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Synthesis of new vinylsilanes containing an asymmetric silicon via platinum catalyzed hydrosilylation of acetylene and monosubstituted alkynes

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Abstract

A series of new racemic vinylsilanes has been obtained by hydrosilylation reaction of acetylene and monosubstituted alkynes with (±)-α-NpPhMeSiH and (±)-$N(CH_2CH_2O)_3SiCH_2PhMeSiH$ in the presence of platinum-containing catalysts.

Introduction

It is accepted in the literature that the initial process in hydrosilylation of alkenes with chiral silanes R_3Si^*H involves stereospecific retentive interaction of the Si*–H bond with the reactive transition metal centre to form a metal–silicon bond which then reacts in a variety of ways with complete retention of silicon atom configuration in hydrosilylation reaction [1]. Thus, the addition of (+)-α-naphtylphenylmethylsilane (R_3Si^*H) to 1-octene proceeds with high chemical yields (up to 85%) and even under relatively strong conditions (130–140°C) with a high degree of stereospecifity in the presence of various platinum catalysts (5% Pt/C, H_2PtCl_6 and $[PtCl_2(C_2H_4)]_2$ [2,3]. All the catalysts permit retention of configuration at the asymmetric silicon centre.

While the addition of various trisubstituted silanes to acetylene and other alkynes has been extensively studied for the last 20 years there have been no reports on the hydrosilylation of the C≡C bond by optically active hydrosilanes. At present there are several points of view on the mechanism of C≡C bond hydrosilylation arising from the regio- and stereoselectivity of this reaction [1,4–6]. That is why it is important to explore the investigations of C≡C bond hydrosilylation with optically active hydrosilanes in order to extend our knowledge about the mechanism of these reactions.

In this work we present our recent results on addition of silanes (±)-α-naphtylphenylmethylsilane (α-NpPhMeSiH) **(1)** and (±)-(silatranylmethyl)methylphenylsilane ($N(CH_2CH_2O)_3SiCH_2PhMeSiH$) **(2)** to acetylene and monosubstituted

alkynes. Our main aim was to find effective and selective catalysts for addition of racemic mixtures of the above silanes to the C≡C bond to produce new vinylsilanes with asymmetric silicon atom. In the further perspective the results obtained will allow us to find the most effective systems for C≡C bond hydrosilylation with optically active silanes, mentioned above.

Results and discussion

Usually, in the presence of platinum complexes trisubstituted silanes undergo *cis*-addition across the C≡C bond to yield the β-adduct with the *trans*-(*E*) configuration [1]. In this work we report on catalytic and synthetic aspects of the hydrosilylation of acetylene and some its monoderivatives by these two silanes leading to formation of new vinylsilanes according to the following equation:

$$\underset{(\mathbf{1,2})}{R_3SiH} + \underset{(\mathbf{3a-e})}{CH{\equiv}CR'} \xrightarrow[25-100°C,\ 6-85\ h]{Cat,\ 10^{-4}\ M} \underset{\alpha}{H_2C{=}CR'(SiR_3)} + \underset{\beta}{R_3SiCH{=}CHR'}$$

$$\underset{(\mathbf{4,\ 5a-e})}{\qquad\qquad} \qquad \underset{(\mathbf{6,\ 7a-e})}{\qquad\qquad}$$

(**1**, **4**, **6**: R_3 = (±)-α-NpPhMe; **2**, **5**, **7**: R_3 = (±)-(N($CH_2CH_2O)_3SiCH_2$)PhMe; **a**: R′ = H; **b**: R′ = Ph; **c**: R′ = COOMe; **d**: R′ = CMe_3; **e**: R′ = $SiMe_3$)

The following five platinum complexes $(PPh_3)_4Pt$, $(PPh_3)_2Pt(C_2H_4)$, $(PPh_3)_2Pt(O_2)$, $(PPh_3)_2PtCl_2$ and H_2PtCl_6 (cyclohexanone) were used to catalyse these reactions.

The results of catalytic experiments leading to optimization of catalyst activity and conditions of the reactions in the synthesis of vinylsilanes **4–7**, **a–e** are compiled in Tables 1 and 2.

