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Penta-coordinated chlorosilanes: reaction chemistry, structure and bonding

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Abstract

The synthesis and reaction behavior of the penta-coordinated chlorosilanes $[C_6H_4CH_2N(CH_3)_2\text{-}2]Si(Cl)(R)(R')$ [**3a**: $R = R' = Cl$; **3b**: $R = R' = CH_3$; **3c**: $R = C1$, $R' = CH_3$; **3d**: $R = Cl$, $R' = CH{=}CH_2$; **3e**: $R = CH_3$, $R' = CH{=}CH_2$] are discussed. Compounds **3a–e** can be obtained by the reaction of $LiC_6H_4CH_2N(CH_3)_2\text{-}2$ (**1**) with stoichiometric amounts of $(R)(R')SiCl_2$ (**2**) in high yields and give access to a versatile reaction chemistry on substitution of the chlorine atoms by many of the diverse nucleophiles used. Hydrolysis of compound **3d** produces oligomeric $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)SiO\}_n$ (**4a**), whereas **3e** yields the disiloxane $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)(CH_3)Si\}_2O$ (**4b**). Alcoholysis of compounds **3d** and **3e** in presence of NEt_3 affords $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)(CH_3)Si(OCH_3)$ (**5a**) or $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)Si(OR)_2$ [**5b**: $R = CH_3$, **5c**: $R = C_2H_5$, **5d**: $R = {}^iC_3H_7$], respectively. Compound **5b** can be transferred to the difluorosilane derivative $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)SiF_2$ (**6**) by its reaction with $BF_3^*O(C_2H_5)_2$, while treatment with $LiAlH_4$ produces the silane $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)SiH_2$ (**7a**). Moreover, hypervalent silanes are accessible by the reaction of chloro-functionalized **3d** or **3e** with $LiAlH_4$ whereby compounds $[C_6H_4CH_2N(CH_3)_2](H_2C{=}CH)Si(H)(R)$ (**7a**: $R = H$; **7b**: $R = CH_3$) are formed in good yields. Metathesis reaction of compounds **3b–e** with LiR reagents [$R = C{\equiv}CR'$, $NHC_6H_2(CH_3)_3\text{-}2,4,6$, $P(C_6H_5)_2$] produces $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)(R)(SiC{\equiv}CR')$ [reaction of **3b** or **3e** with $LiC{\equiv}CR'$; **8a**: $R = CH_3$, $R' = C_6H_5$; **8b**: $R = CH_3$, $R' = Si(CH_3)_3$; **8c**: $R = CH{=}CH_2$, $R' = C_6H_5$; **8d**: $R = CH{=}CH_2$, $R' = Si(CH_3)_3$], $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)Si(C{\equiv}CR')_2$ [reaction of **3c** or **3d** with $LiC{\equiv}CR'$; **9a**: $R = CH_3$, $R' = C_6H_5$; **9b**: $R = CH{=}CH_2$, $R' = C_6H_5$; **9c**: $R = CH{=}CH_2$, $R = Si(CH_3)_3$], $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si[HNC_6H_2(CH_3)_3\text{-}2,4,6]_2$ [reaction of **3d** with $LiNHC_6H_2(CH_3)_3\text{-}2,4,6$; **10**] or $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si[P(C_6H_5)_2]_2$ [reaction of **3d** with $LiP(C_6H_5)_2$; **11**]. The solid state structures of **3c** and **3d** are reported. Complex **3c** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.918(5)$, $b = 11.557(3)$, $c = 12.830(7)$ Å; $\beta = 108.17(4)°$, $V = 1256(5)$ Å^3 and $Z = 4$; **3d** crystallizes in the monoclinic space group $P2_1$ with $a = 6.625(3)$, $b = 8.574(6)$, $c = 11.281(8)$ Å; $\beta = 88.16(5)°$, $V = 640.5(7)$ Å^3 and $Z = 2$. The central silicon atom in compounds **3c** and **3d** shows an essentially distorted trigonal-bipyramidal coordination sphere, with the axial positions occupied by the nitrogen donor atom and one chloro ligand. Dynamic ^{1}H-NMR studies confirm that the same geometry is adopted in solution. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Penta-coordination; Chlorosilanes; Synthesis, Reaction behavior

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1. Introduction

Recently, there has been a wide interest in hypervalent silicon species [1], as these compounds have been proposed as intermediates or transition states in many

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chemical reactions ([1]a,b,f). Auner, Corriu as well as Zybill have shown that hypervalent silicon species of type $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)SiCl_2$ or $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)SiH_2$ are well suited for the synthesis and stabilization of low-valent silanediyl transition metal compounds of type $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)Si{=}ML_n$ ($ML_n = Fe(CO)_4$, $Cr(CO)_5$, $(\eta^5\text{-}C_5H_5)Mn(CO)_2$; R = H, aryl) [2].

In the course of our studies, concerning the synthesis and reaction chemistry of heterobutadiene and heteroallyl π-systems, containing main group elements as well as transition metal atoms [3–5], we were interested in using penta-coordinated silicon compounds, which additionally feature organic π-systems such as vinyl or alkynyl groups in order to synthesize highly unsaturated compounds of type $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)Si{=}ML_n$ (ML_n = 16-valence electron transition metal fragment, R = organic π-system). In these silanediyl complexes, next to an silicon–metal double bond unit an organic π-system is located. This arrangement allows an direct internal comparison of the reaction behavior of both an organometallic and organic π-system next to each other.

In this context, we here report the synthesis and the reaction chemistry of hypervalent chlorofunctionalized silanes, to gain further information on nucleophilic substitution reactions at five-coordinated silicon atoms.

2. Results and discussion

2.1. Synthesis

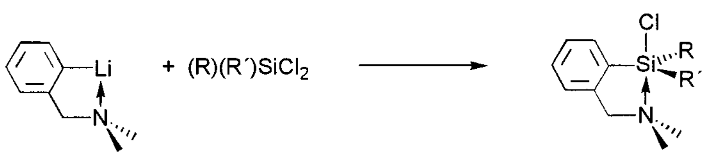
The penta-coordinated chlorosilanes $[C_6H_4CH_2N(CH_3)_2\text{-}2](Cl)Si(R)(R')$ (**3a**: $R = R' = Cl$; **3b**: $R = R' = CH_3$; **3c**: $R = Cl$, $R' = CH_3$; **3d**: $R = Cl$, $R' = CH{=}CH_2$; **3e**: $R = CH_3$, $R' = CH{=}CH_2$) were prepared by reacting equimolar amounts of $LiC_6H_4CH_2N(CH_3)_2\text{-}2$ (**1**) [6] with the appropriate chlorosilanes $(R)(R')SiCl_2$ (**2**) in diethyl ether solutions at ambient temperature, according to methods firstly described by van Koten [7] and Corriu et al. [1,8].

