

Palladium-Induced Intramolecular Coupling Reactions of Some Alkenyl(*o*-iodobenzyl)silanes

by Zhu Teng and Reinhart Keese*

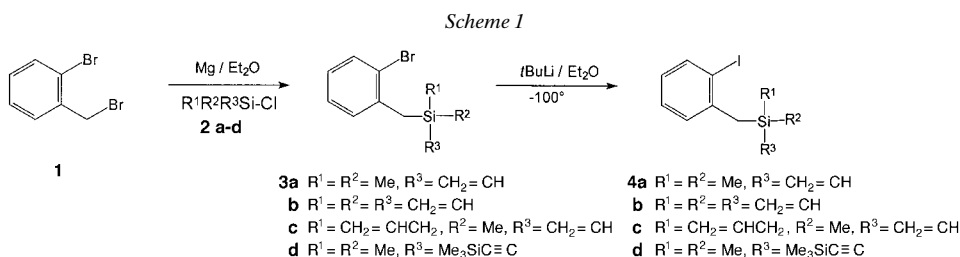
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern

The first examples for the formation of siloles by intramolecular *Heck*-type cyclizations are reported. Upon treatment with $[\text{PdCl}_2(\text{PPh}_3)]$, the (*o*-iodobenzyl)vinylsilanes **4a** and **4c** give the siloles **5a** and **5c** as well as the vinyl-transfer products **6a** and **6c** (*Scheme 2*), respectively. Under CO pressure **4a** and **4c** react to the carbonylation products in modest yields (*Scheme 3*). In addition, carbonylative crossover is observed with **4a**.

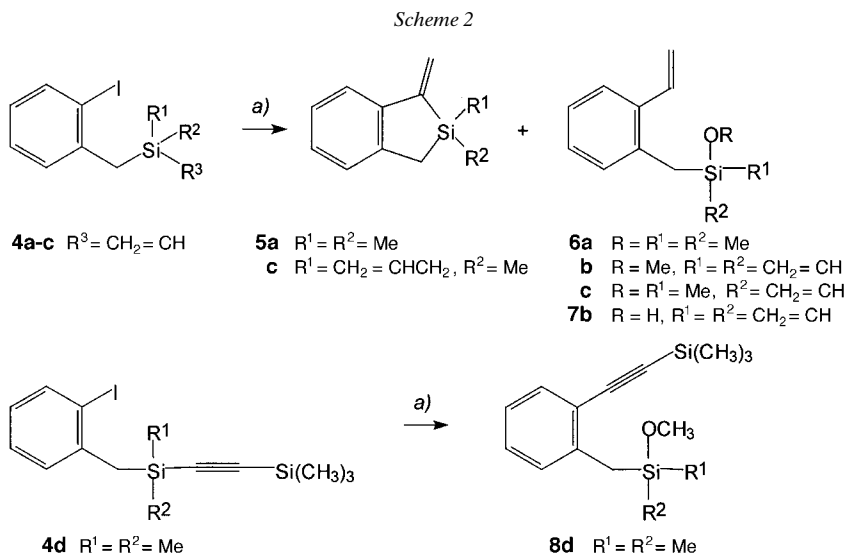
Introduction. – Homogeneous catalysis plays an important rôle in advanced synthesis [1]. An important tool for this type of reactions is provided by the intermolecular as well as the intramolecular *Heck*-type cross-coupling reactions with Pd^0 and Pd^{II} complexes as very efficient catalysts [2]. More recently, the potential of organosilicium compounds in cross-coupling reactions has been explored [3][4]. Thus, iodoarenes and 1-iodoalkenes react with trimethyl(vinyl)silane in the presence of $[\{\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)\}_2]$ as catalyst after activation of the silane with ‘naked’ F^- ions to give vinylarenes and -dienes, respectively. *Hiyama* has also explored the carbonylative coupling of organofluorosilanes with organic iodides and found these reactions to be an efficient process when the vinylic C–Si bond is activated by raising the coordination number of the Si-atom *via* addition of ‘naked’ F^- ions [5][6]. Under these conditions, carbonylation with subsequent intermolecular vinyl transfer is an efficient process and has become a valuable addition to the arsenal of preparative methods.

Within the scope of our interest in Si-heterocyclic compounds, we considered intramolecular *Heck*-type cyclizations of (*o*-iodobenzyl)vinylsilanes with the formation of siloles as a feasible concept. We argued that such reactions might be faster than the intermolecular coupling reactions and that reductive elimination is competitive with the vinyl transfer in the absence of specific activators for the Si–vinyl bond. To explore this approach, we investigated the Pd-induced reactions of the alkenyl(*o*-iodobenzyl)silanes **4a–c** and of the alkynyl(*o*-iodobenzyl)silane **4d**. These compounds were prepared by silylation of the *Grignard* reagent of *o*-bromobenzyl bromide (**1**) with the chlorosilanes **2a–d** *via* the (*o*-bromobenzyl)silanes **3a–d** (*ca.* 50% yield), followed by Li/Br exchange and treatment with I_2 (78–88% yield) (*Scheme 1*).

