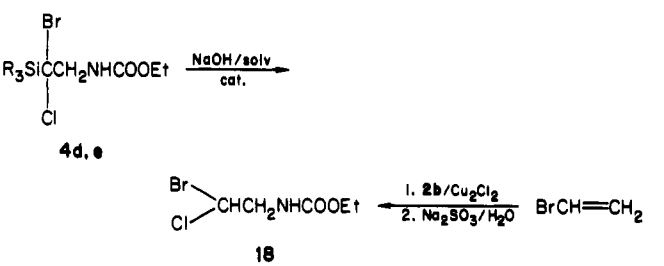


4b **13b** **17**

The results obtained suggest that 1-substituted 2-(trialkylsilyl)-2-haloaziridines may by prepared by intramolecular alkylation of pseudohalogen and (α-bromovinyl)-silane adducts.

However, the experimental findings were somewhat unexpected (Scheme V; Tables VII and VIII). Ethyl [2-chloro-2-bromo-2-(trialkylsilyl)ethyl]carbamates (**4d** and **4e**) in the presence of solid bases and catalyst ($(C_8H_{17})_4N^+Br$ or $Et_3N^+CH_2PhCl$) are converted in satisfactory yields to ethyl (2-chloro-2-bromoethyl)carbamate (**18**), identical with that synthesized by the reaction of vinyl

Scheme V



bromide and dichlorocarbamate **2b** in the presence of Cu_2Cl_2 with subsequent reduction with Na_2SO_3 (Scheme V).

The formation of **18** from **4d** and **4e** also takes place without a catalyst (Table VIII).

Hence, the presence of an additional electron-accepting substituent in the α-position with respect to the silicon atom alters the conversion direction of such carbamates in the presence of bases. In fact, carbamate **4f** in hexane upon contact with NaOH in the presence of $(C_8H_{17})_4N^+Br^-$ is rapidly converted to ethyl [2-chloro-2-(methoxycarbonyl)ethyl]carbamate[26] (**19**) in 57% yield.

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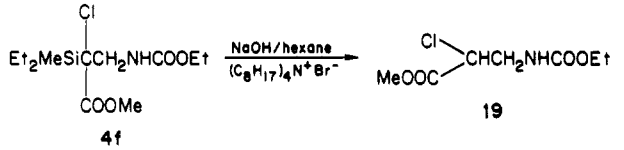

4f 19

These results are in agreement with the data of ref 27 demonstrating that the cleavage of Si–C bond by oxygen-containing bases proceeds particularly readily for molecules containing more than one halogen atom in the α-position.

Experimental Section

^1H NMR spectra were recorded on a Bruker WH-90/DS spectrometer using $CDCl_3$ as solvent and Me_4Si and cyclohexane as internal standards. Mass spectra were obtained on a Kratos MS-25 GC/MS system (70 eV). GLC analysis was conducted with a Chrom-42 instrument equipped with FID detector. A 2.4 m × 3 mm column packed with 10% SE-30 + 2.5% Reoplex-400 on Chromosorb W-AW (60–80 mesh) (A) and a 1.2 m × 3 mm column packed with 5% OV-17 on Chromosorb W-HP (80–100 mesh) (B) were used. Preparative HPLC separations were accomplished on a 22.4 mm × 25 cm column containing ZORBAX Sil (Du Pont 880 Prep). UV detection at 215 nm was used. Melting points were determined with a Fisher "digital melting point and analyser" and are given without correction.

Trimethyl- and triethylvinylsilane and trimethylallylsilane were Fluka products. (α-Bromovinyl)triethylsilane,[28] alkyl dichlorocarbamates[3] and *N,N*-dichloro-*p*-toluenesulfonamide[29] were prepared by conventional procedures.

Addition of Dichlorocarbamates (2) to Vinylsilanes (1) (General Procedure). To a solution of 0.1 mol of **1** in CCl_4 (50 mL) under an argon atmosphere was added **2** (0.1 mol) and Cu_2Cl_2 (1 g) with stirring. The reaction mixture was heated to 45–50 °C. After 25–30 min an exothermic reaction started and continued for 20 min. The mixture was refluxed for another 15 min and cooled. After filtration and removal of the solvent by distillation, the residue was distilled under vacuum. The yields of chlorocarbamates **3** are given in Table I and ^1H NMR spectra in Table II.