Compounds **3a–e** were the only products, which could be isolated by extraction of the reaction residues with dichloromethane, followed by filtration through a pad of Celite. While compounds **3a–d** could be crystallized as colorless solids from saturated dichloromethane/*n*-pentane solutions upon cooling to − 30°C, compound **3e** was obtained as an oil, which could be further purified by vacuum distillation. All compounds synthesized are soluble in most polar organic solvents and decompose rapidly on exposition to air.

Compounds **3a–e** were spectroscopically characterized by dynamic ^{1}H-NMR and temperature dependent $^{29}Si\{^1H\}$-NMR studies ([1]a, [9]). All these compounds contain a CH_2NMe_2 built-in arm, resulting in an penta-coordinated environment around the silicon atom. While hypervalent silicon molecules of the latter type are well studied in solution, only little is known about their solid state structure [8,10].

The X-ray structures of penta-coordinated **3c** and **3d** were determined in order to clearly confirm the intramolecular N–Si coordination of compounds **3a–e** in the solid state. The result of the X-ray structure analysis is shown in Fig. 1. Crystallographic parameters for compounds **3c** and **3d** are listed in Table 1, selected bond lengths and angles are given in Table 2 and atomic coordinates as well as anisotropic thermal parameters are depicted in Tables 3 and 4.

Compounds **3c** and **3d** crystallize in the monoclinic space group $P2_1/c$ (**3c**) and $P2_1$ (**3d**). Both compounds are characterized by a slightly distorted trigonal-bipyramidal coordinated silicon atom. The nitrogen atom N1 of the $C_6H_4CH_2N(CH_3)_2$ ligand is dative bonded to the silicon center and occupies an apical position of the trigonal bipyramid. Additionally, in both structures a chlorine atom (Cl1) is found in the apical position: This atom and the dative bonded nitrogen atom N1 are facing each other. This is in agreement with the increased ease of stretching the Cl–Si bond in comparison with the Si–C bonds of the methyl or vinyl groups present in compounds **3c** or **3d**. The N–Si distances of 2.183(3) and 2.257(7) Å in **3c** and **3d**, respectively, are relatively short, indicating a substantial bonding inter-



1 **2**

3a: R = R' = Cl
3b: R = R' = CH_3
3c: R = Cl, R' = CH_3
3d: R = Cl, R' = $CH{=}CH_2$
3e: R = CH_3, R' = $CH{=}CH_2$

action as compared with isostructural $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiF_2$ ([10]e). The shorter Si1–N1 bond in **3c** in contrast to the corresponding Si1–N1 bond in compound **3d** is reflected in a longer Si–Cl1 bond in **3c** (2.233(1) Å) than in **3d** (2.194(3) Å) (Table 2). In both compounds the N1–Si1–Cl1 axis are essentially linear [**3c** 176.3(1), **3d** 175.0(2)°] (Table 2). The vinyl group in **3d** is not in-plane bonded with the atoms C1, C10, Cl2 and Si1 [interplanar angle C1, C10, Cl2, Si1/Si1, C10, C11: 54.9(5)°]. An internal comparison of the Si–Cl bond distances Si_{ax}–Cl and Si_{eq}–Cl in compounds **3c** [Si1–Cl1 2.233(1), Si1–Cl2 2.087(2) Å] and **3d** [Si1–Cl1 2.194(3), Si1–Cl2 2.081(3) Å] (Table 2) shows that in each case the Si_{ax}–Cl distances are significantly elongated as compared with the appropriate Si_{eq}–Cl bond lengths ([1]a,d, [10]). The Si–C separations found in compounds **3c** and **3d** are in the range of values usually found for tetravalent derivatives [11].

The structures of molecules **3a–e** adopted in the solid state could also be confirmed in solution by temperature dependent ^{1}H-NMR (**3b–e**) or ^{29}Si{^{1}H}-NMR experiments (**3a–e**) (Sections 2.3 and 3) [12].

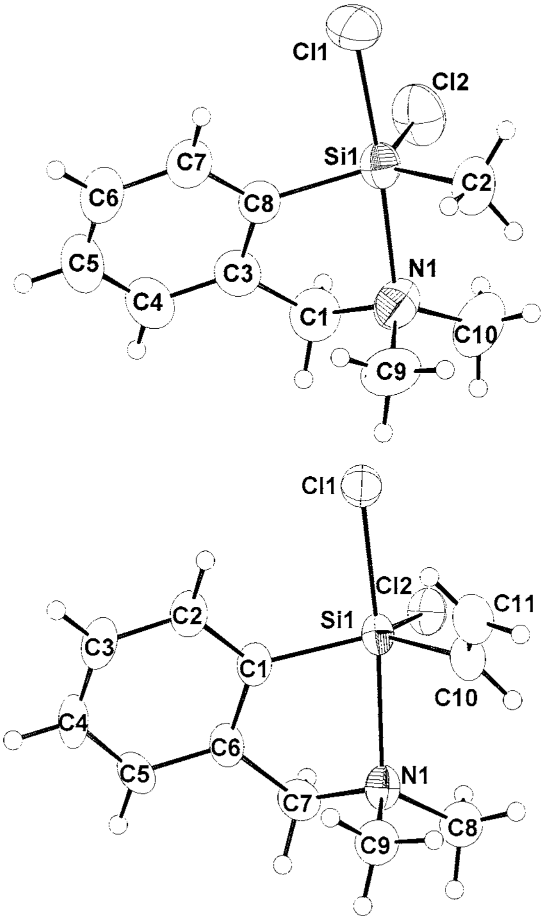


Fig. 1. ZORTEP drawings (drawn at 50% probability level) of compounds **3c** (top) and **3d** (bottom) with the atom numbering schemes.

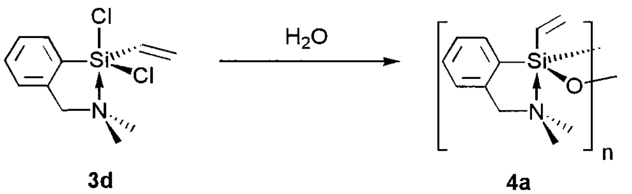
Table 1
Crystallographic parameters for compounds **3c** and **3d**

	3c	**3d**
Formula	$C_{10}H_{15}Cl_2NSi$	$C_{11}H_{15}Cl_2NSi$
FW	248.21	260.23
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a (Å)	8.918(5)	6.625(3)
b (Å)	11.557(3)	8.574(6)
c (Å)	12.830(7)	11.281(8)
β (°)	108.17(4)	88.16(5)
V (Å^3)	1256.4(10)	640.5(7)
$D_{calc.}$ (g cm^{-3})	1.31	1.35
Z	4	2
Crystal size (mm^3)	0.30 × 0.25 × 0.25	0.25 × 0.30 × 0.50
Diffraction model	Siemens R3m/V	Siemens R3m/V
μ (mm^{-1})	0.58	0.57
Radiation (λ, Å)	Mo–K_α (0.71073)	Mo–K_α (0.71073)
T (K)	293	272
Scan mode	ω-Scan	ω-Scan
Scan range $\Delta\omega$ (°)	0.75	0.75
Scan speed (° min^{-1})	2.3–29.3	2.3–29.3
2θ range (°)	3.0–51.0	3.6–48
Index ranges	$-10 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 15$	$-4 \leq h \leq 7$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$
Unique reflections	2340	1069
Observed [$I \geq 2\sigma(I)$]	1431	1026
Refined parameters	130	143
Largest difference peak and hole (e Å^{-3})	0.234/−0.279	0.675/−0.650
R_1/wR_2^a [$I > 2\sigma(I)$]	0.0462/0.1134	0.0559/0.1522
R_1/wR_2^a (all)	0.0957/0.1281	0.0595/0.1533
S (goodness-of-fit)^b on F^2	1.174	0.980