Results and Discussion. – When the (*o*-iodobenzyl)silane **4a** was treated with $[\text{PdCl}_2(\text{PPh}_3)]$ in refluxing MeCN/benzene in the presence of MeOH, the products **5a** and **6a** were obtained in isolated yields of 23 and 60%, respectively (*Scheme 2*). Similarly, **4c** gave **5c** and **6c** in 21 and 52% yields, respectively. Vinyl transfer only was observed in the case of (*o*-iodobenzyl)trivinylsilane (**4b**) to give **6b** in 47% yield. Similarly, **4d** underwent only transfer of the ethynyl group furnishing **8d** in 72% yield,



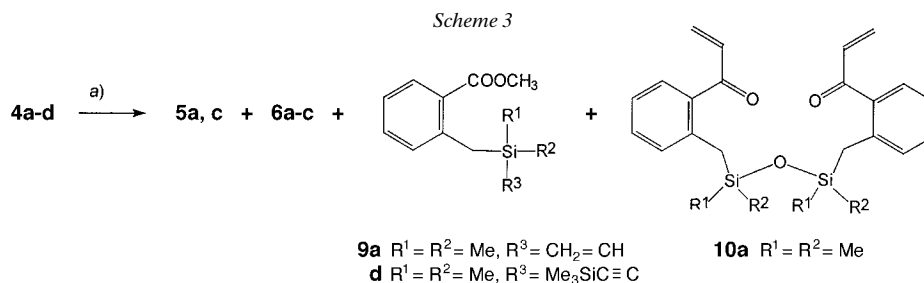
while the potential cyclization product was again absent. When the reaction of **4b** was performed in the absence of MeOH, the hydroxy compound **7b** was obtained after aqueous workup. Since **5a** is stable under the conditions of its formation, ring cleavage of this silole to give **6a** can be excluded. Thus, it is established that an intramolecular cyclization reaction can be competitive with an intramolecular cross-coupling reaction involving the transfer of a vinyl or (trimethylsilyl)ethynyl group, respectively. In the case of **4c**, the intermediate leading to **5c** might have led to a further ring-closure reaction involving the allyl group. However, no such bicyclic product was observed.



a) 5 mol-% of $[\text{PdCl}_2(\text{PPh}_3)_2]$, 4 equiv. of Et_3N , 2 equiv. of MeOH, MeCN/ C_6H_6 1:1, reflux 4 h.

In view of the well-established cyclocarbonylation of 1-alkenyl-2-iodobenzenes promoted by Pd^0 catalysts and the carbonylative intermolecular cross coupling mentioned above, it was of interest to explore cyclizations of the silanes **4a** and **4c** in the presence of CO [5][7]. Thus, when **4a** or **4c** was treated with $[\text{Pd}(\text{dba})_2]$ (dba = dibenzylideneacetone = 1,5-diphenylpenta-1,4-dien-3-one) or $[\text{Pd}(\text{PPh}_3)_4]$ in MeOH in the presence of Et_3N under 40–100 atm of CO for 1–48 h, the silole **5a** (28%) or **5c** (19%), and the crossover product **6a** (12%) or **6c** (11%), respectively, were isolated (*Scheme 3*). Under similar conditions, only a trace of the crossover product **6b** was

obtained from **4b**. From the reaction of **4a** with CO and [Pd(dba)₂] as catalyst in the presence of MeOH, small amounts of the carbonylation product **9a** (5%) and a trace of **10a** were obtained. Surprisingly, the reaction of **4a** with [PdCl₂(PPh₃)₂] as catalyst under 40 atm of CO and at 100° gave, after aqueous workup, **10a** as the major product (26–36%). With **4d** and [PdCl₂(PPh₃)₂] as well as [Pd(dba)₂] as catalyst under 40 and 100 atm of CO, respectively, **9d** was obtained as the sole product in 58 and 45% yield, respectively. This result differs from *Hijama*'s observation that 1-phenyl-2-(trimethylsilyl)ethyne reacts with 4-iodoacetophenone under 30 atm of CO only to 4-(2-phenylethynyl)acetophenone rather than to the CO-insertion product [4].



a) 5 mol-% of Pd-catalyst, 4 equiv. of Et₃N, 2 equiv. MeOH, 40 or 100 atm, CO, 100°.

Concluding Remarks. – The first examples for the formation of siloles by the intramolecular cyclization reaction of (*o*-iodobenzyl)vinylsilanes are described. The reaction of **4a,c** with a Pd⁰ catalyst in the presence or absence of CO to the silole **5a,c** establishes that ring-closing reactions preserving two Si–C bonds can be competitive with an intramolecular transfer of a Si-bonded vinyl group. The different behaviour of the (*o*-iodobenzyl)vinylsilane **4a** and the (*o*-iodobenzyl)ethynylsilane **4d** in the Pd-induced carbonylation reactions suggests that the aptitude for the intramolecular transfer of an Si-bound vinyl group is larger than that of an Si-bound ethynyl group. Furthermore, the reaction of the aryl iodides **4** with CO leading potentially to **9** seems to be competitive with the direct, most likely intramolecular transfer of the Si-bound vinyl group. This is further supported by the observation that methyl benzoate was isolated in 81% yield as the sole product in the carbonylation reaction of iodobenzene in the presence of trimethyl(vinyl)silane

This work was supported by the *Swiss National Science Foundation* (project No. 2000-050731.97). We thank Prof. P. Rys and Mr. F. Luck, Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, Zürich, for help and support with the high-pressure experiments.