Reduction of Chlorocarbamates 3 (General Procedure). To a solution of **3** (0.05 mol) in 50 mL of hexane cooled to 5–10 °C was added 50 mL of 20% aqueous Na_2SO_3, and the mixture was stirred for 4 h at room temperature. The organic layer was separated, dried with anhydrous Na_2SO_4, and filtered and the solvent distilled off. The residue was distilled under vacuum or recrystallized. The yields of carbamates **4** are summarized in Table I, and ^1H NMR and mass spectra are presented in Table III and IV.

Addition of *N,N*-Dichloro-*p*-toluenesulfonamide (5) to Vinylsilanes (1a and 1c). To a solution of **1a** or **1c** (0.1 mol) in 50 mL of CCl_4 under an argon atmosphere was added 0.1 mol of **5** in 50 mL of CCl_4 and Cu_2Cl_2 (1 g). The reaction mixture was heated to 45–50 °C. After 25–30 min an exothermal reaction commenced and continued for 20 min. The mixture was heated at reflux for another 15 min. After the catalyst was removed by filtration, the solution was concentrated by evaporation, and (1,2-dichloroethyl)trimethylsilane (**8**) was distilled off. The residue was dissolved in benzene (100 mL), cooled to 5–10 °C, treated with a 20% aqueous solution of Na_2SO_3 (70 mL), and stirred for 4 h at room temperature. The organic layer was separated, dried, and filtered. After the solvent was removed by distillation, the residue was recrystallized. Sulfonamides **7a** and **7c** were obtained (see Tables I, III, and IV).

Addition of Ethyl Dichlorocarbamate (2b) to Trimethylallylsilane (9). To 0.03 mol of **9** in CCl_4 (20 mL) was added 0.03 mol of **2b** and Cu_2Cl_2 (1 g) under an argon atmosphere with stirring. The stirring was continued for 4 h at room temperature. Following solvent removal by distillation, the residue was dissolved in hexane (50 mL), cooled to 5–10 °C, and treated with a 20% aqueous solution of Na_2SO_3 (30 mL). The reaction mixture was stirred for 4 h at room temperature. The organic layer was separated and dried with anhydrous Na_2SO_4. After removal of the solvent, a mixture of **10** and **11** (1:1) was obtained (see Tables I, III, and IV) which was resolved by preparative HPLC (ether–hexane (1:1) was used as eluent).

Addition of *N,N*-Dichloro-*p*-toluenesulfonamide (5) to Trimethylallylsilane (9). To a solution of **9** (0.03 mol) in 20 mL of CCl_4 cooled to 0–5 °C was added a solution of **5** (0.03 mol) in CCl_4 (15 mL) in air with stirring. The stirring was continued for 4 h at room temperature. After the solvent was removed by distillation, the residue was dissolved in benzene and then treated with aqueous Na_2SO_3 as described above. The resulting sulfonamide **12** was recrystallized from petroleum ether (see Tables I, III, and IV). The reaction of **9** and **5** in the presence of Cu_2Cl_2 was carried out as specified for the addition of **5** to **1a** and **1c**.

Ethyl (2-Bromo-2-chloroethyl)carbamate (18). Carbamate **18** was obtained by reacting vinyl bromide (0.05 mol) and **2b** (0.05 mol) in CCl_4 (50 mL) in the presence of Cu_2Cl_2 (1 g) as described above for the reaction of **1** and **2**: yield 76%; mp 48 °C; ^1H NMR [δ, *J* (Hz)] 1.27 (3 H, t, *J* = 6.5, OCH_2CH_3), 3.81 (2 H, m, CH_2N), 4.04 (2 H, q, *J* = 6.5, OCH_2CH_3), 5.24 (1 H, b s, NH), 5.78 (1 H, t, *J* = 6, HC(Cl)Br); mass spectrum, *m/e* (relative abundance, %) 229 (M^+ (^{35}Cl, ^{79}Br), 1), 184 (M^+ – OEt, 3), 141 (M^+ – NHCOOEt, 10), 102 (100), 58 (11), 45 (16).