It should be pointed out that hydrosilylation of acetylene gives vinylsilane which is accompanied by a small amount (5–10%) of bissilylethane. The reaction of monosubstituted acetylenes brings about predominantly a formation of a mixture of β-(*trans*) (**6**, **7b–e**) and α-adducts (**4**, **5b–e**) with a preponderance of the β-form. The addition of these silanes to alkynes with strong electron-donor substituents e.g. $C(CH_3)_3$ takes place regiospecifically with *anti*-Markovnikov selectivity to give β-adduct with most of the catalysts used (similarly to trialkylsilanes [7]).

On the other hand, very low yields of the hydrosilylation reaction of HC≡CCOOMe (**3c**) were noted for most of the catalysts. An exceptionally high yield (but low regioselectivity) was found using $Pt(PPh_3)_4$ as a catalyst for the reaction with both hydrosilanes. However our experiments showed that hydrosilylation of methyl propiolate (**3c**) with both hydrosilanes proceeds almost quantitatively in THF with the same regioselectivity as that obtained without solvent.

H_2PtCl_6 (cyclohexanone) and $(PPh_3)_2Pt(C_2H_4)$ appeared to be very effective catalysts particularly in the hydrosilylation of phenylacetylene even at room temperature. At ambient temperatures phosphine complexes of platinum(0) [e.g. $Pt(PPh_3)_4$ and $Pt(PPh_3)_2(C_2H_4)$] are the most active and regioselective catalysts for almost all reactions examined. It is worthy of note that selective monoaddition is observed in these processes (except in the case of the reaction with acetylene) which is due to steric effects caused by substituents at silicon. Besides, no dehydrocondensation reactions accompany the hydrosilylation.

Table 1

Catalytic hydrosilylation of alkynes with (±)α-NpPhMeSiH [a]

Alkyne	Catalyst (10^{-4} M%)	Conditions Temp./time (°C/h)	Products, yield [b] (%) ($\beta:\alpha$)
HC≡CH	H_2PtCl_6/cyclohexanone	45/6	95 –
		60/6	99 –
HC≡CPh	$(PPh_3)_4Pt$	25/85	64(91:9)
		60/15	91(87:13)
	$(PPh_3)_2Pt(C_2H_4)$	25/85	90(72:28)
		60/15	99(92:8)
	$(PPh_3)_2Pt(O_2)$	25/85	38(91:9)
		60/15	90(93:7)
	$(PPh_3)_2PtCl_2$	25/85	31(92:8)
		60/15	7(96:4)
	H_2PtCl_6/cyclohexanone	25/85	99(87:13)
HC≡CCOOMe	$(PPh_3)_4Pt$	60/15	80(56:44)
			99(56:44) [c]
	$(PPh_3)_2Pt(C_2H_4)$	60/15	3(66:34)
	$(PPh_3)_2Pt(O_2)$	60/15	0
	$(PPh_3)_2PtCl_2$	60/15	0
	H_2PtCl_6/cyclohexanone	25/85	10(89:11)
HC≡CCMe$_3$	$(PPh_3)_4Pt$	60/15	99(100:0)
	$(PPh_3)_2Pt(C_2H_4)$	60/15	99(100:0)
	$(PPh_3)_2Pt(O_2)$	60/15	99(76:24)
	$(PPh_3)_2PtCl_2$	60/15	40(61:39)
	H_2PtCl_6/cyclohexanone	25/85	98(100:0)
HC≡CSiMe$_3$	$(PPh_3)_4Pt$	60/15	99(100:0)
	$(PPh_3)_2Pt(C_2H_4)$	60/15	99(100:0)
	$(PPh_3)_2Pt(O_2)$	60/15	99(100:0)
	$(PPh_3)_2PtCl_2$	60/15	7(100:0)
	H_2PtCl_6/cyclohexanone	25/85	99(89:11)

[a] [alkyne]:[silane] = 1:1. [b] GC data. [c] THF used as a solvent.

It should be noted that the adducts ratio obtained ($\beta:\alpha$) is similar to those observed in the case of hydrosilylation reactions of the same monosubstituted alkynes with aryl- and hetarylhydrosilanes [8,9].

These experimental studies enable the hydrosilylation of acetylene and monosubstituted acetylenes catalyzed by complexes of platinum to be applied to the synthesis of a new group of vinylsilanes with high yield and high regioselectivity. Under some conditions (substituents at the C≡C bond, selected catalysts and temperature) the reaction occurs regiospecifically giving exclusively the *β-trans* adduct.

All details on synthesis procedures and spectroscopic identification of products are presented in the Experimental section.