Experimental Part

General. All reactions were performed under Ar or N₂. Chemicals were purchased from commercial suppliers and used without further purification. *t*-BuLi (*Aldrich, pract.*) was used as a 1.7 M soln. in pentane. After workup by pouring the reaction mixture onto ice and extraction of the aq. phase with Et₂O, the extract was dried (MgSO₄) and evaporated and the residue purified by flash chromatography (FC) or chromatography (CC). TLC: silica gel plates SIL G/UV₂₅₄ (*Macherey & Nagel*). GC: *Hewlett-Packard-HP-5890* instrument, *HP-5-Ultra* capillary column (length 10 m, i.d. 0.2 mm); temp. program 40–220° (3°/min); *t_R* in min. Prep. HPLC: 715004-ET-250/10-Nuc-50-7 column (*Macherey & Nagel*); flow 12 ml/min. IR Spectra: *Perkin-Elmer-782*

spectrophotometer; in cm^{-1} . NMR Spectra: *Bruker-AC-300* (^1H , 300 MHz; ^{13}C , 75 MHz) and *-DRX-500* spectrometer (^{29}Si , 99.325 MHz); in CHCl_3 and CDCl_3 (locked to internal CHCl_3 (δ 7.27), resp.; chemical shifts δ in ppm rel. to SiMe_4 (δ 0.0) for ^1H , CDCl_3 (δ 77.0) for ^{13}C , and SiMe_4 (δ 0.0) for ^{29}Si ; coupling constants J in Hz; GC/MS: *VG-Autospec* spectrometer. MS: *Varian-MAT-CH7A* (70 eV, EI) and *Fisons-Autospec-Q* spectrometer; in m/z (rel. %).

(*Chloro*)ethenyl(methyl)(*prop-2-enyl*)silane (**2c**) [8][9]. To a soln. of dichloro(ethenyl)methylsilane (7.05 g, 0.05 mol) in dry THF, 2M (prop-2-enyl)magnesium chloride in THF (25 ml) was added dropwise at 0° . After reaching r.t. and stirring for 1 h, the mixture was evaporated and the residue distilled: 4.4 g (60%) of **2c**. B.p. $80-90^\circ/200$ Torr.

(*Chloro*)dimethyl[(trimethylsilyl)ethynyl]silane (**2d**) was prepared according to [10].

(*o*-Bromobenzyl)silanes **3**: *General Procedure*. To Mg (0.24 g, 0.01 mol) in dry Et_2O (40 ml), a soln. of *o*-bromobenzyl bromide (**1**; 2.5 g, 0.01 mol) in Et_2O (10 ml) was added at -5° [11]. The mixture was stirred at -5° until the Mg had disappeared completely. The chlorosilane **2** (1.2 equiv.) was added and the mixture refluxed for 24 h. After workup with aq. NH_4Cl soln. and extraction ($2 \times$) of the aq. phase with Et_2O , the combined org. phase was dried (MgSO_4) and evaporated, and the residue purified by FC (hexane): **3** colourless oil.

[(2-Bromophenyl)methyl]ethenyldimethylsilane (**3a**): Yield 0.25 g (54%). R_f 0.54 (hexane). IR: 1405s, 1250s, 1155s, 1020s, 1005s, 955s. $^1\text{H-NMR}$: 0.147 (s, 3 H); 2.42 (s, 2 H); 5.71 (*dd*, $J=20.2$, 3.69, 1 H); 6.01 (*dd*, $J=14.7$, 4.05, 1 H); 6.21 (*dd*, $J=19.8$, 14.3, 1 H); 6.93–6.99 (*m*, 1 H); 7.07–7.11 (*m*, 1 H); 7.16–7.21 (*m*, 1 H); 7.51–7.55 (*m*, 1 H). $^{13}\text{C-NMR}$: -3.23 (*q*); 25.73 (*t*); 123.63 (*s*); 125.66 (*d*); 126.99 (*d*); 129.79 (*d*); 132.21 (*d*); 132.72 (*d*); 138.12 (*t*); 140.13 (*s*). $^{29}\text{Si-NMR}$: -5.137 . MS: 256 (100, $[M+2]^+$), 254 (98, M^+), 241 (38), 239 (40), 175 (36), 159 (28), 137 (30), 117 (72), 86 (52). HR-MS: 254.0112 ($\text{C}_{11}\text{H}_{15}\text{BrSi}^+$; calc. 254.0126).

