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Preparation of carbazolylsilanes *

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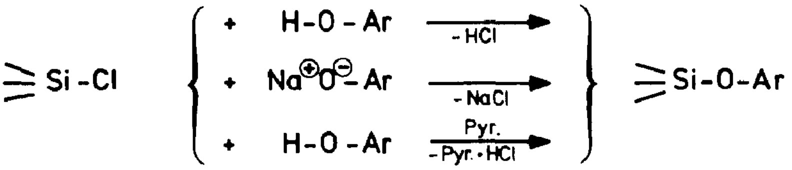
Abstract

Metallation at the heteroatom of carbazole results in a reactive derivative of carbazole that reacts smoothly with chlorosilanes. Nine carbazolylsilanes have been prepared in high yields by this route. Physical and spectroscopic data and representative chemical properties of the compounds obtained are described.

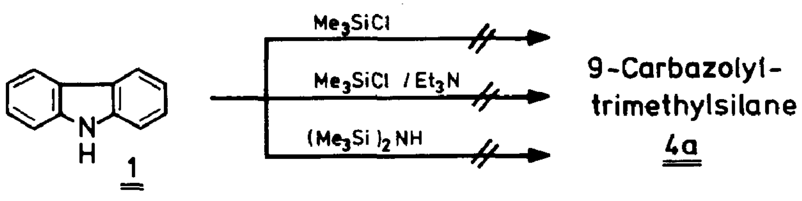
Introduction

Hydroxy-substituted polyaromatic hydrocarbons react smoothly with chlorosilanes [1–3]. In many cases the reaction rate is increased by conversion of the hydroxy compound into a salt or by adding a base, such as pyridine or a tertiary amine.



(1)

Aromatics containing an NH group, like carbazole (**1**), do not react either in the absence or presence of bases owing to the low acidity of the NH group, and so the chemistry of **1** is different from that of amines, such as $ArNH_2$ or phenols. It was found that direct silylation of **1** is impossible:



(2)

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* Dedicated to Professor Dr.Dr.h.c. Heinz-Gerhard Franck (Ruetgerswerke AG) on the occasion of his 65th birthday.

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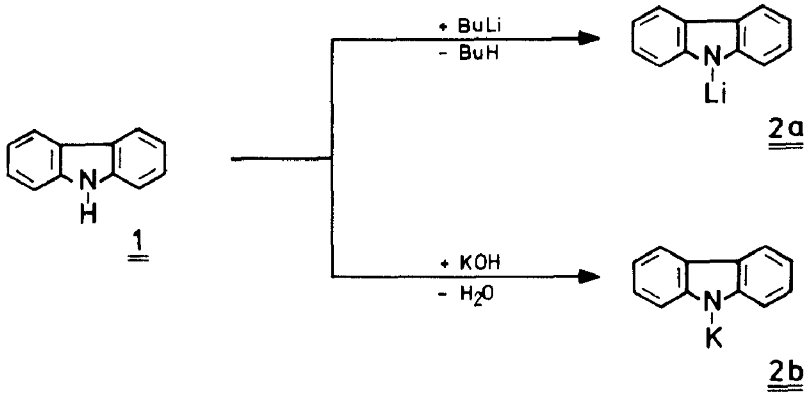
The first example of a silylated carbazole, di-9-carbazolyldichlorosilane (**4h**), was prepared by reaction of 9-sodiocarbazole with $SiCl_4$ (**3d**) [4]. The objective of the work described here was the preparation and characterisation of the carbazolylsilanes **4a–4i**, and to examine some reactions of these compounds.

(A) Preparation of carbazolylsilanes (*4a–4i*) via 9-lithiocarbazole (*2a*) or 9-potassiocarbazole (*2b*), respectively

The precursor in the preparation of carbazolylsilanes (**4a–4i**) is 9-lithiocarbazole (**2a**) or 9-potassiocarbazole (**2b**), respectively. **2a** was prepared by treating a suspension of **1** in toluene, xylene, or 1,2,3,4-tetramethylbenzene with n-butyllithium in hexane and heating the mixture until no more butane was evolved. **2b** was prepared by heating a suspension of **1** and KOH in xylene and removing the water continuously.