Experimental

Materials

The alkynes were purchased mainly from Fluka AG and starting hydrosilanes were prepared according to the literature; α-NpPhMeSiH (**1**) [10] and

Table 2

Catalytic hydrosilylation of alkynes with (±)-[$N(CH_2CH_2O)_3SiCH_2$]PhMeSiH [a]

Alkyne	Catalysts (10^{-4} M%)	Conditions Temp./time (°C/h)	Products. yield [b] (%) ($\beta:\alpha$)
HC≡CH	H_2PtCl_6/cyclohexanone	45/6	97 –
		60/6	99 –
HC≡CPh	$(PPh_3)_4Pt$	25/85	43(58:42)
		40/24	67(77:23)
		60/6	87(73:27)
		60/15	99(81:19)
		100/6	98(84:16)
	$(PPh_3)_2Pt(C_2H_4)$	25/85	97(85:15)
		40/24	58(76:24)
		60/6	56(74:26)
		60/15	93(71:'29)
		100/6	99(81:19)
	$(PPh_3)_2Pt(O_2)$	25/85	41(85:15)
		40/24	52(81:19)
		60/15	85(78:29)
		100/6	99(77:23)
	$(PPh_3)_2PtCl_2$	25/85	34(76:24)
		40/24	44(83:17)
		60/6	52(78:22)
		60/15	85(78:22)
		100/6	44(83:17)
	H_2PtCl_6/cyclohexanone	25/85	95(73:27)
HC≡CCOOMe	$(PPh_3)_4Pt$	60/15	14(61:39)
			99(57:43) [c]
	$(PPh_3)_2Pt(C_2H_4)$	60/15	6(60:40)
	$(PPh_3)_2Pt(O_2)$	60/15	16(60:40)
	$(PPh_3)_2PtCl_2$	60/15	3(55:45)
	H_2PtCl_6/cyclohexanone	25/85	4(71:29)
$HC{\equiv}CCMe_3$	$(PPh_3)_4Pt$	60/15	99(100:0)
	$(PPh_3)_2Pt(C_2H_4)$	60/15	99(100:0)
	$(PPh_3)_2Pt(O_2)$	60/15	99(100:0)
	$(PPh_3)_2PtCl_2$	60/15	99(100:0)
	H_2PtCl_6/cyclohexanone	25/85	93(100:0)
$HC{\equiv}CSiMe_3$	$(PPh_3)_4Pt$	60/15	99(71:29)
	$(PPh_3)_2Pt(C_2H_4)$	60/15	85(80:20)
	$(PPh_3)_2Pt(O_2)$	60/15	99(64:36)
	$(PPh_3)_2PtCl_2$	60/15	75(79:21)
	H_2PtCl_6/cyclohexanone	25/85	97(70:30)

[a] [alkyne]:[silane] = 1:1. [b] GC data. [c] THF used as a solvent.

$N(CH_2CH_2O)_3SiCH_2SiPhMeSiH$ (**2**) [11]. The platinum catalysts were prepared according to the literature: $(PPh_3)_4Pt$ [12], $(PPh_3)_2Pt(C_2H_4)$ [13], $[(PPh_3)_2Pt(O_2)]$ [12], $[(PPh_3)_2PtCl_2]$ [12] and H_2PtCl_6 (cyclohexanone) [14]. Acetylene was Analytical Grade (Polish Technical Gases).

Products examination

^1H NMR spectra were recorded with a Bruker WH-90/DS and WM-360 spectrometers in $CDCl_3$ using TMS as internal standard. Mass spectra were

recorded with a Kratos MS-25 GC-MS (70 eV). GC analysis was carried out with a Chrom-5 apparatus equipped with a flame-ionization detector. Glass columns (1.2 m × 3 mm) packed with 3% JXR/Chromosorb W-AW (60-80 mesh) were used for analysis, the carrier gas was helium (50 ml/min).

Hydrosilylation reactions of acetylene (general procedure)

The reaction was performed in a 10 ml all glass flow reactor. The temperature of the reactor was kept constant (±0.5°C) by oil under thermostatic control circulated through the heating jacket. Acetylene was bubbled (0.25 l/h) through mixture containing a 10% solution of hydrosilane in benzene and 10^{-4} *M*% of catalyst at 45 or 60°C for 6 h. Full details of the procedure have been described previously [15].