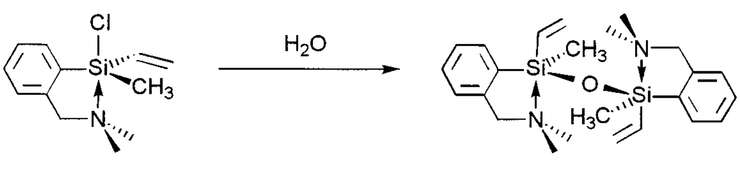
[a] $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]$, $wR_2 = \Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{0.5}$.
[b] $S = \Sigma w(F_o^2 - F_c^2)^2]/(n-p)^{0.5}$; n, number of reflections; p, parameters used.
Definition of w (where $P = (F_o^2 + 2F_c^2)/3]$:
3c: $w = 1/[\sigma^2(F_o^2) + (0.0716P)^2 + 0.0000P]$
3d: $w = 1/[\sigma^2(F_o^2) + (0.1121P)^2 + 0.4098P]$.

2.2. Reaction behavior

The intramolecular N–Si coordination found for all compounds **3a–e** is accompanied by an enhanced reactivity of these compounds when compared with tetravalent silicon species [1,2]. For example, hydrolysis of molecules **3d** or **3e** produces without added catalyst at low temperature the polymeric siloxane $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiO\}_n$ (**4a**) or the disiloxane $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(CH_3)Si\}_2O$ (**4b**) at 25°C in THF.

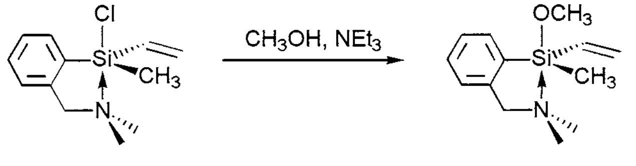


3d **4a**

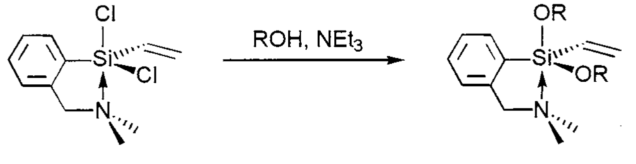


3e **4b**

While hydrolysis of compounds **3d** and **3e** is straightforward, the reaction of these compounds with less acidic alcohols requires the presence of a Lewis base, such as triethylamine. The chlorosilanes **3d** and **3e** were therefore refluxed with $N(C_2H_5)_3$ in alcoholic solutions (CH_3OH, C_2H_5OH, $^iC_3H_7OH$), causing the precipitation of $N(C_2H_5)_3 \cdot HCl$. The mono- (**5a**) or disubstituted silylethers (**5b–d**) are obtained as colorless oils in yields between 48–65% after appropriate work-up.



3e **5a**

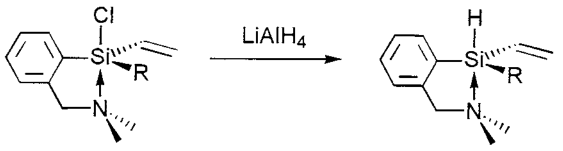


3d

5b: R = CH_3
5c: R = C_2H_5
5d: R = $^iC_3H_7$

Compound **5b** can successfully be used as a starting material for the synthesis of the hypervalent difluorosilane **6** or the silane **7a** by treatment with $(C_2H_5)_2O \cdot BF_3$ in *n*-pentane or with $LiAlH_4$ in diethyl ether solutions at 25°C.

A further possibility for the preparation of five-coordinated vinylated silanes is given by the reaction of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(R)SiCl$ (**3d**: R = Cl, **3e**: R = CH_3) with $LiAlH_4$ in diethyl ether at 25°C. The silanes $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_2{=}CH)(R)SiH$ [**7a**: R = H, **7b**: R = CH_3] are formed in 57 or 54% yield, respectively.

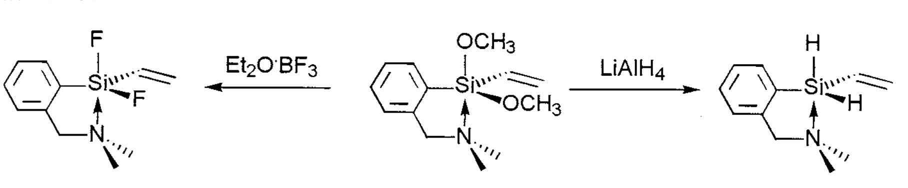


3d: R = Cl
3e: R = CH_3

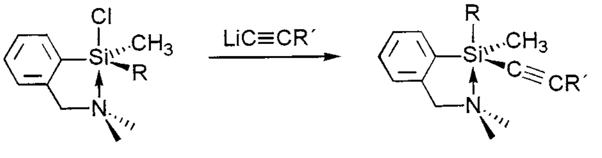
7a: R = H
7b: R = CH_3

Likewise, the chloro atoms in compounds **3b–e** can be replaced by different organic entities, e.g. alkynyls, amines and phosphines.

The mono- and di-alkynyl substituted silanes $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)(R)Si(C{\equiv}CR')$ [**8a**: R = CH_3, R′ = C_6H_5; **8b**: R = CH_3, R′ = $Si(CH_3)_3$; **8c**: R = $CH{=}CH_2$, R′ = C_6H_5; **8d**: R = $CH{=}CH_2$, R′ = $Si(CH_3)_3$] and $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)Si(C{\equiv}CR')_2$ [**9a**: R = CH_3, R′ = C_6H_5; **9b**: R = $CH{=}CH_2$, R′ = C_6H_5; **9c**: R = $CH{=}CH_2$, R′ = $Si(CH_3)_3$] can be synthesized by reacting equimolar amounts of the chlorosilane starting materials **3b–e** with $LiC{\equiv}CR'$ in diethlyl ether solutions at ambient temperature. Depending on the nature of the organic ligands R and R′, compounds **8** and **9** can be obtained in 50–85% yield.