(3)

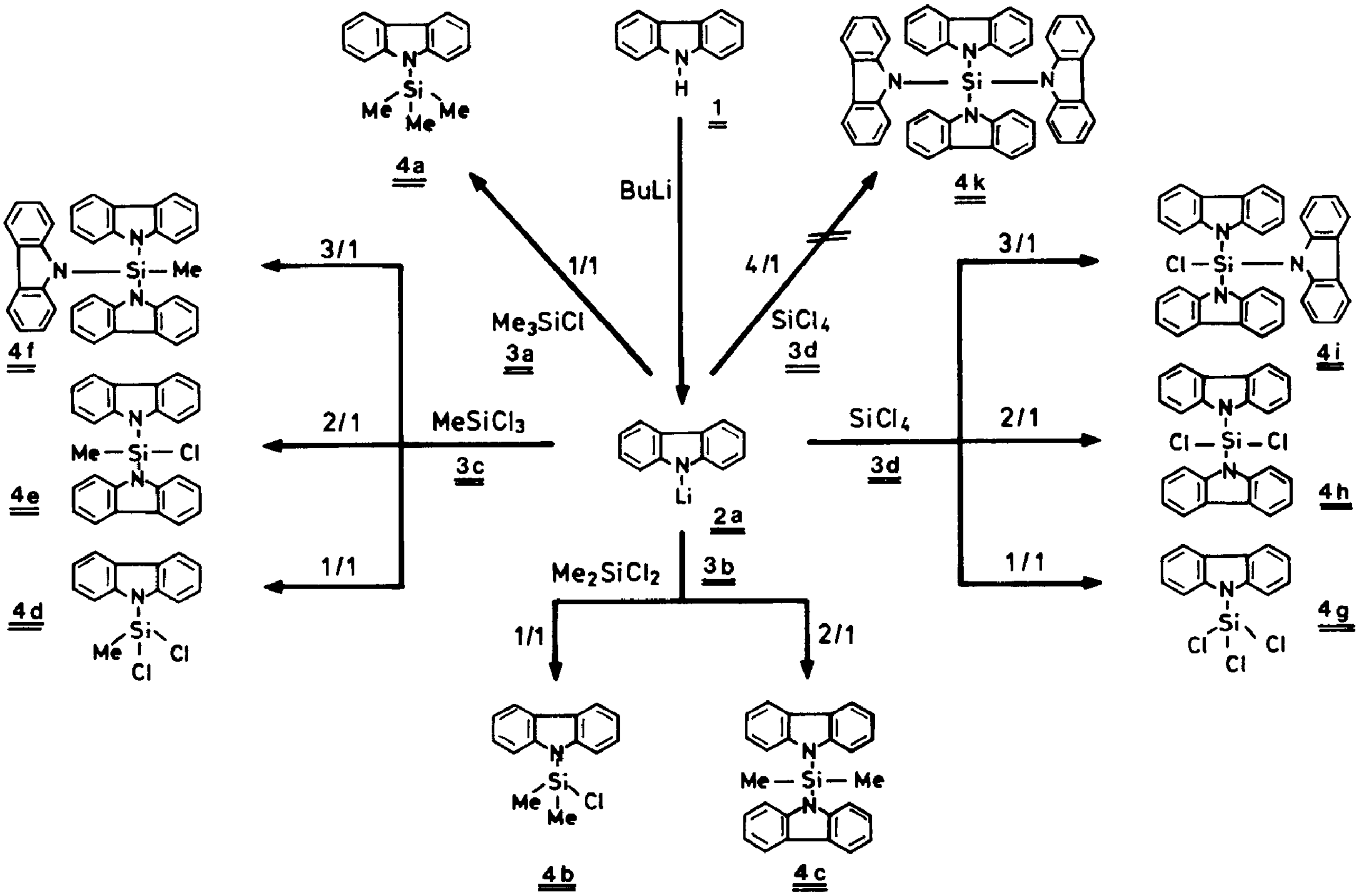
2a was used for most of the experiments performed. Suspensions of **2a** were found to react with the chlorosilanes **3a–3d** in various molar ratios, and Scheme 1 shows the molar ratio used (above the arrows) and the products obtained. The course of the reactions is mainly determined by the following factors (see also Table 2):

(a) The number of carbazolyl substituents in the silane formed increases with increasing reaction temperature. For example, only 3% of methyltri-9-carbazolylsilane (**4f**) was obtained in boiling xylene (140 ° C) compared to 78% **4f** in boiling 1,2,3,4-tetramethylbenzene (204 ° C).

(b) To obtain chlorinated monocarbazolylsilanes in high yields, a suspension of **2a** is added to **3b–3d** at temperatures below 20 ° C. Addition at temperatures above 20 ° C or mixing of the reagents in reverse order gives dicarbazolylsilanes in high yields. In the preparation of di- and tricarbazolylsilanes (**4e**, **4h**, **4i**) the second or third carbazolylation is controlled by steric effects.

(c) As is well known, **3d** is much more reactive than **3c** or **3b** and so the second or third carbazolylation can be achieved under milder conditions for **3d** than for **3c**.