1-(Alkoxycarbonyl)- and 1-(*p*-Tolylsulfonyl)-2-(trialkylsilyl)aziridines (13a–c and 14). To a solution containing 0.0024 mol of carbamate **4a–c** or sulfonamide **12** in 30 mL of appropriate solvent (Table V) supplemented with 0.00024 mol (10 mol %) of $(C_8H_{17})_4N^+Br^-$ or $Et_3N^+CH_2PhCl^-$ was added finely pulverized NaOH or K_2CO_3 (0.0048 mol) (Table V), and the mixture was stirred at room temperature. The course of the reaction was monitored by GLC (column A for **4a–c** cyclization and column B for 12 cyclization). As soon as the starting compound had disappeared, the reaction mixture was filtered through neutral Al_2O_3 and the solvent was removed by distillation under vacuum to yield aziridines **13a–c** and **14** (see Tables V–VII).

1-(Ethoxycarbonyl)-2-[(trimethylsilyl)methyl]aziridine (15). To a solution containing 0.0033 mol of an equimolar mixture of **10** and **11** in hexane (30 mL) and $(C_8H_{17})_4N^+Br^-$ (0.00033 mol) was added NaOH powder (0.0033 mol), and the mixture was stirred for 1 h at room temperature (GLC on column A was used as control). After filtration through neutral Al_2O_3 and removal of hexane by distillation in vacuo, **15** was obtained at 20% yield (see Tables V–VII).

1-(*p*-Tolylsulfonyl)-2-[(trimethylsilyl)methyl]aziridine (16). A mixture of sulfonamide **12** (0.0025 mol), $(C_8H_{17})_4N^+Br^-$ (0.00025 mol) and solid NaOH (0.0025 mol) in hexane (30 mL) was stirred for 2 h at 25 °C (GLC on column B was used as control). During this time the starting compound **12** completely disappeared from the solution containing **16** (see Tables V–VII).

Cyclization of Ethyl [2-Chloro-2-(trimethylsilyl)ethyl]carbamate (4b) under Ultrasonic Irradiation. A 25 cm^3 pyriform flask containing the solution of **4b** (0.6 g) in hexane (10 mL) and KOH powder (0.3 g) was placed in the center of an ultrasonic cleaner (Branson B-220, 100 W, 55 KHz) and was irradiated with ultrasound. The course of the reaction was monitored by GLC analysis (column A).

The amount of aziridine **13b** reached its peak (45%) after 0.5 h (see text).

Ethyl (2-Chloro-2-bromoethyl)carbamate (18) from Ethyl [2-Chloro-2-bromo-2-(trialkylsilyl)ethyl]carbamate (4d and 4e). To a solution of **4d** or **4e** in an appropriate solvent was added finely pulverized base and catalyst (see Table VIII). The mixture was stirred at room temperature until the starting substance **4d** or **4e** disappeared from the reaction mixture (GLC on column A was used as control). The reaction time and yield of **18** are given in Table VIII. The resulting product was identical (^1H NMR, mass spectroscopy data, and GLC retention time) to carbamate **18** obtained by the addition of *N,N*-dichlorourethane to vinyl bromide (see Tables III and IV).

Ethyl [2-Chloro-2-(methoxycarbonyl)ethyl]carbamate (19) from Ethyl [2-Chloro-2-(methoxycarbonyl)-2-(diethylmethylsilyl)ethyl]carbamate (4f). To a solution of **4f** (0.0024 mol) and $(C_8H_{17})_4N^+Br^-$ (0.00024 mol) was added NaOH powder

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(0.0048 mol), and the mixture was stirred at room temperature for 2 h (GLC on column B was used as control). After standard workup, there was obtained **19**, which was identical with that prepared from *N,N*-dichlorourethane and methyl acrylate:[26] yield 57% (GLC data).