Hydrosilylation reactions of monosubstituted alkynes (general procedure)

Mixtures of 0.3 mmol of hydrosilane, 0.3 mmol of alkyne and 10^{-4} *M*% of catalyst were stirred for 6, 15 or 24 h at 24, 40, 60 or 100°C in a glass microautoclave (Pierce). Processes were controlled by GC. Products were separated with HPLC Gilson apparatus equipped with semipreparative column (250 × 10 mm) packed with Silasorb SPH-9μ.

Spectroscopic data of products

*(±)-Methylnaphtylphenylsilylethene (**4a**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.78 (s, 3H, Si–CH_3); 5.81 (dd, 1H, α-H, J_{ac} 19.5 Hz, J_{ab} 3.7 Hz); 6.21 (dd, 1H, b-H, J_{bc} 14.2 Hz, J_{ab} 3.7 Hz); 6.64 (dd, 1H, c-H, J_{bc} 14.2 Hz, J_{ac} 19.5 Hz); 7.31–8.01 (m, 12H, Si–C_6H_5, Si–$C_{10}H_7$); Mass spectrum *m/e* (rel. intensity, %): 274(M^+, 49), 216(6), 260(25), 259(100), 248(6), 247(25), 234(5), 233(23), 231(12), 229(6), 215(7), 203(7), 202(10), 197(14), 196(45), 195(20), 183(8), 182(7), 181(31), 171(12), 170(23), 169(23), 168(7), 167(17), 156(7), 155(39), 154(6), 153(9), 152(13), 147(8), 146(14), 145(6), 141(11), 131(6), 129(12), 128(7), 127(5), 123(12), 122(6), 121(34), 120(9), 115(5), 107(6), 105(33), 103(6), 79(6), 77(9), 53(23), 51(8), 43(20); IR (cm^{-1}): 1598(ν(C=C)).

*(±)-1-Methylnaphtylphenylsilyl-1-phenylethene (**4b**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.78 (s, 3H, Si–CH_3); 5.59 (d, 1H, *J* 2.5 Hz), 5.70 (d, 1H, *J* 2.5 Hz); 7.08-8.13 (m, 17H, Si-C_6H_5, Si-$C_{10}H_7$, C-C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 350 (M^+, 36), 335(13), 272(14), 259(13), 257(15), 249(7), 248(23), 247(100), 245(5), 231(7), 229(7), 228(6), 197(6), 170(7), 169(27), 167(12), 155(8), 136(6), 129(5), 121(6), 105(12), 103(5), 77(7), 53(8); IR (cm^{-1}): 1608(ν(C=C)).

*(±)-1-Methylnaphtylphenylsilyl-1-methoxycarbonylethene (**4c**).* ^{1}H NMR ($CDCl_3$, δ, ppm): 0.92 (s, 3H, Si-CH_3); 3.6 (s, 3H, C–OCH_3); 5.96 (d, 1H, *J* 2.78 Hz); 7.03 (d, 1H, *J* 2.78 Hz); 7.25–7.98 (m, 12H, Si–C_6H_5, Si–$C_{10}H_7$); Mass spectrum *m/e* (rel, intensity, %): 332(M^+, 38), 318(13), 317(46), 287(19), 285(34), 277(12), 263(32), 257(19), 255(20), 254(12), 247(26), 245(17), 239(11), 233(15), 231(19), 223(22), 206(15), 205(81), 203(20), 202(36), 201(19), 195(14), 175(20), 171(16), 169(33), 167(23), 166(18), 165(100), 155(29), 153(14), 152(16), 151(61), 141(15), 137(12), 129(46), 128(17), 123(12), 121(36), 115(20), 105(28), 103(11), 102(16), 91(17), 77(15), 59(27), 53(25), 43(17); IR (cm^{-1}): 1595 (ν(C=C)).

*(±)-1-Methylnaphtylphenylsilyl-1-trimethylsilylethene (**4e**).* Mass spectrum *m/e* (rel. intensity, %): 346(M^+, 17), 272(6), 257(6), 253(13), 249(6), 248(24), 247(100),

210(7), 196(15), 195(11), 185(12), 169(16), 167(7), 155(6), 135(19), 105(8), 73(22), 45(6), 43(8).