[(2-Bromophenyl)methyl]triethenylsilane (**3b**). Yield 0.26 g (52%). R_f 0.45 (hexane). IR: 1400s, 1155m, 1020s, 1005s, 960s. $^1\text{H-NMR}$: 2.57 (s, 2 H); 5.81 (*dd*, $J=16.9$, 7.35, 3 H); 6.12–6.20 (*m*, 6 H); 6.94–7.00 (*m*, 1 H); 7.13–7.22 (*m*, 2 H); 7.52–7.55 (*m*, 1 H). $^{13}\text{C-NMR}$: 23.51 (*t*); 123.95 (*s*); 125.92 (*d*); 126.95 (*d*); 130.12 (*d*); 132.68 (*d*); 133.63 (*d*); 135.29 (*t*); 139.09 (*s*). $^{29}\text{Si-NMR}$: -21.288 . MS: 280 (100, $[M+2]^+$), 278 (100, M^+), 251 (40), 199 (30), 171 (68), 161 (52), 145 (42), 117 (60), 109 (55). HR-MS: 278.0123 ($\text{C}_{13}\text{H}_{15}\text{BrSi}^+$; calc. 278.0126).

[(2-Bromophenyl)methyl]ethenyl(methyl)(*prop-2-enyl*)silane (**3c**). Yield 0.26 g (48%). R_f 0.38 (hexane). IR: 1630s, 1590m, 1460s, 1435s, 1400s, 1250s, 1155s, 1020s, 1000s, 950s. $^1\text{H-NMR}$: 0.12 (s, 3 H); 1.69 (*d*, $J=8.5$, 2 H); 2.44 (s, 2 H); 4.88–4.95 (*m*, 2 H); 5.67–5.85 (*m*, 2 H); 6.00–6.22 (*m*, 2 H); 6.93–6.99 (*m*, 1 H); 7.08–7.11 (*m*, 1 H); 7.15–7.21 (*m*, 1 H); 7.50–7.53 (*m*, 1 H). $^{13}\text{C-NMR}$: -5.69 (*q*); 21.83 (*t*); 24.02 (*t*); 113.84 (*t*); 123.68 (*s*); 125.80 (*d*); 127.05 (*d*); 129.89 (*d*); 132.74 (*d*); 133.25 (*t*); 134.06 (*d*); 136.13 (*d*); 139.77 (*s*). $^{29}\text{Si-NMR}$: -6.426 . MS: 282 (12, $[M+2]^+$), 280 (10, M^+), 267 (10), 255 (20), 242 (100), 240 (90), 213 (15), 199 (15), 159 (82), 151 (27), 145 (25), 131 (60), 125 (50), 111 (43). HR-MS: 280.0272 ($\text{C}_{13}\text{H}_{15}\text{BrSi}^+$; calc. 280.0283).

[(2-Bromophenyl)methyl]dimethyl[(trimethylsilyl)ethynyl]silane (**3d**). Yield 0.33 g (54%). R_f 0.23 (hexane). IR: 1470s, 1205s, 1210s, 1160s, 1020s. $^1\text{H-NMR}$: 0.21 (s, 9 H); 0.23 (s, 6 H); 2.48 (s, 2 H); 6.95–7.00 (*m*, 1 H); 7.17–7.26 (*m*, 2 H); 7.52–7.54 (*m*, 1 H). $^{13}\text{C-NMR}$: -1.55 (*q*); -0.16 (*q*); 26.06 (*t*); 111.87 (*s*); 115.69 (*s*); 123.75 (*s*); 125.97 (*d*); 126.96 (*d*); 130.17 (*d*); 132.63 (*d*); 139.15 (*s*). $^{29}\text{Si-NMR}$: -18.849 ; -17.355 . MS: 325 (44, $[M+1]^+$), 323 (41, $[M-1]^+$), 310 (18), 308 (18), 244 (100), 170 (14), 168 (11), 154 (63), 138 (12), 97 (16), 73 (32). HR-MS: 324.0363 ($\text{C}_{14}\text{H}_{21}\text{BrSi}_2^+$; calc. 324.0365).

(*o*-Iodobenzyl)silanes: *General Procedure* [12]. To an Et_2O soln. of (*o*-bromobenzyl)silane **3** (1 mmol) in dry Et_2O (10 ml), 1 equiv. of *t*-BuLi was added at -100° (TLC monitoring). When the starting material had disappeared (after ca. 10 min), I_2 (1.2 equiv.) in Et_2O (5 ml) was added and the mixture slowly warmed to r.t. After workup with 5% aq. Na_2SO_3 soln., the residue was purified by CC (hexane): **4** colourless oil.