For isolation of the desired silane the solvent was distilled off and the residue fractionated by vacuum distillation. **4a** and **4c** can also be obtained in pure form by


1
BuLi
2a
Me3SiCl
3a
1/1
4a
SiCl4
3d
4/1
4k
MeSiCl3
3c
3/1
2/1
1/1
4f
4e
4d
SiCl4
3d
3/1
2/1
1/1
4i
4h
4g
Me2SiCl2
3b
1/1
2/1
4b
4c

Scheme 1

Table 1

Solubility of solid carbazolylsilanes (mg/μL solvent) at 20° C (RT) and in boiling solvent (BT)

		Benzene	Ether	THF	$CHCl_3$	CCl_4	CS_2
4a	RT	1/1	1/1	1/1	1/1	1/2	1/2
4c	RT	1/10		1/4	1/5	1/20	1/20
	BT	1/5	1/65	1/3	1/3	1/6	
4e	RT	1/8		1/6	1/7	1/22	1/10
	BT	1/2	1/100	1/3	1/3	1/6	
4h	RT	1/10		1/5	1/5	1/11	1/10
	BT	1/2	1/35	1/2	1/2	1/3	
4f	RT	1/25	1/260	1/20	1/30	1/90	1/90
4i	RT	1/18	1/200	1/15	1/17	1/60	1/90
1	RT			1/7			
	BT	1/30	1/300	1/5	1/40	1/160	1/120

crystallisation of the residue from $CHCl_3$ or CCl_4. Under the conditions used **4k** could not be prepared. Table 2 shows the conditions used and the product yields.

Carbazolylsilanes **4a**, **4c** and **4h** were also obtained by reaction of **2b** with the silanes **3a**, **3b**, and **3d**. Reagent **2b** can be prepared by heating molar amounts of **1** and KOH in V2A-vessels at 220–230 °C, but this is not recommended since **1** and **2b** sublime at this temperature and furthermore coloured products are formed owing to the long reaction time. For preparation of **2b** heating a suspension of **1** and KOH (NaOH gave much lower yields) in xylene with continuous removal of water is much better. The amount of solvent is only about 1/5 of that used in the preparation of **2a**. Reaction of **2b** with **3a** gives **4a** in 88% (based on **1**) or 66% (based on **3a**) yield.

(B) Solubility of solid carbazolylsilanes

Mono- and di-carbazolylsilanes have higher solubilities in various solvents than carbazole, while the solubilities of tricarbazolylsilanes are comparable to those of carbazole (see Table 1).

(C) Some reactions of carbazolylsilanes

The reactions of **1** with β-bromo-α-methylstyrene [5], β-bromostyrene [6*], (vinylation), and acetyl chloride (acylation) have been studied.

The reaction temperature, the solvent and the concentration of the starting material were varied, and in some cases catalysts ($Cu^{I}Cl$ or $AlCl_3$) were used, but vinylcarbazoles could not be obtained. On the other hand reaction of **4a** with acetyl chloride in the presence of an equimolar amount of $AlCl_3$ or $Cu^{I}Cl$ yielded 63% or 46%, respectively, of acetylcarbazole.

The reaction of chlorinated carbazolylsilanes with water is also of interest. In a Japanese patent [4] it was stated that hydrolysis of **4h** yields the corresponding dihydroxy derivative. In our experiments, however, carbazole was the only product formed (94% yield) under various conditions.