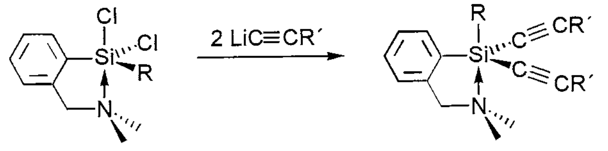


6 **5b** **7a**



3b: R = CH_3
3e: R = C_2H_3

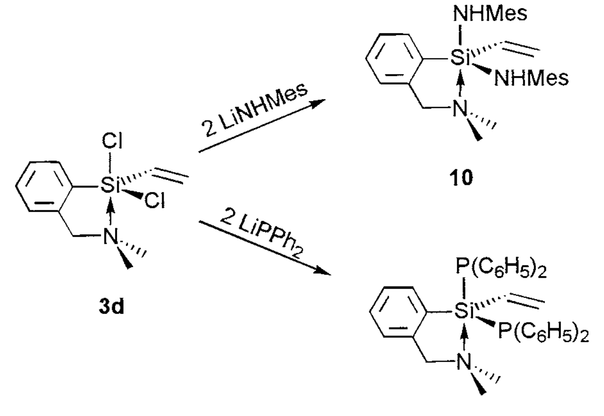
8a: R = CH_3, R′= C_6H_5
8b: R = CH_3, R′= $Si(CH_3)_3$
8c: R = C_2H_3, R′= C_6H_5
8d: R = C_2H_3, R′= $Si(CH_3)_3$



3c: R = CH_3
3d: R = C_2H_3

9a: R = CH_3, R′= C_6H_5
9b: R = C_2H_3, R′= C_6H_5
9c: R = C_2H_3, R′= $Si(CH_3)_3$

An access to amino- or phosphino-functionalized penta-coordinated silicon compounds is given by the reaction of the hypervalent dichlorosilane **3d** with two equivalents of LiNHMes (Mes = $C_6H_2(CH_3)_3$-2,4,6; synthesis of compound **10**) or $LiP(C_6H_5)_2$ (synthesis of compound **11**).



10

3d

11

Compounds **8–11** carry alkynyl, amino or phosphino groups, which should allow an attractive coordination chemistry. Hence, compounds **8** and **9** were reacted with a variety of inorganic and organic copper(I) compounds $[CuX]_n$. However, even at −100°C, only off-white or yellow polymeric products are formed, which are insoluble in most common organic solvents. IR spectroscopic studies confirm a η^2-coordination of the alkynyl ligands to the Group 11 metal atom, but the constitution of the latter complexes could not be assigned unequivocally.

2.3. Spectroscopic studies

The new synthesized compounds represent colorless oils (**3e** and **4–7**) or solids (**3a–d** and **8–11**: colorless; **10**: orange; **11**: off-white). While compounds **4–9** are soluble in most common organic solvents, molecules **3**, **10** and **11** can only be dissolved in polar solvents, such as dichloromethane, THF or acetone. Compounds **5–7**, as well as **10** and **11**, can be handled in air only for very short periods of time, whereas the oligosiloxane **4a**, the disiloxane **4b** and the alkynyl functionalized silanes **8** and **9** are stable to air.

Compounds **3–11** were completely characterized by elemental analysis and spectroscopic studies (IR, ^{1}H-, ^{13}C{^{1}H}-, ^{29}Si{^{1}H}-, ^{31}P{^{1}H}-NMR, MS).

The utilization of IR spectroscopy represents a reliable method for the rapid identification of the different functional ligands present in compounds **3–11**. IR spectra show the characteristic frequencies in the expected region of the functionalized groups, e.g. Si–O, Si–H, N–H, C=C and C≡C. The most remarkable feature in compounds $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(R)SiH$ [**7a**: R = H; **7b**: R = CH_3] is the observation of two Si–H stretching vibrations Si–H_{eq} and Si–H_{ax} at 2135 (vs) and 2081 (m) cm^{-1} in **7a** or 2133 (vs) and 2094 (m) cm^{-1} in **7b**. This is of major importance to clearly determine the structure of the hypervalent hydridosilanes **7a** and **7b**. It points out that at least different

Table 2
Selected bond lengths (Å) and angles (°) for compounds **3c** and **3d**[a]

3c		**3d**	
Bond lengths (Å)			
Si1–N1	2.183(3)	Si1–N1	2.257(7)
Si1–Cl1	2.233(1)	Si1–Cl1	2.194(3)
Si1–Cl2	2.087(2)	Si1–Cl2	2.081(3)
Si1–C2	1.863(3)	Si1–C10	1.850(7)
Si1–C8	1.873(3)	Si1–C1	1.880(7)
N1–C1	1.492(4)	N1–C7	1.461(10)
N1–C9	1.488(4)	N1–C8	1.490(10)
N1–C10	1.484(4)	N1–C9	1.498(10)
Bond angles (°)			
Cl1–Si1–Cl2	92.9(1)	Cl1–Si1–Cl2	93.4(1)
N1–Si1–Cl1	176.3(1)	N1–Si1–Cl1	175.0(2)
N1–Si1–Cl2	88.6(1)	N1–Si1–Cl2	86.7(2)
C2–Si1–Cl2	115.7(1)	C1–Si1–C12	115.2(2)
C8–Si1–Cl2	111.4(1)	C10–Si1–C12	113.6(2)
C2–Si1–C8	131.7(2)	C1–Si1–C10	128.2(3)
Si1–N1–C1	102.3(2)	C7–N1–C8	110.2(6)
S1–N1–C9	109.8(2)	C7–N1–C9	109.1(6)
Si1–N1–C10	118.3(2)	C7–N1–Si1	101.9(5)
C1–N1–C9	107.8(3)	C8–N1–C9	106.8(7)
C1–N1–C10	110.2(3)	C8–N1–Si1	119.0(5)
C9–N1–C10	108.0(3)	C9–N1–Si1	109.5(5)
		Si1–C10–C11	125.0(6)

[a] Estimated S.D. in units of the last significant figure in parentheses.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for **3c** ($Å^2 \times 10^3$)[a]

Atom	x/a	y/b	z/c	U_{eq}
Si1	2433(1)	2503(1)	7787(1)	44(1)
Cl1	2108(1)	688(1)	8275(1)	69(1)
Cl2	2328(1)	2015(1)	6200(1)	70(1)
N1	2905(3)	4273(2)	7385(2)	55(1)
C1	4591(4)	4208(3)	7418(3)	61(1)
C2	531(4)	2976(3)	7966(3)	61(1)
C3	5439(4)	3476(3)	8391(3)	49(1)
C4	7020(4)	3613(3)	8960(3)	62(1)
C5	7718(4)	2935(4)	9854(3)	68(1)
C6	6848(4)	2122(3)	10189(3)	62(1)
C7	5269(4)	1958(3)	9618(3)	51(1)
C8	4523(3)	2637(3)	8699(2)	40(1)
C9	2811(5)	5071(3)	8273(4)	77(1)
C10	1925(5)	4764(4)	6322(3)	80(1)

[a] Estimated S.D. in units of the last significant figure in parentheses; U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

isomers are formed in which the hydrogen atoms occupy axial or equatorial positions as well. Due to the unequal ratio of $\nu(Si–H_{eq})/\nu(Si–H_{ax})$, whereby the latter vibration is less intensive for both compounds, one can conclude that the equatorial positions in the trigonal bipyramid are preferentially occupied. Similar results were concluded by Corriu et al. on dihydridosilanes of type $[C_6H_4CH_2N(CH_3)_2\text{-}2](R)SiH_2$ and $[C_{10}H_6CH_2N(CH_3)_2\text{-}8](R)SiH_2$ ($R = C_6H_5$, α-$C_{10}H_7$) by dynamic NMR studies [9]. Compared with tetravalent silanes [13], the Si–H frequencies in the penta-coordinated silicon compounds **7a** and **7b** are shifted to lower wavenumbers.