Ethenyl[(2-iodophenyl)methyl]dimethylsilane (**4a**). Yield 0.25 g (84%). R_f 0.50 (hexane). IR: 3050m, 3000s, 2950s, 1590m, 1470s, 1430m, 1400s, 1240s, 1160s, 1000vs, 960s. $^1\text{H-NMR}$: 0.20 (s, 6 H); 2.49 (s, 2 H); 5.74 (*dd*, $J=20.2$, 3.69, 1 H); 6.04 (*dd*, $J=14.7$, 3.66, 1 H); 6.25 (*dd*, $J=20.2$, 14.7, 1 H); 6.78–6.83 (*m*, 1 H); 7.10–7.13 (*m*, 1 H); 7.22–7.26 (*m*, 1 H); 7.82–7.85 (*m*, 1 H). $^{13}\text{C-NMR}$: -3.01 (*q*); 30.59 (*t*); 100.46 (*s*); 125.81 (*d*); 127.87 (*d*); 128.48 (*d*); 132.30 (*t*); 138.07 (*d*); 139.41 (*d*); 143.65 (*s*). $^{29}\text{Si-NMR}$: -5.081 . MS: 302 (100, M^+), 287 (30), 218 (30), 185 (22), 175 (72), 117 (38), 85 (72), 59 (46). HR-MS: 301.9982 ($\text{C}_{11}\text{H}_{15}\text{ISi}^+$; calc. 301.9988).

Triethenyl[(2-iodophenyl)methyl]silane (**4b**). Yield 0.26 g (81.0%). R_f 0.50 (hexane). IR: 3060m, 1470s, 1435m, 1405vs, 1210vs, 1005vs, 960s. $^1\text{H-NMR}$: 2.59 (s, 2 H); 5.79 (*dd*, $J=16.9$, 6.6, 3 H); 6.10–6.23 (*m*, 6 H); 6.75–6.80 (*m*, 1 H); 7.10–7.13 (*m*, 1 H); 7.17–7.20 (*m*, 1 H); 7.77–7.80 (*m*, 1 H). $^{13}\text{C-NMR}$: 28.47 (*t*); 101.02 (*s*); 126.08 (*d*); 127.86 (*d*); 128.93 (*d*); 133.65 (*d*); 135.34 (*t*); 139.39 (*d*); 142.62 (*s*). $^{29}\text{Si-NMR}$: -21.278 . MS: 326

(100, M^+), 299(20), 209(32), 199(20), 183(15), 171(54), 116(46), 109(68), 83(44). HR-MS: 325.9974 ($C_{13}H_{15}Si^+$; calc. 325.9988).

Ethenyl[(2-iodophenyl)methyl]methyl(prop-2-enyl)silane (4c). Yield 0.26 g (79.6%). R_f 0.38 (hexane). IR: 3010s, 2970m, 2900w, 1620vw, 1520m, 1460m, 1400m, 1210s, 1150m, 1040s, 1005s, 925m. 1H -NMR: 0.16 (s, 3 H); 1.73 (d, $J=8.1$, 2 H); 2.50 (s, 2 H); 4.91–4.97 (m, 2 H); 5.68–5.88 (m, 2 H); 6.02–6.26 (m, 2 H); 6.77–6.82 (m, 1 H); 7.10–7.12 (m, 1 H); 7.21–7.26 (m, 1 H); 7.80–7.83 (m, 1 H). ^{13}C -NMR: 5.48 (q); 21.94 (t); 28.94 (t); 100.56 (s); 113.88 (t); 125.96 (d); 127.95 (d); 128.64 (d); 133.35 (t); 134.03 (d); 136.15 (d); 139.45 (d); 143.34 (s). ^{29}Si -NMR: –6.389. MS: 328 (4, M^+), 313(8), 301(7), 288(100), 255(8), 197(11), 159(46), 145(18), 131(28), 111(12). HR-MS: 328.0138 ($C_{13}H_{17}Si^+$; calc. 328.0143).

[(2-Iodophenyl)methyl]dimethyl(trimethylsilyl)ethynylsilane (4d). Yield 0.33 g (88.1%). R_f 0.24 (hexane). IR: 3020s, 2960s, 2915m, 1590m, 1560w, 1465s, 1430m, 1410m, 1250s, 1210vs, 1160m, 1045m, 1010s, 935m. 1H -NMR: 0.21 (s, 9 H); 0.25 (s, 6 H); 2.51 (s, 2 H); 6.78–6.83 (m, 1 H); 7.23–7.25 (m, 2 H); 7.79–7.82 (m, 1 H). ^{13}C -NMR: –1.34 (q); 0.16 (q); 30.88 (t); 100.56 (s); 111.91 (s); 115.88 (s); 126.15 (d); 127.87 (d); 128.96 (d); 139.36 (d); 142.81 (s). ^{29}Si -NMR: –18.849, –17.299. MS: 372 (54, M^+), 358(18), 246(26), 245(100), 218(10), 156(32), 155(84), 145(10), 97(10). HR-MS: 372.0228 ($C_{14}H_{21}Si_2^+$; calc. 372.0227).