Registry No. **1a**, 754-05-2; **1c**, 1112-54-5; **1d**, 13683-41-5; **1e**, 18276-17-0; **1f**, 97042-85-8; **2a**, 16487-46-0; **2b**, 13698-16-3; **3a**, 91935-98-7; **3b**, 97042-67-6; **3c**, 97042-68-7; **3d**, 97042-69-8; **3e**, 97042-70-1; **3f**, 97042-71-2; **4a**, 91935-99-8; **4b**, 97042-72-3; **4c**, 97042-73-4; **4d**, 97042-74-5; **4e**, 97059-47-7; **4f**, 97042-75-6; **5**, 473-34-7; **7a**, 97042-76-7; **7c**, 97042-84-7; **7d**, 97042-77-8; **9**, 762-72-1; **10**, 91936-03-7; **11**, 91936-04-8; **12**, 97042-78-9; **13a**, 91936-00-4; **13b**, 97042-79-0; **13c**, 97042-80-3; **14**, 97042-81-4; **15**, 91936-05-9; **16**, 97042-82-5; **18**, 97042-83-6; **19**, 13698-14-1; CH_2=CHBr, 593-60-2.

Supplementary Material Available: Tables IV and VII, mass spectra (3 pages). Ordering information is given on any current masthead page.

Modeling Macroscale Metal Vapor Reactions. 2.† Bis(arene)iron Revisited

Pascale D. Morand and Colin G. Francis*

Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1062

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The reaction of iron vapor with naphthalene and 1-methylnaphthalene was studied by metal atom matrix optical spectroscopy in the temperature range 30–290 K. Two different products were obtained, which have been assigned to a highly unstable, 16-electron bis(η^4-naphthalene)iron(0) and a room-temperature-stable, 20-electron bis(η^6-naphthalene)iron(0) species. The former is observed in the range 30–77 K, while the latter forms at $T \geq 150$ K. Assignments for these complexes were based on an extensive study involving iron atoms and selected arene ligands, also including cyclohexadiene as a model for η^4-binding.

Introduction

The versatility of arene ligands in their mode of coordination to transition metals represents a fundamental concept in the current understanding of homogeneous[1] and heterogeneous[2] catalytic processes involving aromatic molecules. Interest in such systems has resulted in an extensive research effort directed toward the structural, electronic, and catalytic properties of (arene)metal complexes.[3] Our studies have recently focused on the interaction of iron atoms with aromatic molecules, the primary motivation being our interest in the ligand properties of fused rings such as naphthalene.[4] In addition, we[5] and others[6] have shown that thermally unstable complexes, specifically bis(toluene)iron, provide valuable precursors for the preparation of supported metal particles. The need to obtain precisely defined materials by reproducible doping procedures has prompted us to pose several questions regarding the nature and behavior of the products formed when iron atoms are allowed to react with aromatic ligands at low temperature.

It is perhaps surprising that, in spite of the considerable attention the Fe/arene system has received, the identity of the initially formed species remains unresolved. Although the product can be intercepted at low temperature by stabilizing ligands, such as phosphine, phosphite, or selected dienes,[7] resulting in the isolation of complexes of the form (η^6-arene)FeL_n, its poor thermal stability has prevented its definitive characterization in macroscale metal vapor reactions.

Attempts to elucidate the nature of the product by matrix-isolation spectroscopic studies have led so far to differing conclusions. It has been reported,[8] on the basis of infrared spectroscopy, that iron reacts with benzene in C_6H_6/Ar matrices at 10–12 K *and* in pure C_6H_6 matrices at 77 K to yield a monoarene species, (η^6-C_6H_6)Fe. However, other workers have expressed their preference for a bis(arene)iron formulation.[9,10] Indeed, it could be argued that one would not anticipate a monoarene complex to be favored in neat C_6H_6 matrices. The reaction of iron with toluene in solution-phase experiments at 150 K,[11] as observed by UV–visible spectroscopy, reveals the formation of a single species, suggested to be (η^6-$C_6H_5CH_3$)Fe(η^4-$C_6H_5CH_3$), *but* two species on cocondensation at 77 K, viz., the η^6:η^4 complex and another species of uncertain composition. Keeping in mind the existence of (η^6-C_6Me_6)$_2$Fe,[12]

† For part 1 of this series, see: Morand, P. D.; Francis, C. G. *Inorg. Chem.* **1985**, *24*, 56.

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