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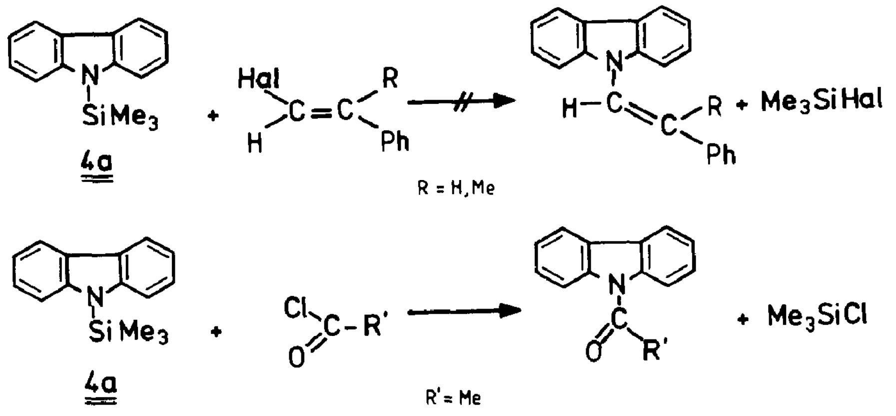
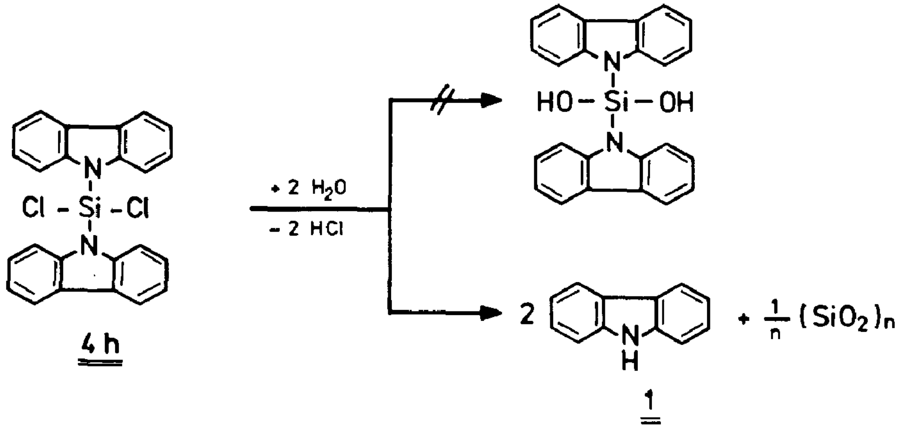
* Reference number with asterisk indicates a note in the list of references.



(5)



(6)

Carbazolylsilanes containing no chlorine, viz. **4a**, **4c** and **4f**, did not react with water.

Experimental

General. All reactions were carried out under argon as most of the silicon compounds are sensitive towards moisture. The solvents were dried by standard methods and distilled under argon. The silanes, n-butyllithium (2.5 *M* solution in hexane), KOH and carbazole were commercial samples. The ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on a Varian XL-200 spectrometer at 200 MHz; chemical shifts are in ppm relative to Me_4Si as internal reference. Mass spectra were recorded on a Hewlett–Packard mass spectrometer mod 5995A, UV spectra on a Zeiss PMQ II and IR spectra on a Perkin–Elmer 283B spectrophotometer. Elemental analyses were by the analytical laboratories of Malissa & Reuter, Engelskirchen.

*General procedures for preparing carbazolylsilanes via 9-lithiocarbazole (**2a**).* Variant A. A solution of 50 mmol n-BuLi in hexane is added to a suspension of carbazole (8.4 g, 50 mmol) in 100 ml of toluene at 20 °C. The stirred suspension is then heated at 110 °C until no more butane is evolved, than cooled to 20 °C and Me_3SiCl (5.4 g, 50 mmol) is added dropwise. The mixture is kept under reflux for 1 h and the solvent then evaporated off. Residual solvent **4a** is isolated by fractional distillation under reduced pressure. (Other products, for example **4c**, require isolation by sublimation.)

Variant B. Reagent **2a** is prepared as described above, then the suspension is cooled to < 20 °C and added to Me_2SiCl_2 (6.5 g, 50 mmol) in 15 ml of toluene. The mixture is then kept under reflux for 1 h, and the solvent subsequently evaporated off **4b** is isolated by fractional distillation under reduced pressure.

Amounts of starting materials, reaction conditions and yields for **4a–4i** are given in Table 2.

*9-Carbazolyltrimethylsilane (**4a**).* Yield 10.2 g (85%); colourless solid; mp. 85 °C; bp. 149 °C/0.1 mmHg; ^1H NMR ($CDCl_3$) δ 0.70 (s, 9H, $SiCH_3$), 7.1–7.4 (m, 4H, CH_{Ar}), 7.6 (m, 2H, CH_{Ar}), 8.1 (m, 2H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 1.7 ($SiCH_3$), 113.1, 119.5, 120.0, 125.4 (CH), 126.2, 144.2 (C_q); ^{29}Si NMR ($CDCl_3$) δ 10.4; MS (70 eV, 160 °C): *m/e* (relative intensity) 239 (83%, M^+), 224 (53%, $M^+ - Me$), 166 (18%, $C_{12}H_8N^+$), 140 (13%, $C_{11}H_8{}^+$), 73 (100%, Me_3Si^+); UV (cyclohexane): ϵ (wavelength) 4570 (332), 18200(293), 44680 (230 nm); IR (KBR-pellet): 3040 (CH_{Ar}, m), 2950 (CH, m), 1900–1700 (Ar, w), 1650/1590 (C=C, m), 1470/1450(s), 1300–1250(s), 1250–1200(m), 970(s), 840(s), 760(s), 730(s) cm^{-1}. Elemental analysis: Found: C, 75.26; H, 7.16; N, 5.83; Si, 11.80. $C_{15}H_{17}NSi$ (239.39) calcd.: C, 75.26; H, 7.16; N, 5.85; Si, 11.73%.