However, for compound **7a** the formation of different isomers as revealed by IR spectroscopic studies is not observed by ^{1}H-NMR studies down to -100°C. Similar observations were made for all synthesized compounds with exception of compounds **3** and **6**. This phenomenon can be explained by the increased tendency of the halide substituents in accepting electron density as compared to alkyl, alkenyl, alkynyl and alkoxy groupings as well as H atoms.

Moreover, the silicon atom in compound **7b** is surrounded by a benzyl, vinyl and methyl unit as well as by a H atom and is thus chiral. The chirality is directly reflected in diastereotopic methylene protons of the $CH_2N(CH_3)_2$ entity, which is observed by the existence of two resonance signals at 3.59 and 3.61 ppm, respectively. However, of the insignificantly magnetic difference of the two protons, a splitting into doublets, which should be caused by a $^2J_{HH}$ coupling, is not observed. In contrast, the chirality of **3e** causes the magnetically inequivalent methylene protons of the $CH_2N(CH_3)_2$ unit, which leads to a separation of two doublets ($^2J_{HH} = 3.3$ Hz), already at 25°C.

As typical for hypervalent silicon compounds, compared with tetravalent ones, the $^{29}Si\{^1H\}$-NMR resonance signals of compounds **3–11** are shifted upfield [14]. The presence of two fluoro atoms in compound **6**, as well as two diphenyl–phosphino groups in compound **11** leads to a splitting of the $^{29}Si\{^1H\}$-NMR resonance signals to triplets with $^1J_{SiF} = 260$ Hz and $^1J_{SiP} = 49.3$ Hz, respectively.

In conclusion, the synthesis, reaction behavior, structure and bonding of highly functionalized hypervalent silicon compounds was described. For the first time monodentate bonded alkynyl, amino or phosphino groups could be introduced in this type of molecules.

3. Experimental section

3.1. General comments

All reactions were carried out in an atmosphere of nitrogen, using standard Schlenk techniques. Solvents were purified by distillation. *n*-Pentane and dichloromethane: calcium hydride; diethyl ether and THF: sodium/benzophenone ketyl; triethylamine and alcohols: sodium. Water was deoxygenated at 0°C/10^{-3} mbar and saturated with nitrogen. Chlorosilanes were distilled from magnesium and stored over magnesium at 0°C. IR spectra were obtained with a Perkin-Elmer 983G spectrometer as KBr pellets or as film between NaCl plates. NMR spectra were recorded on a Bruker AC 200 spectrometer, operating in the Fourier transform mode,^{1}H-NMR spectra were recorded at 200.132 MHz (internal standard relative to $CDCl_3$, $\delta = 7.27$); $^{13}C\{^1H\}$-NMR spectra were recorded at 50.323 MHz (standard intern, rel. $CDCl_3$, $\delta = 77.0$); $^{29}Si\{^1H\}$-NMR

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for **3d** ($Å^2 \times 10^3$)[a]

Atom	x/a	y/b	z/c	U_{eq}
Si1	1043(3)	8072(2)	7995(2)	29(1)
Cl1	2560(3)	5831(2)	8266(2)	39(1)
Cl2	−1826(2)	7086(2)	8091(2)	37(1)
N1	−495(9)	10336(8)	7546(5)	37(2)
C1	2107(10)	8411(9)	6452(6)	32(2)
C2	3901(10)	7764(10)	5980(6)	36(2)
C3	4566(10)	8120(11)	4832(6)	41(2)
C4	3445(13)	9079(10)	4134(6)	43(2)
C5	1657(12)	9724(9)	4564(7)	38(2)
C6	1035(11)	9420(9)	5738(6)	33(2)
C7	−838(11)	10142(10)	6282(7)	40(2)
C8	−2418(12)	10759(12)	8189(8)	48(2)
C9	937(13)	11664(9)	7711(7)	44(2)
C10	1782(11)	9020(9)	9390(6)	35(2)
C11	3s42(12)	8841(11)	9892(7)	43(2)

[a] Estimated S.D. in units of the last significant figure in parentheses; U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

spectra at 39.763 MHz (standard extern, rel. $Si(CH_3)_4$, $\delta = 0$) and $^{31}P\{^1H\}$-NMR spectra at 81.015 MHz (standard extern, rel. 85% H_3PO_4, with $P(OMe)_3$ $\delta = 139$ ppm). Chemical shifts are reported in δ units (ppm) downfield from TMS with the solvent as reference signal. FD and EI mass spectra were recorded on a Finnigan 8400 mass spectrometer, operating in the positive-ion mode. Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organisch-Chemisches Institut der Universität Heidelberg.

3.2. General procedure for the synthesis of compounds **3a–e**

According to the procedure described by van Koten and coworkers [7], 100 mmol of ^{n}BuLi (40 ml 2.5 M solution in *n*-hexane) are added dropwise to 100 mmol $C_6H_5CH_2N(CH_3)_2$-2 (13.5 g) in 300 ml of diethyl ether at − 30°C. The reaction mixture is allowed to warm to 25°C and stirred at this temperature for 7 days. The formed colorless suspension of $LiC_6H_4CH_2N(CH_3)_2$-2 is added at − 30°C, via a teflon cannula, to 100 mmol of the appropriate chlorosilane (**3a**: 17.0 g $SiCl_4$; **3b**: 12.9 g $(CH_3)_2SiCl_2$; **3c**: 15.0 g $(CH_3)SiCl_3$; **3d**: 16.2 g $(H_2C{=}CH)SiCl_3$; **3e**: 14.1 g $(CH_3)(H_2C{=}CH)SiCl_2$) dissolved in 200 ml of diethyl ether. The reaction mixture is allowed to warm to 25°C overnight. After filtration through a pad of Celite, all volatile materials are removed in vacuum and the obtained residues are crystallized from concentrated dichloromethane/*n*-pentane (**3a–c**; ratio 5:1) or diethyl ether/*n*-pentane (**3d**; ratio 1:1) solutions at − 30°C. Compound **3e** is purified by vacuum distillation.

3.2.1. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2]SiCl_3$ (**3a**)

Yield: 25.0 g (93.1 mmol, 93%, rel. $SiCl_4$). M.p. 112°C. ^1H-NMR ($CDCl_3$): δ 2.46 (s, 6 H, NCH_3), 3.83 (s, 2 H, CH_2), 7.1–7.2 (m, 1 H, C_6H_4), 7.4–7.5 (m, 2 H, C_6H_4), 8.2–8.3 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 46.1 (NCH_3), 61.9 (CH_2), 125.5, 128.0, 132.2, 132.9, 139.3, 142.1 (C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ − 62.6. EI MS *m/e* (rel. int.): M^+, 267 (13); $M^+ - Cl$, 232 (62); $M^+ - 2Cl$, 197 (12); $CH_2N(CH_3)_2^+$, 58 (100). Anal. Calc. for $C_9H_{12}NCl_3Si$ (268.63): C, 40.24; H, 4.50. Found: C, 40.01; H, 3.99%.