(±)-Methylphenyl(silatranylmethyl)silylethene (5a). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.07 (s, 2H, Si–CH_2), 0.41 (s, 3H, Si–CH_3), 2.77 (t, 6H, N–CH_2), 3.71 (t, 6H, O–CH_2), 5.80 (dd, 1H, α-H, $J_{ac} = 19.4$ Hz, $J_{ab} = 5.0$ Hz), 5.99 (dd, 1H, b-H, $J_{bc} = 14.7$ Hz, $J_{ab} = 5.0$ Hz), 6.56 (dd, 1H, c-H, $J_{bc} = 14.7$ Hz, $J_{ac} = 19.4$ Hz), 7.20–7.61 (m, 5H, C_6H_5) Mass spectrum *m/e* (rel. intensity, %): 335 (M^+, 0.4), 321(6), 320(23), 309(10), 308(38), 259(7), 258(33), 195(6), 175(13), 174(100), 145(6), 121(7), 105(7), 103(5), 91(8), 56(9), 45(7), 43(7), 42(8), 41(6); IR (cm^{-1}): 1600(ν(C=C)).

(±)-1-Methylphenyl(silatranylmethyl)silyl-1-phenylethene (5b). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.10 (s, 2H, Si–CH_2); 0.46 (s, 3H, Si–CH_3); 2.67 (t, 6H, CH_2); 3.64 (t, 6H, O–CH_2), 5.71 (d, 1H, *J* 3.2 Hz); 5.90 (d, 1H, *J* 3.2 Hz); 7.18–8.17 (m, 10H, Si–C_6H_5, C–C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 396(M^+ – Me, 2), 310(10), 308(100), 264(5), 195(12), 174(23), 105(6), 103(6), 91(6), 56(6), 42(5); IR (cm^{-1}): 1610(ν(C=C)).

(±)-1-Methylphenyl(silatranylmethyl)silyl-1-methoxycarbonylethene (5c). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.09 (d, 1H, CH_2, *J* 13.6 Hz); 0.25 (d, 1H, CH_2, *J* 13.6 Hz); 0.48 (s, 3H, Si–CH_3); 2.72 (t, 6H, CH_2); 3.62 (s, 3H, O–CH_3); 3.65 (t, 6H, O–CH_2); 6.02 (d, 1H, *J* 3.23 Hz); 6.78 (d, 1H, *J* 3.23 Hz); 7.19–7.65 (m, 5H, Si–C_6H_5); Mass spectrum, *m/e* (rel. intensity, %): 378(M^+ – Me, 2.5), 324(19), 316(6), 310(6), 309(10), 308(27), 264(6), 263(5), 262(29), 195(5), 176(7), 175(14), 174(100), 145(5), 121(5), 91(6), 78(6), 69(6), 56(8), 55(6), 42(6); IR (cm^{-1}): 1595(ν(C=C)).

(±)-1-Methylphenyl(silatranylmethyl)silyl-1-tert-butylethene (5d). Mass spectrum, *m/e* (rel. intensity, %): 391(M^+, 0.3), 378(5), 377(12), 376(39), 334(12), 316(5), 315(11), 314(42), 310(11), 309(26), 308(100), 231(6), 195(9), 188(5), 181(5), 179(5), 175(10), 174(70), 145(7), 135(7), 121(9), 119(7), 105(18), 103(5), 91(9), 73(5), 70(6), 69(6), 56(10), 55(9), 54(5), 45(6), 43(8), 42(9), 41(16), 39(5), 29(7).

(±)-1-Methylphenyl(silatranylmethyl)silyl-1-trimethylsilylethene (5e). ^{1}H NMR ($CDCl_3$, δ, ppm): –0.06(s, 9H, Si–CH_3); 0.09 (d, 2H, Si–CH_2); 0.42 (s, 3H, Si–CH_3); 2.69 (t, 6H, CH_2); 3.62 (t, 6H, O–CH_2); 6.38 (s, 1H); 7.18–7.61 (m, 5H, Si–C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 407(M^+, 0.1), 392(8), 330(6), 310(11), 309(26), 308(100), 195(8), 174(21), 135(6), 73(14), 70(5), 56(5), 41(5); IR (cm^{-1}): 1565(ν(C=C)).