*9-Carbazolylchlorodimethylsilane (**4b**).* Yield 16.7 g (65%); colourless solid; m.p. 46 °C; b.p. 150 °C/0.1 mmHg; ^1H NMR ($CDCl_3$) δ 1.10 (s, 6H, $SiCH_3$), 7.2–7.5 (m, 4H, CH_{Ar}), 7.7 (m, 2H, CH_{Ar}), 8.0–8.1 (m, 2H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 4.8 ($SiCH_3$), 113.5, 120.1, 120.7, 125.8 (CH), 126.6, 143.2 (C_q); ^{29}Si NMR ($CDCl_3$) δ 14.9; MS (70 eV, 160 °C): *m/e* (relative intensity) 261/259 (35/100%, M^+), 246/244 (5/18%, $M^+ - Me$), 166 (10%, $C_{12}H_8N^+$), 95/93 (6/20%, $SiMe_2Cl^+$), 65/63 (5/5%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 3470 (323), 3890 (311), 12590 (290), 11480 (284), 50120 (243), 47860 (234 nm); IR (film): 3040 (CH_{Ar}, m), 2960 (CH, m), 2000–1750 (Ar, m), 1620/1595 (C=C, m), 1450–1350(s), 1300–1200(s), 1150(s), 1120(s), 970(s), 870–775(s), 755(s), 725(s) cm^{-1}. Elemental analysis: Found: C, 65.78; H, 5.49; Cl, 11.60; N, 5.53; Si, 11.10. $C_{14}H_{14}ClNSi$ (259.81) calcd.: C, 64.72; H, 5.43; Cl, 13.65; N, 5.39; Si, 10.81%.

*Di-9-carbazolyldimethylsilane (**4c**).* Yield 7.4 g (76%); colourless solid; m.p. 199–200 °C; b.p. $>$ 225 °C/0.1 mmHg; ^1H NMR ($CDCl_3$) δ 1.25 (s, 6H, $SiCH_3$), 7.2–7.4 (m, 8H, CH_{Ar}), 7.4–7.5 (m, 4H, CH_{Ar}), 8.1 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 2.5 ($SiCH_3$), 112.9, 120.2, 120.5, 126.0 (CH), 126.6, 143.2 (C_q); ^{29}Si NMR ($CDCl_3$) δ 0.8; MS (70 eV, 180 °C): *m/e* (relative intensity) 390 (12%, M^+), 224 (40%, $M^+ - C_{12}H_8N$), 206 (21%), 194 (42%, $C_{12}H_8NSi^+$), 180 (48%), 166 (86%, $C_{12}H_8N^+$), 140 (100%, $C_{11}H_8{}^+$), 115 (26%, $C_9H_7{}^+$); UV (cyclohexane): ϵ (wavelength) 7940 (325), 8710 (312), 30200 (290), 87100 (232 nm); IR (KBr-pellet): 3060(CH_{Ar}, w), 2970(CH, w), 1950–1780(Ar, w), 1620/1600(C=C, m), 1470(m), 1450–1400(s), 1350–1320(m), 1300–1180(s), 1155(m), 1120(m), 1030(m), 975(s), 870/860/835(m), 815(s), 760(s), 730(s) cm^{-1}. Elemental analysis: Found: C, 79.72; H, 5.89; N, 7.17; Si, 7.24. $C_{26}H_{22}N_2Si$ (390.56) calcd.: C, 79.96; H, 5.68; N, 7.17; Si, 7.19%.

*9-Carbazolyldichloromethylsilane (**4d**).* Yield 21.4 g (76%); colourless liquid; b.p.