Pd-Catalyzed Reactions of the (o-Iodobenzyl)silanes 4: General Procedure. A mixture of (*o*-iodobenzyl)silane **4** (1 mmol), $[PdCl_2(PPh_3)]$ (5 mol-%), Et_3N (4 equiv.), MeOH (2 equiv.) in MeCN/ C_6H_6 1:1 (6 ml) was refluxed for 4 h. After evaporation, the residue was purified by FC (hexane/ Et_2O 60:1).

2,3-Dihydro-2,2-dimethyl-1-methylidene-1H-2-silaindene (5a): Yield 0.040 g (23%). R_f 0.60 (hexane/ Et_2O 60:1). IR: 1600s, 1520m, 1210vs, 1040s, 925s. 1H -NMR: 0.29 (s, 6 H); 2.07 (s, 2 H); 5.49 (d, $J=2.19$, 2 H); 6.24 (d, $J=2.19$, 1 H); 7.16–7.19 (m, 2 H); 7.27–7.29 (m, 1 H); 7.56–7.59 (m, 1 H). ^{13}C -NMR: –2.40 (q); 18.78 (t); 117.89 (t); 121.05 (d); 125.88 (d); 127.97 (d); 130.37 (d); 142.87 (s); 143.05 (s); 150.53 (s). ^{29}Si -NMR: 7.472. MS: 175 (44, $[M+1]^+$), 174 (100, M^+), 160(44), 159(97), 145(20), 133(45), 131(73), 105(30). HR-MS: 174.0862 ($C_{11}H_{14}Si^+$; calc. 174.0865).

Control experiment: A soln. of **5a** (1 mmol, 174 mg), $[PdCl_2(PPh_3)]$ (5 mol-%), Et_3N (4 mol-equiv.) and MeOH (2 mol-equiv.) in MeCN/ C_6H_6 1:1 (6 ml) was refluxed under Ar for 4 h (TLC monitoring (hexane/ Et_2O 60:1)). Only starting material (95%) was recovered.

2,3-Dihydro-2-methyl-1-methylidene-2-(prop-2-enyl)-1H-2-silaindene (5c): Yield 42 mg (21%). R_f 0.65 (hexane/ Et_2O 60:1). IR: 1600s, 1258m, 1066m. 1H -NMR: 0.31 (s, 3 H); 1.76 (d, $J=7.71$, 2 H); 2.01 (d, $J=18.0$, 1 H); 2.13 (d, $J=17.7$, 1 H); 4.85–4.97 (m, 2 H); 5.50 (d, $J=1.83$, 1 H); 5.74–5.88 (m, 1 H); 6.27 (d, $J=1.83$, 1 H); 7.16–7.19 (m, 2 H); 7.26–7.30 (m, 1 H); 7.55–7.58 (m, 1 H). ^{13}C -NMR: –4.59 (q); 16.94 (t); 22.03 (t); 113.90 (t); 118.71 (t); 120.98 (d); 125.93 (d); 128.03 (d); 130.37 (d); 133.64 (d); 142.82 (s); 142.87 (s); 148.66 (s). ^{29}Si -NMR: 6.109. MS: 200 (40, M^+), 185(7), 172(15), 160(45), 159(100), 158(72), 145(20), 133(28), 131(45), 115(15), 105(17). HR-MS: 200.1014 ($C_{13}H_{16}Si^+$; calc. 200.1021).

[(2-Ethenylphenyl)methyl]methoxydimethylsilane (6a): Yield 0.124 g (60%). R_f 0.20 (hexane/ Et_2O 60:1). IR: 1595m, 1400m, 1150m, 1070s, 1010s. 1H -NMR: 0.10 (s, 6 H); 2.29 (s, 2 H); 3.14 (s, 3 H); 5.27 (dd, $J=11.0$, 1.47, 1 H); 5.62 (dd, $J=17.3$, 1.47, 1 H); 6.96 (dd, $J=17.3$, 11.0, 1 H); 7.03–7.18 (m, 3 H); 7.45–7.49 (m, 1 H). ^{13}C -NMR: –2.47 (q); 23.39 (t); 50.55 (q); 114.87 (t); 124.70 (d); 125.83 (d); 127.61 (d); 129.46 (d); 135.49 (d); 135.68 (s); 136.81 (s). ^{29}Si -NMR: 17.018. MS: 206 (100, M^+), 191(21), 174(36), 163(12), 159(34), 145(9), 131(10), 115(12), 89(51). HR-MS: 206.1126 ($C_{12}H_{18}OSi^+$; calc. 206.1127).

Diethenyl[(2-ethenylphenyl)methyl]methoxysilane (6b): Yield 0.108 g (47%). R_f 0.40 (hexane/ Et_2O 60:1). IR: 1478m, 1224s, 1070m, 1046s, 928s. 1H -NMR: 2.02 (s, 2 H); 3.44 (s, 3 H); 5.26 (dd, $J=11.0$, 1.47, 1 H); 5.59 (dd, $J=17.6$, 1.47, 1 H); 5.81–5.89 (m, 2 H); 6.00–6.17 (m, 4 H); 6.97 (dd, $J=17.6$, 11.0, 1 H); 7.06–7.18 (m, 3 H); 7.44–7.47 (m, 1 H). ^{13}C -NMR: 21.21 (t); 51.20 (q); 115.02 (t); 124.91 (d); 125.86 (d); 127.51 (d); 129.86 (d); 133.20 (d); 135.68 (s); 135.86 (t); 136.06 (s). ^{29}Si -NMR: –9.434. MS: 230 (22, M^+), 202(40), 189(66), 162(10), 145(11), 115(30), 114(30), 113(100), 87(53). HR-MS: 230.1127 ($C_{14}H_{18}OSi^+$; calc. 230.1127).