(±)-(E)-1-Methylnaphtylphenylsilyl-2-phenylethene (6b). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.84 (s, 3H, Si–CH_3); 6.87 (d, 1H, *J* 18 Hz, α-H); 6.97 (d, 1H, *J* 18 Hz, b-H); 7.17–8.07 (m, 17H, Si–C_6H_5, Si–$C_{10}H_7$, C–C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 350(M^+, 72), 336(7), 335(29), 273(13), 272(41), 260(24), 256(100), 258(19), 257(81), 255(6), 248(5), 247(23), 245(7), 234(8), 233(33), 232(8), 231(22), 230(14), 229(27), 228(19), 222(9), 215(9), 208(11), 207(52), 205(5), 203(6), 202(10), 198(12), 197(62), 195(5), 184(8), 183(40), 181(9), 180(5), 179(8), 171(13), 170(23), 169(23), 168(6), 167(17), 156(10), 155(64), 154(5), 153(6), 152(12), 146(8), 145(39), 136(23), 135(9), 131(6), 129(15), 128(14), 122(7), 121(48), 120(11), 119(6), 107(8), 106(6), 105(54), 103(8), 102(9), 91(6), 79(7), 78(12), 77(12), 55(6), 53(20), 51(11), 50(6), 43(26); IR (cm^{-1}): 1603(ν(C=C)).

(±)-(E)-1-Methylnaphtylphenylsilyl-2-methoxycarbonylethene (6c). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.82 (s, 3H, Si–CH_3); 3.71 (s, 3H, C–OCH_3); 6.34 (d, 1H, *J* 18.9

Hz, α-H); 7.67 (d, 1H, *J* 18 Hz, b-H); 7.24–7.96 (m, 12H, Si–C_6H_5, Si–$C_{10}H_7$); Mass spectrum *m/e* (rel. intensity, %): 332(M^+, 31), 331(23), 317(22), 259(7), 257(15), 247(14), 242(10), 233(12), 231(11), 229(10), 226(7), 205(10), 203(9), 202(15), 201(34), 196(8), 195(13), 181(8), 171(12), 169(18), 167(12), 165(12), 155(20), 153(10), 152(22), 151(100), 137(12), 129(9), 123(14), 121(26), 116(7), 105(19), 91(11), 77(8), 59(15), 53(18), 43(10); IR (cm^{-1}): 1595(ν(C=C)).

(±)-(E)-1-Methylnaphtylphenylsilyl-2-tert-butylethene (6d). ^1H NMR ($CDCl_3$, δ, ppm): 0.71 (s, 3H, Si–CH_3); 1.00 (s, 9H, C–CH_3); 5.97 (d, 1H, *J* 19.8 Hz, α-H); 6.18 (d, 1H, *J* 19.8 Hz, b-H); 7.10–8.06 (m, 12H, Si–C_6H_5, Si–$C_{10}H_7$); Mass spectrum *m/e* (rel. intensity, %): 330(M^+, 41), 316(15), 275(7), 274(26), 273(100), 260(7), 259(8), 257(6), 248(14), 247(57), 246(7), 245(18), 234(16), 233(69), 232(7), 231(20), 215(8), 203(8), 202(12), 197(5), 196(16), 195(79), 187(8), 185(8), 183(8), 182(11), 181(7), 179(8), 172(5), 171(24), 170(21), 169(34), 168(7), 167(20), 165(12), 156(7), 155(43), 154(6), 153(6), 146(5), 145(28), 140(12), 135(20), 129(13), 128(9), 123(7), 122(8), 121(59), 120(5), 119(5), 115(6), 105(36), 91(6), 83(7), 79(6), 78(6), 77(6), 73(10), 67(8), 59(14), 57(15), 55(9), 53(21), 51(6), 43(25), 41(24); IR (cm^{-1}): 1620(νC=C)).

(±)-(E)-1-Methylnaphtylphenylsilyl-2-trimethylsilylethene (6e). ^1H NMR ($CDCl_3$, δ, ppm.): 0.09 (s, 9H, Si–CH_3); 0.75 (s, 3H, Si–CH_3); 6.80 (d, 1H, *J* 22.5 Hz, α-H); 7.02 (d, 1H, *J* 22.5 Hz, b-H), 7.25-8.03 (m, 12H, Si–C_6H_5, Si–$C_{10}H_7$); Mass spectrum *m/e* (rel. intensity, %): 346(M^+, 13), 331(15), 273(14), 272(6), 269(11), 268(36), 258(9), 257(24), 253(7), 248(17), 247(69), 244(15), 234(7), 233(30), 231(12), 228(10), 219(7), 218(28), 215(6), 212(7), 211(23), 210(18), 208(7), 203(12), 202(7), 297(10), 196(40), 195(100), 186(16), 185(32), 181(12), 179(7), 171(13), 170(9), 169(40), 168(6), 167(21), 161(18), 155(22), 146(10), 145(26), 136(8), 135(51), 129(10), 128(6), 121(25), 119(5), 115(6), 105(25), 83(6), 77(5), 74(9), 73(3), 59(32), 58(5) 53(19), 45(25), 43(27); IR (cm^{-1}): 1595 (ν(C=C)).