Table 2

Reaction conditions and yields

Product	Carbazole		n-Buli (mmol)	Solvent [a] (ml)	Silane				Variant	Yield [b] (g/%)	Remarks [c]
	(g)	(mmol)				(g)	(mmol)	(ml)			
4a	8.4	50	50	100 T	Me_3SiCl	5.4	50	6.3	A	10.2/85	
	83.6	500	500	1000 T	(**3a**)	54.4	500	63.0	A	102.0/85	
4b	16.7	100	100	200 T	Me_2SiCl_2 (**3b**)	16.0	124	15.0	B	16.7/65	1
4c	8.4	50	50	100 T	Me_2SiCl_2	3.2	25	3.0	A	7.4/76	
	83.6	500	500	1000 T	(**3b**)	32.3	250	30.3	A	60.2/62	
4d	16.7	100	100	200 T	$MeSiCl_3$ (**3c**)	16.4	110	12.9	B	21.4/76	2
4e	8.4	50	50	100 T	$MeSiCl_3$ (**3c**)	3.7	25	2.9	A,B	8.2/80	3
4f	25.1	150	150	300 X	$MeSiCl_3$	7.5	50	5.8	A	0.8/3	4
	16.7	100	100	50 Tmb	(**3c**)	5.0	33	3.9	A	14.1/78	5
4g	16.7	100	100	200 T	$SiCl_4$ (**3d**)	18.7	110	12.6	B	14.8/49	6
4h	83.6	500	500	1000 T	$SiCl_4$ (**3d**)	42.5	250	28.7	A,B	97.0/90	
4i	12.6	75	75	50 Tmb	$SiCl_4$ (**3d**)	4.3	25	2.9	A	10.8/77	5
4k	16.7	100	100	50 Tmb	$SiCl_4$ (**3d**)	4.3	25	2.9	A	–/–	5, 7

[a] T = toluene, X = xylene, Tmb = 1,2,3,4-tetramethylbenzene. [b] Based on inserted **1**. [c] 1, 2nd fraction (sublimate) 5.4 g (27%) [b] **4c**; 2, 2nd fraction (sublimate) 4.2 g (20%) [b] **4e**; 3, **4f** detected in traces by GC–MS; 4, after addition of **3c** (3.7 g, 25 mmol, 2.9 ml): 1st fraction (sublimate) 22.3 g (73%) [b] **4e**; 5, reaction time: 10 h; 6, 2nd fraction (sublimate) 8.6 g (40%) [b] **4h**; 7, Isolation of 10.8 g (77%) 4i.

155–160 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 3H, $SiCH_3$), 7.2–7.5 (m, 4H, CH_{Ar}), 7.80 (m, 2H, CH_{Ar}), 8.05 (m, 2H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 8.3 ($SiCH_3$), 113.9, 120.2, 121.6, 126.2 (CH), 126.8, 142.3 (C_q); ^{29}Si NMR ($CDCl_3$) δ −0.7; MS (70 eV, 160 °C): *m/e* (relative intensity) 281/279 (38/58%, M^+), 166 (53%, $C_{12}H_8N^+$), 140 (48%, $C_{11}H_8{}^+$), 139 (35%, $C_{11}H_7{}^+$), 115/113 (73/100%, $MeSiCl_2{}^+$), 65/63 (14/50%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 4270 (317), 4570 (306), 16030 (288), 10000 (255), 46770 (229 nm); IR (film): 3070 (CH_{Ar}, m), 2920 (CH, m), 1950–1840 (Ar, w), 1620/1600 (C=C, m), 1500–1400(s), 1270/1250(s), 1200(s), 1160(m), 1120(m), 995(s), 800(s), 750(s), 725(s) cm^{-1}. Elemental analysis: Found: C, 57.34; H, 4.17; Cl, 23.94; N, 4.90; Si, 9.44. $C_{13}H_{11}Cl_2NSi$ (280.23) calcd.: C, 55.72; H, 3.96; Cl, 25.30; N, 5.00; Si, 10.02%.

Di-9-carbazolylchloromethylsilane (4e). Yield 8.2 g (80%); colourless solid; mp. 191–193 °C; bp. > 225 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H, $SiCH_3$), 7.1–7.3 (m, 8H, CH_{Ar}), 7.4–7.5 (m, 4H, CH_{Ar}), 8.0–8.1 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 5.1 ($SiCH_3$), 113.7, 120.2, 121.5, 126.4 (CH), 127.0, 142.4 (C_q); ^{29}Si NMR ($CDCl_3$) δ −11.8; MS (70 eV, 180 °C): *m/e* (relative intensity) 412/410 (40/100%, M^+), 246/244 (21/51%, $M^+ - C_{12}H_8N$), 206 (17%), 180 (39%), 166 (23%, $C_{12}H_8N^+$), 140 (26%, $C_{11}H_8{}^+$), 139 (18%, $C_{11}H_7{}^+$), 65/63 (17/50%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 8511 (319), 9120 (307), 35480 (288), 120230 (229 nm). Elemental analysis: Found: C, 73.03; H, 4.76; Cl, 8.62; N, 6.85; Si, 6.83%. $C_{25}H_{19}ClN_2Si$ (410.98) calcd.: C, 73.06; H, 4.66; Cl, 8.63; N, 6.82; Si, 6.90%.