[(2-Ethenylphenyl)methyl]methoxy(methyl)(prop-2-enyl)silane (6c). Yield 0.121 g (52%). R_f 0.23 (hexane/ Et_2O 60:1). IR: 3062m, 3024s, 3012s, 2836m, 1630m, 1482m, 1448m, 1418m, 1258s, 1188m, 1160s, 1082s, 990m, 902s. 1H -NMR: 0.08 (s, 3 H); 1.60–1.74 (m, 2 H); 2.30 (d, $J=3.3$, 2 H); 3.41 (s, 3 H); 4.89–4.97 (m, 2 H); 5.28 (dd, $J=11.0$, 1.47, 1 H); 5.63 (dd, $J=17.3$, 1.47, 1 H); 5.70–5.85 (m, 1 H); 6.97 (dd, $J=17.3$, 11.0, 1 H); 7.04–7.19 (m, 3 H); 7.46–7.49 (m, 1 H). ^{13}C -NMR: –4.63 (q); 21.85 (t); 22.63 (t); 50.95 (q); 114.27 (t); 114.99 (t); 124.82 (d); 125.88 (d); 127.65 (d); 129.54 (d); 133.40 (t); 135.42 (d); 135.77 (s); 136.46 (s). ^{29}Si -NMR: 12.946. MS: 232 (20, M^+), 191(48), 164(18), 163(100), 161(28), 159(72), 131(18), 115(29). HR-MS: 232.1277 ($C_{14}H_{20}OSi^+$; calc. 232.1283).

{[2-[(Methoxydimethylsilyl)methyl]phenyl]ethynyl}trimethylsilane (**8d**): Yield 0.20 g (72%). R_f 0.15 (hexane/Et₂O 60:1). IR: 1250s, 1080s. ¹H-NMR: 0.13 (s, 6 H); 0.27 (s, 9 H); 2.49 (s, 2 H); 3.47 (s, 3 H); 7.01–7.11 (m, 2 H); 7.17–7.23 (m, 1 H); 7.41–7.44 (m, 1 H). ¹³C-NMR: –2.55 (q); 0.015 (q); 24.94 (t); 50.52 (q); 97.74 (s); 104.96 (s); 121.58 (s); 124.06 (d); 128.38 (d); 128.46 (d); 132.47 (d); 142.12 (s). ²⁹Si-NMR: –18.083; 17.355. MS: 276 (68, M⁺), 261 (20), 231 (20), 188 (17), 172 (100), 157 (23), 147 (14), 89 (62). HR-MS: 276.1359 (C₁₅H₂₄O₂Si₂; calc. 276.1366).

Diethenyl[(2-ethenylphenyl)methyl]silanol (**7b**). The reaction of **4b** was performed as described above for **4** in the absence of MeOH: 91 mg (42%) of **7b**. R_f 0.19 (hexane/Et₂O 7:1). IR: 1625m, 1595m, 1480m, 1450m, 1405s, 1005s, 960s. ¹H-NMR: 1.88 (s, 1 H); 2.41 (s, 2 H); 5.30 (dd, $J = 11.0, 1.11, 1$ H); 5.63 (dd, $J = 17.3, 1.11, 1$ H); 5.82–5.90 (m, 2 H); 6.07–6.14 (m, 4 H); 6.99 (dd, $J = 17.3, 11.0, 1$ H); 7.05–7.20 (m, 3 H); 7.45–7.48 (m, 1 H). ¹³C-NMR: 22.72 (t); 115.39 (t); 125.04 (d); 126.06 (d); 127.72 (d); 129.76 (d); 134.84 (d); 135.06 (t); 135.74 (d); 135.78 (s); 135.94 (s). ²⁹Si-NMR: –10.835. MS: 217 (69, [M+1]⁺), 216 (98, M⁺), 198 (61), 189 (100), 176 (70), 161 (60), 147 (71), 142 (42), 128 (88), 115 (93), 101 (82), 91 (60). HR-MS: 216.0962 (C₁₃H₁₆O₂Si⁺; calc. 216.0970).

General Procedure for the Pd-Catalyzed Reaction of the (o-Iodobenzyl)silanes **4a–c** with CO: A mixture of **4a–d** (1 mmol), [PdCl₂(PPh₃)] (5 mol-%) or the Pd⁰ complex (cf. below), Et₃N (4 equiv.), and MeOH (2 equiv.) in MeCN/C₆H₆ 1:1 (6 ml) was heated in an autoclave under a CO pressure of 40–100 atm to 100° for 1–24 h (cf. below). After removing CO and the solvent, the products were separated by FC (hexane/Et₂O 60:1 and 7:1).