3.2.2. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)_2SiCl$ (**3b**)

Yield: 23.0 g [100.0 mmol, 100%, rel. $(CH_3)_2SiCl_2$]. M.p. 98°C. ^1H-NMR ($CDCl_3$): δ 0.83 (s, 6 H, $SiCH_3$), 2.16 (s, 6 H, NCH_3), 3.64 (s, 2 H, CH_2), 7.1–7.2 (m, 1 H, C_6H_4), 7.4–7.5 (m, 2 H, C_6H_4), 8.2–8.3 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 3.5 ($SiCH_3$), 46.5 (NCH_3), 60.0 (CH_2), 125.7, 127.9, 132.6, 132.9, 139.4, 143.0 (C_6H_4). EI MS *m/e* (rel. int.): M^+, 227 (26); $M^+ - CH_3$, 212 (86); $M^+ - Cl$, 192 (12); $CH_2N(CH_3)_2^+$, 58 (100). Anal. Calc. for $C_{11}H_{18}NClSi$ (227.79): C, 58.00; H, 7.96. Found: C, 57.87; H, 7.70%.

3.2.3. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)SiCl_2$ (**3c**)

Yield: 24.0 g (96.7 mmol, 97%, rel. $(CH_3)SiCl_3$). M.p. 94°C. ^1H-NMR ($CDCl_3$): δ 1.03 (s, 3 H, $SiCH_3$), 2.28 (s, 6 H, NCH_3), 3.70 (s, 2 H, CH_2), 7.1–7.2 (m, 1 H, C_6H_4), 7.3–7.4 (m, 2 H, C_6H_4), 8.2–8.3 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 9.3 ($SiCH_3$), 44.9 (NCH_3), 62.7 (CH_2), 126.1, 127.2, 131.1, 132.9, 138.6, 144.0 (C_6H_4) $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ − 24.1. EI MS *m/e* (rel. int.): M^+, 248 (66); $M^+ - CH_3$, 233 (6); $M^+ - Cl$, 213 (44); $M^+ - 2Cl$, 178 (100); $C_6H_5Si^+$, 105 (45). Anal. Calc. for $C_{10}H_{15}NCl_2Si$ (248.21): C, 48.39; H, 6.09; N, 5.64. Found: C, 48.84; H, 6.58; N, 5.52%.

3.2.4. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (**3d**)

Yield: 21.5 g (83.0 mmol, 83%, rel. $(H_2C{=}CH)SiCl_3$) . M.p. 104°C. IR (NaCl, cm^{-1}): $\nu_{C=C} = 1589$ (m). ^1H-NMR ($CDCl_3$): δ 2.26 (s, 6 H, NCH_3), 3.70 (s, 2 H, CH_2), 5.9–6.1 (m, 2 H, C_2H_3), 6.3–6.5 (m, 1 H, C_2H_3), 7.1–7.2 (m, 1 H, C_6H_4), 7.3–7.4 (m, 2 H, C_6H_4), 8.3–8.4 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 45.2 (NCH_3), 62.5 (CH_2), 125.9 (C_6H_4), 127.4 (C_6H_4), 130.4 (C_2H_3), 131.4 (C_6H_4), 131.9 (C_6H_4), 136.1 (C_2H_3), 139.2 (C_6H_4), 144.0 (C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ − 41.0. EI MS *m/e* (rel. int.): M^+, 259 (10); $M^+ - CH_3$, 255 (8); $M^+ - Cl$, 225 (44); $M^+ - N(CH_3)_2$, 216 (65); $N(CH_3)_3^+$, 59 (100). Anal. Calc. for $C_{11}H_{15}NCl_2Si$ (260.23): C, 50.77; H, 5.81; N, 5.38. Found: C, 50.92; H, 6.05; N, 5.17%.

3.2.5. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)(H_2C{=}CH)SiCl$ (**3e**)

Yield: 17.6 g (73.6 mmol, 74%, rel. $(CH_3)(H_2C{=}CH)SiCl_2$). B.p. 115–118°C/10^{-2} mbar. IR (NaCl, cm^{-1}): $\nu_{C=C} = 1588$ (s). ^1H-NMR ($CDCl_3$): δ 0.79 (s, 3 H, $SiCH_3$), 2.15 (s, 6 H, NCH_3), 3.51 (br s, 1 H, CH_2), 3.60 (br s, 1 H, CH_2), 5.84 (dd, $^2J_{HH} = 3.3$ Hz, $^3J_{HH} = 19.9$ Hz, 1 H, C_2H_3), 6.02 (dd, $^2J_{HH} = 3.3$ Hz, $^3J_{HH} = 14.5$ Hz, 1 H, C_2H_3), 6.41 (dd, $^3J_{HH} = 14.5$ Hz, $^3J_{HH} = 19.9$ Hz, 1 H, C_2H_3), 7.1–7.2 (m, 1 H, C_6H_4), 7.3–7.4 (m, 2 H, C_6H_4), 8.2–8.4 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 2.5 ($SiCH_3$), 44.9 (NCH_3), 63.7 (CH_2), 126.5 (C_6H_4), 126.9 (C_6H_4), 129.9 (C_2H_3), 130.3 (C_6H_4), 133.5 (C_6H_4), 137.1 (C_2H_3), 138.3 (C_6H_4), 144.6 (C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ − 21.0. EI MS *m/e* (rel. int.): M^+, 239 (12); $M^+ - CH_3$, 224 (13); $M^+ - Cl$, 204 (39); $M^+ - C_2H_3\text{–}CH_3$, 196 (100); $M^+ - Cl\text{–}C_2H_3$, 178 (60); $(C_6H_5)(C_2H_3)Si^+$, 132 (22); $(C_6H_5)Si^+$, 105 (15). Anal. Calc. for $C_{12}H_{18}NClSi$ (239.81): C, 60.10; H, 7.56. Found: C, 59.25; H, 8.02%.

*3.3. X-ray structure determinations of compounds **3c** and **3d** [16]*

The structures of compounds **3c** and **3d** were determined from single crystal X-ray diffraction data, which were collected using a Siemens R3 m/V (Nicolet Syntex) diffractometer. Crystallographic data for **3c** and **3d** are given in Table 1. All structures were solved by direct methods (SHELX-97) [17]. An initial empirical absorption correction was applied. The structures of compounds **3c** and **3d** were refined by the least-squares method based on F^2 with all reflections (SHELX-97). All non-H atoms were refined anisotropically; the H atons were placed in calculated positions. The structure plots have been made using ZORTEP [18].