Methyltri-9-carbazolylsilane (4f). Yield 14.1 g (78%); colourless solid; m.p. 271–274 °C; b.p. > 300 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 3H, $SiCH_3$), 6.7–7.2 (m, 18H, CH_{Ar}), 8.0–8.1 (m, 6H, CH_{Ar}); ^{13}C NMR ($CDCl_3$) δ 3.3 ($SiCH_3$), 113.7, 120.1, 121.4, 126.5 (CH), 127.1, 142.6 (C_q); ^{29}Si NMR ($CDCl_3$) δ −24.2; MS (70 eV, 200 °C): *m/e* (relative intensity) 541 (100%, M^+), 375 (45%, $M^+ - C_{12}H_8N$), 359 (23%, $M^+ - C_{13}H_{12}N$), 208 (26%, $M^+ - C_{24}H_{17}N_2$), 194 (32%, $C_{12}H_8NSi^+$), 167 (66%, $C_{12}H_9N^+$), 166 (38%, $C_{12}H_8N^+$), 140 (49%, $C_{11}H_8{}^+$), 139 (28%, $C_{11}H_7{}^+$), 115 (15%, $C_9H_7{}^+$); UV (cyclohexane): ϵ (wavelength) 15850 (320), 14790 (310), 52480 (290), 173800 (231 nm); IR (KBr-pellet): 3070 (CH_{Ar}, m), 2915 (CH, w), 1990–1775 (Ar, w), 1620/1600 (C=C, m), 1500–1400(s), 1260(s), 1210(s), 1160(m), 1125(m), 995(s), 870/855(m), 800(s), 750(s) 720(s) cm^{-1}. Elemental analysis: Found: C, 81.93; H, 5.06; N, 7.73; Si, 4.96. $C_{37}H_{27}N_3Si$ (541.73) calcd.: C, 82.03; H, 5.02; N, 7.76; Si, 5.19%.

9-Carbazolyltrichlorosilane (4g). Yield 14.8 g (49%); colourless liquid; b.p. 142–143 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.2–7.5 (m, CH_{Ar}), 8.0 (m, CH_{Ar}), intensity 1/1; ^{13}C NMR ($CDCl_3$) δ 114.4, 120.2, 122.4, 126.5 (CH), 127.0, 141.7 (C_q); ^{29}Si NMR ($CDCl_3$) δ −27.5; MS (70 eV, 160 °C): *m/e* (relative intensity) 303/301/299 (31/99/89%, M^+), 265/263 (5/6%, $M^+ - Cl$), 166 (100%, $C_{12}H_8N^+$), 140 (49%, $C_{11}H_8{}^+$), 139 (49%, $C_{11}H_7{}^+$), 137/135/133 (15/27/29%, $SiCl_3{}^+$), 65/63 (7/27%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 3800 (314), 14450 (290), 12600 (255), 39800 (230 nm); IR (film): 3080 (CH_{Ar}, m), 2930 (CH, m), 1950–1720 (Ar, w), 1620/1600 (C=C, m), 1490/1470/1445(s), 1320/1300(m), 1250/1200/1160/1140(s), 1030(m), 1000(s), 870(m), 850(m), 750(s), 725(s), 700(m) cm^{-1}. Elemental analysis: Found: C, 49.44; H, 3.03; Cl, 33.75; N, 4.60; Si, 8.85. $C_{12}H_8Cl_3NSi$ (300.65) calcd.: C, 47.94; H, 2.68; Cl, 35.38; N, 4.66; Si, 9.34%.

Di-9-carbazolyldichlorosilane (4h). Yield 97.0 g (90%); colourless solid; m.p. 173–176 °C; b.p. > 225 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.1–7.3 (m, CH_{Ar}), 7.5–7.6 (m, CH_{Ar}), 8.0 (m, CH_{Ar}), intensity 2/1/1; ^{13}C NMR ($CDCl_3$) δ 114.3, 120.2, 122.4, 126.7 (CH), 127.2, 141.7 (C_q); ^{29}Si NMR ($CDCl_3$) δ −36.6; MS (70 eV, 180 ° C): *m/e* (relative intensity) 434/432/430 (9/40/51%, M^+), 166 (100%, $C_{12}H_8N^+$), 140 (60%, $C_{11}H_8{}^+$), 139 (39%, $C_{11}H_7{}^+$), 65/63 (8/29%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 9120 (313), 10000 (303), 34670 (287), 25700 (255), 123030 (229 nm). Elemental analysis: Found: C, 66.74; H, 3.85; Cl, 16.50; N, 6.52; Si, 6.58. $C_{24}H_{16}Cl_2N_2Si$ (431.40) calcd.: C, 66.82; H, 3.74; Cl, 16.44; N, 6.49; Si, 6.51%.