Methyl 2-[(Ethenyldimethylsilyl)methyl]benzoate (**9a**): Yield 3.0, 5.0, and 13%, with 100, 100, and 40 atm of CO for 48, 8, and 1 h, resp.; catalyst [Pd(dba)₂]. R_f 0.27 (hexane/Et₂O 60:1). IR: 1715s, 1260s, 1105s. ¹H-NMR: 0.029 (s, 6 H); 2.74 (s, 2 H); 3.87 (s, 3 H); 5.62 (dd, $J = 19.9, 4.05, 1$ H); 5.93 (dd, $J = 14.7, 4.05, 1$ H); 6.10 (dd, $J = 19.9, 14.7, 1$ H); 7.06–7.16 (m, 2 H); 7.32–7.37 (m, 1 H); 7.86–7.89 (m, 1 H). ¹³C-NMR: –3.54 (q); 24.39 (t); 51.65 (q); 123.96 (d); 127.98 (s); 130.72 (d); 130.82 (d); 131.60 (d); 131.94 (t); 138.27 (d); 142.95 (s); 168.35 (s). ²⁹Si-NMR: –5.025. MS: 234 (57, M⁺), 219 (82), 206 (100), 204 (92), 201 (45), 193 (32), 187 (75), 169 (38), 143 (28), 129 (34), 118 (60), 90 (42). HR-MS: 234.1046 (C₁₃H₁₈O₂Si⁺; calc. 234.1076).

Methyl 2-[[Dimethyl[(trimethylsilyl)ethynyl]silyl]methyl]benzoate (**9d**): Yield 45 and 58%, with 100 and 40 atm of CO, resp., for 4 h; catalyst: 5 mol-% of [Pd(dba)₂] or [PdCl₂(PPh₃)₂]. R_f 0.24 (hexane/Et₂O 60:1). IR: 1570m, 1435s, 1300m, 1255s, 1105s, 1070s. ¹H-NMR: 0.13 (s, 6 H); 0.16 (s, 9 H); 2.80 (s, 2 H); 3.87 (s, 3 H); 7.13–7.23 (m, 2 H); 7.34–7.49 (m, 1 H); 7.90–7.93 (m, 1 H). ¹³C-NMR: –1.80 (q); –0.18 (q); 24.81 (t); 51.64 (q); 112.30 (s); 115.23 (s); 124.28 (d); 127.92 (s); 130.86 (d); 131.04 (d); 131.65 (d); 142.12 (s); 168.18 (s). ²⁹Si-NMR: –8.313; 5.941. MS: 303 (5, [M–1]⁺), 289 (46), 275 (28), 274 (72), 273 (100), 231 (11), 193 (10), 155 (33), 118 (32). HR-MS: 304.1251 (C₁₆H₂₄O₂Si₂⁺; calc. 304.1315).

1,1'-[Oxybis(dimethylsilylene)methylene-2,1-phenylene]bis[prop-2-en-1-one] (**10a**): Yield 13, 26, and 36%, with 100, 40, and 40 atm of CO for 8, 4, and 1 h, resp.; catalyst: 5 mol-% of [PdCl₂(PPh₃)]. R_f 0.38 (hexane/Et₂O 7:1). IR: 1670s, 1650s, 1605s, 1565m, 1400s, 1250s, 1150s, 1050s, 990s, 960s. ¹H-NMR: –0.035 (s, 12 H); 2.45 (s, 4 H); 5.94 (dd, $J = 10.3, 1.47, 2$ H); 6.20 (dd, $J = 17.1, 1.47, 2$ H); 6.83 (dd, $J = 17.1, 10.3, 2$ H); 7.09–7.17 (m, 4 H); 7.29–7.34 (m, 2 H); 7.47–7.50 (m, 2 H). ¹³C-NMR: 0.36 (q); 26.07 (t); 123.67 (d); 129.29 (d); 130.22 (t); 130.70 (d); 130.83 (d); 136.17 (d); 136.47 (s); 140.36 (s); 195.56 (s). ²⁹Si-NMR: 5.959. MS: 422 (8, M⁺), 407 (48), 351 (43), 335 (13), 278 (100), 261 (62), 203 (68), 187 (15), 149 (39), 133 (40), 129 (43). HR-MS: 422.1725 (C₂₄H₃₀O₃Si₂⁺; calc. 422.1734).

Methyl Benzoate was obtained from iodobenzene by carbonylation in the presence of ethenyltrimethylsilane (100 mg, 1 mmol), [PdCl₂(PPh₃)₂] (5 mol-%), and MeOH as described above for **4**. FC (hexane/Et₂O 10:1) gave iodobenzene (100 mg; 50%) and methyl benzoate (55 mg, 81%) which was identified by its ¹H- and ¹³C-NMR.

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Received February 4, 1999