(±)-(E)-1-Methylphenyl(silatranylmethyl)silyl-2-phenylethene (7b). ^1H NMR ($CDCl_3$, δ, ppm): 0.10 (s, 2H, Si–CH_2); 0.46 (s, 3H, Si–CH_3); 2.67 (t, 6H, CH_2); 3.64 (t, 6H, O–CH_2); 6.72 (d, 1H, *J* 19.1 Hz, α-H); 6.92 (d, 1H, *J* 19.1 Hz, b-H); 7.18–8.17 (m, 10H, Si–C_6H_5, C–C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 411 (M^+, 14), 397(10), 396(29), 335(6), 334(20), 309(10), 308(39), 233(6), 232(13), 231(65), 230(6), 195(9), 189(7), 188(32), 181(7), 179(8), 176(6), 175(14), 174(100), 145(10), 135(9), 130(6), 121(11), 119(8), 117(7), 115(6), 105(14), 104(12), 103(10), 102(7), 91(12), 89(6), 78(8), 77(7), 70(6), 56(13), 54(5), 51(6), 45(8), 43(10), 42(10), 41(7); IR (cm^{-1}): 1610(ν(C=C)).

(±)-(E)-1-Methylphenyl(silatranylmethyl)silyl-2-methoxycarbonylethene (7c). ^1H NMR ($CDCl_3$, δ, ppm): 0.04 (d, 1H, CH_2, *J* 19.5 Hz); 0.11 (d, 1H, CH_2, *J* 19.9 Hz); 0.42 (s, 3H, Si–CH_3); 2.75 (t, 6H, CH_2); 3.69 (t, 6H, O–CH_2); 3.72 (s, 3H, O–CH_3); 6.22 (d, 1H, *J* 18.8 Hz, α-H); 7.40 (d, 1H, *J* 18.8 Hz, b-H); 7.26–7.81 (m, 5H, Si–C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 379(6), 378(M^+ – Me, 16), 316(16), 310(7), 309(5), 308(13), 176(6), 175(16), 174(100), 121(5), 91(6), 42(5), 29(6); IR (cm^{-1}): 1605(ν(C=C)).

(±)-(E)-1-Methylphenyl(silatranylmethyl)silyl-2-tert-butylethene (7d). ^1H NMR ($CDCl_3$, δ, ppm.): 0.008 (s, 2H, Si–CH_2); 0.34 (s, 3H, Si–CH_3); 1.00 (s, 9H, C–CH_3); 2.72 (t, 6H, CH_2); 3.66 (t, 6H, O–CH_2); 5.73 (d, 1H, *J* 18.93 Hz, α-H); 6.10 (d, 1H, *J* 18.93 Hz, b-H); 7.20–7.67 (m, 5H, Si–C_6H_5); Mass spectrum *m/e*

(rel. intensity, %): 376(3.5), 314(7), 310(24), 308(100), 195(9), 174(26), 41(6); IR (cm^{-1}): 1620(ν(C=C)).

(±)-(E)-1-Methylphenyl(silatranylmethyl)silyl-2-trimethylsilylethene (7e). ^1H NMR ($CDCl_3$, δ, ppm): 0.02 (s, 2H, Si–CH_2); 0.05 (s, 9H, Si–CH_3); 0.36 (s, 3H, Si–CH_3); 6.61 (d, 1H, *J* 22.6 Hz, α-H); 6.82 (d, 1H, *J* 22.45 Hz, b-H); 7.64–7.22 (m, 5H, C_6H_5); Mass spectrum *m/e* (rel. intensity, %): 392(2), 310(10), 309(25), 308(100), 228(5), 195(8), 174(16), 135(5), 73(5), 70(5); IR (cm^{-1}): 1565(ν(C=C)).

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