*3.4. General procedure for the synthesis of compounds **4a** and **4b***

10.0 mmol of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(R)SiCl$ (**3d**: R = Cl, 2.6 g; **3e**: R = CH_3, 2.4 g) are dissolved in 50 ml of THF and 2 ml of water are added in one portion at 25°C. The reaction mixture is refluxed for 30 min and then all volatile materials are removed under vacuum at 25°C. The residue obtained is dissolved in 50 ml of dichloromethane and dried over $MgSO_4$. After removing the solvent under vacuum, compounds **4a** and **4b** are obtained as a colorless oil and powder, respectively.

*3.4.1. Data for $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiO\}_n$ (**4a**)*

Yield: 1.71 g (8.3 mmol, 83%, rel. **3b**). Mol. wt.: 600 g mol^{-1} (cryoscopic measurement in benzene [15]); $\tilde{n}$ = 2.9. IR (NaCl, cm^{-1}): ν_{OH} = 3381 (vs), $\nu_{C=C}$ = 1594 (w), ν_{SiO} = 1080 (vs). ^{1}H-NMR ($CDCl_3$): δ 2.0–2.3 (m, 6 H, NCH_3), 3.4–3.7 (m, 2 H, NCH_2), 5.6–6.4 (m, 3 H, C_2H_3), 7.0–8.0 (m, 4 H, C_6H_4). Anal. Calc. for $[C_{11}H_{15}ONSi]_n$ $(205.32)_n$: C, 64.35; H 7.36. Found: C, 63.85; H, 6.98%.

*3.4.2. Data for $\{[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(CH_3)Si\}_2O$ (**4b**)*

Yield: 1.70 g (4.0 mmol, 80%, rel. **3e**). IR (KBr, cm^{-1}): ν_{CH} = 2944 (vs), 2817 (vs), 2777 (vs); $\nu_{C=C}$ = 1588 (w); ν_{SiO} = 1044 (vs). ^{1}H-NMR ($CDCl_3$): δ 0.53 (s, 6 H, $SiCH_3$), 2.26 (s, 12 H, NCH_3), 3.33 (d, $^2J_{HH}$ = 12.2 Hz, 2 H, NCH_2), 3.83 (d, $^2J_{HH}$ = 12.2 Hz, 2 H, NCH_2), 5.8–6.5 (m, 6 H, C_2H_3), 7.2–7.6 (m, 6 H, C_6H_4), 7.8–7.9 (m, 2 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −1.5 ($SiCH_3$), 45.0 (NCH_3), 64.2 (NCH_2), 126.0–145.0 (C_2H_3 and C_6H_5). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −20.3. FAB MS *m/e* (rel. int.): M^+, 425 (9); $M^+ - CH_3$, 410 (19); $M^+ - C_2H_3$, 398 (10); $M^+ - N(CH_3)_2–C_2H_3–CH_3$, 338 (79); $[C_6H_4CH_2N(CH_3)_2](C_2H_3)(CH_3)Si^+$, 204 (60). Anal. Calc. for $C_{24}H_{36}N_2OSi_2$ (424.73): C, 65.11; H, 8.65 Found: C, 65.65; H, 7.99%.

*3.5. General procedure for the synthesis of compounds **5a–d***

A total of 50.0 ml of methanol (39.5 g, 1.23 mol), ethanol (39.5 g, 0.86 mol) or *i*-propanol (39.0 g, 0.65 mol) and 40 ml of triethylamine (29.2 g, 0.29 mol) are mixed and cooled to 0°C. To this mixture, 15.0 mmol $[C_6H_4CH_2N(CH_3)_2\text{-}2](C_2H_3)(R)SiCl$ (**3d**: R = Cl, 3.9 g; **3e**: R = CH_3, 3.6 g) are added slowly in four steps. An exothermic reaction is observed each time. To complete the reaction, the mixture is refluxed for 30 min and then filtered through a pad of Celite. After removal of all volatile materials under vacuum, the colorless oils obtained are purified by vacuum distillation.

*3.5.1. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)(CH_3)Si(OCH_3)$ (**5a**)*

Yield: 2.3 g (9.8 mmol, 65%, rel. **3e**). B.p. 130°C/10^{-1} mbar (ball tube distillation). IR (NaCl, cm^{-1}): ν_{CH} = 3044 (s), 2965 (vs), 2938 (vs), 2897 (s), 2851 (vs), 2811 (vs); $\nu_{C=C}$ = 1587 (m); ν_{SiO} = 1076 (vs). ^{1}H-NMR ($CDCl_3$): δ 0.59 (s, 3 H, $SiCH_3$), 2.10 (s, 6 H, NCH_3), 3.36 (d, $^2J_{HH}$ = 13.1 Hz, 1 H, CH_2), 3.46 (s, 3 H, OCH_3), 3.53 (d, $^2J_{HH}$ = 13.1 Hz, 1 H, CH_2), 5.79 (dd, $^2J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 19.7 Hz, 1 H, C_2H_3), 5.98 (dd, $^2J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 15.4 Hz, 1 H, C_2H_3), 6.27 (dd, $^3J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 19.7 Hz, 1 H, C_2H_3), 7.2–7.3 (m, 3 H, C_6H_4), 7.7–7.8 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −0.8 ($SiCH_3$), 44.8 (NCH_3), 50.4 (OCH_3), 64.1 (CH_2), 126.3, 128.2, 129.3, 139.4, 132.5, 135.7, 136.3, 145.7 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −12.4. EI MS *m/e* (rel. int.): M^+, 235 (6); $M^+ - CH_3$, 220 (17); $M^+ - CH_3–C_2H_4$, 192 (43); $M^+ - 2CH_3–C_2H_3$, 178 (100). Anal. Calc. for $C_{13}H_{21}NOSi$ (235.40): C, 66.33; H, 8.99. Found: C, 66.13; H, 8.78%.

*3.5.2. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si(OCH_3)_2$ (**5b**)*

Yield: 1.8 g (7.2 mmol, 48%, rel. **3d**). B.p. 118°C/10^{-1} mbar. IR (NaCl, cm^{-1}): ν_{CH} = 3047 (s), 2967 (s) 2933 (vs), 2948 (m), 2827 (s), 2811 (s), 2771 (s); $\nu_{C=C}$ = 1588 (m); ν_{SiO} 1084 (vs). ^{1}H-NMR ($CDCl_3$): δ 2.16 (s, 6 H, NCH_3), 3.51 (s, 2 H, CH_2), 3.59 (s, 6 H, OCH_3), 5.8–5.9 (m, 1 H, C_2H_3), 6.0–6.2 (m, 2 H, C_2H_3), 7.3–7.4 (m, 3 H, C_6H_4), 7.8–7.9 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 44.7 (NCH_3), 50.1 (OCH_3), 63.8 (CH_2), 126.1, 128.0, 129.9, 131.7, 133.4, 133.7, 136.5, 146.5 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −32.67. EI MS *m/e* (rel. int.): M^+, 251 (24); $M^+ - CH_3$, 236 (50); $M^+ - C_2H_3–CH_4$, 208 (100). Anal. Calc. for $C_{13}H_{21}NO_2Si$ (251.40): C, 62.11; H, 8.42. Found: C, 62.48; H, 8.89%.