*Chlorotri-9-carbazolylsilane (**4i**).* Yield 10.8 g (77%); colourless solid; m.p. 308–309 ° C; b.p. > 275 ° C/0.1 mmHg; ^1H NMR ($CDCl_3$) δ 6.8–7.0 (m, CH_{Ar}), 7.1–7.2 (m, CH_{Ar}), 8.0 (m, CH_{Ar}), intensity 2/1/1; ^{13}C NMR ($CDCl_3$) δ 114.4, 120.1, 122.3, 126.7 (CH), 127.4, 141.8 (C_q), ^{29}Si NMR ($CDCl_3$) δ −45.9; MS (70 eV, 200 ° C): *m/e* (relative intensity) 563/561 (24/41%, M^+), 395/393 (15/19%, $M^+ - C_{12}H_8N$), 359 (60%, $M^+ - C_{12}H_8NCl$), 231/229 (7/19%, $M^+ - C_{24}H_{16}N_2$), 167 (100%, $C_{12}H_9N^+$), 166 (75%, $C_{12}H_8N^+$), 140 (87%, $C_{11}H_8{}^+$), 139 (50%, $C_{11}H_7{}^+$), 65/63 (25/71%, $SiCl^+$); UV (cyclohexane): ϵ (wavelength) 15850 (314), 16600 (303), 43650 (286), 33100 (255), 41700 (245), 165960 (228 nm). Elemental analysis: Found: C, 77.11; H, 4.45; Cl, 6.42; N, 7.35; Si, 4.80. $C_{36}H_{24}ClN_3Si$ (562.15) calcd.: C, 76.92; H, 4.30; Cl, 6.30; N, 7.48; Si, 5.00%.

*Preparation of **4a** via 9-potassiocarbazole (**2b**).* A mixture of KOH (34.0 g) and **1** (84.0 g, 0.5 mol) in 200 ml of xylene was refluxed until the evolution of water was complete (about 13 ml H_2O). Chlorosilane **3a** (54.4 g, 0.5 mol, 63.3 ml) was then added at 40 ° C and the mixture was refluxed for 1 h then cooled to 20 ° C. The solid was filtered off and dried (57.0 g). It was then worked-up by refluxing with water (500 ml) and **1** (21.0 g) was isolated. For isolation of **4a** the mother liquor after the filtration was distilled at low pressure to give 79.1 g (88% based on recovered **1**; 66% based on inserted **3a**) of product.

*Reaction of **4a** with bromostyrenes.* A solution of **4a** (12.0 g, 50 mmol) in 40 ml of benzene was added to one of β-bromo-α-methylstyrene (9.8 g, 50 mmol) in 10 ml of benzene. After 1 h refluxing no vinylcarbazole could be detected by GC-MS. $AlCl_3$ (0.07 g) was then added and the mixture was refluxed for 1 h; traces of carbazole (**1**) were detected by GC-MS. After addition of an equimolar amount of $AlCl_3$ (6.7 g, 50 mmol), refluxing the mixture for 1 h and hydrolysis with ice/HCl, **1** (8.2 g, 50 mmol) was isolated from the organic layer. No vinylated carbazole could be detected by GC-MS.

Analogous results were obtained in experiments with Cu^ICl as catalyst, or with β-bromostyrene as substrate, or toluene as solvent.

*Reaction of **4a** with acetylchloride.* A solution of **4a** (12.0 g, 50 mmol) in 40 ml of benzene was treated with one of acetyl chloride (3.9 g, 50 mmol, 4.3 ml) in 10 ml of benzene at 0 ° C. The mixture was kept at 20 ° C for 1 h, refluxed for 1 h, treated with $AlCl_3$ (0.07 g), and refluxed again for 1h. 9-Acetylcarbazole was detected in traces by GC-MS. After addition of an equimolar amount of $AlCl_3$ (6.7 g, 50 mmol), refluxing the mixture for 1 h, and hydrolysis with ice/HCl, 9-acetylcarbazole (5.3 g, 63%) was isolated from the organic layer. Analogous results were obtained in experiments with Cu^ICl as catalyst (yield: 46%).

*Reaction of **4h** with water.* **4h** (1.00 g, 2.32 mmol) was stirred with water (10 ml) for 1 h at 20 ° C. Carbazole (**1**) formed was filtered off (m.p. 240 ° C, yield: 0.72 g (94%)).

Analogous results were obtained by treating a solution of **4h** in toluene (10 ml) with water (10 ml) and stirring the mixture for 1 h at 20 ° C.

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