*3.5.3. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si(OC_2H_5)_2$ (**5c**)*

Yield: 2.3 g (8.3 mmol, 55%, rel. **3d**). B.p. 110°C/10^{-2} mbar. IR (NaCl, cm^{-1}): ν_{CH} = 3048 (s), 2966 (s), 2937 (vs), 2873 (m), 2810 (s), 2768 (s); $\nu_{C=C} = 1588$ (m); $\nu_{SiO} = 1079$ (vs). ^{1}H-NMR ($CDCl_3$): δ 1.20 (t, $^3J_{HH} = 7.0$ Hz, 6 H, $OCH_2C\mathit{H}_3$), 2.16 (s, 6 H, $NC\mathit{H}_3$), 3.48 (s, 2 H, $NC\mathit{H}_2$), 3.77 (q, $^3J_{HH} = 7.0$ Hz, 4 H, $OC\mathit{H}_2CH_3$), 5.7–5.9 (m, 1 H, $C_2\mathit{H}_3$), 6.0–6.1 (m, 2 H, $C_2\mathit{H}_3$), 7.1–7.2 (m, 1 H, $C_6\mathit{H}_4$), 7.3–7.4 (m, 2 H, $C_6\mathit{H}_4$), 7.7–7.8 (m, 1 H, $C_6\mathit{H}_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 18.2 ($OCH_2\mathit{C}H_3$), 45.0 ($N\mathit{C}H_3$), 58.0 ($O\mathit{C}H_2CH_3$), 63.8 ($N\mathit{C}H_2$), 126.0, 128.2, 129.9, 132.6, 133.9, 134.2, 136.4, 146.4 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ -40.0. EI MS *m*/*e* (rel. int.): M^+, 279 (20); $M^+ - CH_3$, 264 (52); $M^+ - CH_3{-}C_2H_4$, 236 (100); $M^+ - OCH_2CH_3$, 234 (37). Anal. Calc. for $C_{15}H_{25}NO_2Si$ (279.46): C, 64.47; H, 9.02. Found: C, 63.99; H, 9.60%.

*3.5.4. Data for [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)Si($O^iC_3H_7$)$_2$ (**5d**)*

Yield: 2.5 g (8.1 mmol, 54%, rel. **3d**). IR (NaCl, cm^{-1}): $\nu_{CH} = 3049$ (m), 2965 (vs), 2936 (vs), 2882 (m), 2810 (s), 2767 (s); $\nu_{C=C} = 1588$ (m); $\nu_{SiO} = 1029$ (vs). ^{1}H-NMR ($CDCl_3$): δ 1.3 [m[1], 12 H, $OCH(C\mathit{H}_3)_2$], 2.25 (s, 6 H, $NC\mathit{H}_3$), 3.66 (s, 2 H, $NC\mathit{H}_2$), 4.28 [m, 2 H, $OC\mathit{H}(CH_3)_2$], 6.0–6.2 (m, 3 H, $C_2\mathit{H}_3$), 7.3–7.6 (m, 3 H, $C_6\mathit{H}_4$), 7.8–7.9 (m, 1 H, $C_6\mathit{H}_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 25.0[2] [$OCH(\mathit{C}H_3)_2$], 25.6[2] [$OCH(\mathit{C}H_3)_2$], 45.2 ($N\mathit{C}H_3$), 63.5 ($N\mathit{C}H_2$), 65.2 [$O\mathit{C}H(CH_3)_2$], 125.8, 128.1, 129.9, 133.2, 134.5, 134.9, 136.2, 146.0 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ -42.3. EI MS *m*/*e* (rel. int.): M^+, 307 (33); $M^+ - CH_3$, 292 (64); $M^+ - CH(CH_3)_2$, 264 (100); $M^+ - OCH(CH_3)_2$, 248 (58). Anal. Calc. for $C_{17}H_{29}NO_2Si$ (307.51): C, 66.40; H, 9.50. Found: C, 66.61; H, 9.16%.

*3.6. Synthesis of [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)SiF_2 (**6**)*

Freshly distilled $BF_3 \cdot O(C_2H_5)_2$ [870 mg (6.1 mmol)] are added dropwise to a solution of 1.53 g (6.1 mmol) [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)Si(OCH_3)$_2$ (**5b**) in 30 ml of *n*-pentane at 25°C. The reaction mixture is stirred for 30 min and then all volatile materials are removed under vacuum. The yellow oil obtained is purified by ball tube distillation (temperature of the air bath 170°C/10^{-1} mbar). 1.1 g (4.84 mmol, 79%, rel. compound **5b**) of **6** are obtained as a colorless oil.

IR (NaCl, cm^{-1}): $\nu_{CH} = 3053$ (s), 2998 (s), 2946 (s), 2868 (s), 2835 (s), 2789 (m); $\nu_{C=C} = 1591$ (s); $\nu_{SiF} = 853$ (vs). ^{1}H-NMR ($CDCl_3$): δ 2.30 (s, 6 H, $NC\mathit{H}_3$), 3.62 (s, 2 H, $NC\mathit{H}_2$), 6.0–6.1 (m, 3 H, $C_2\mathit{H}_3$), 7.1–7.2 (m, 1 H, $C_6\mathit{H}_4$), 7.3–7.4 (m, 2 H, $C_6\mathit{H}_4$), 7.9–8.0 (m, 1 H, $C_6\mathit{H}_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 45.2 ($N\mathit{C}H_3$), 62.9 ($N\mathit{C}H_2$), 125.5, 127.2, 131.1 (t, $^3J_{CF} = 23.0$ Hz), 132.8 (t, $^3J_{CF} = 22.0$ Hz), 131.3, 134.2, 137.5, 145.2 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ -62.6 (t, $^1J_{SiF} = 258.8$ Hz). EI MS *m*/*e* (rel. int.): M^+, 227 (39); $M^+ - CH_3$, 212 (41); $M^+ - C_2H_3$, 200 (22); $M^+ - C_2H_3{-}CH_4$, 184 (57); $M^+ - C_2H_3{-}CH_3 - 2F$, 132 (23); $CH_2N(CH_3)_2^+$, 58 (100). Anal. Calc. for $C_{11}H_{15}NF_2Si$ (227.33): C, 58.12; H, 6.65. Found: C, 57.73; H, 7.03%.

*3.7. Synthesis of [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)SiH_2 (**7a**) from **5b***

At 0°C 31.0 g (124.0 mmol) of [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)Si(OCH_3)$_2$ (**5b**) are dissolved in 300 ml of diethyl ether and added slowly to a suspension of 2.6 g (68.4 mmol) $LiAlH_4$ in 500 ml of diethyl ether. The gray slurry is slowly warmed to 25°C and the solvent is distilled off. To the residue obtained 400 ml of *n*-pentane are added and filtered through a pad of Celite. After removal of the solvent the colorless oil is further purified by vacuum distillation (64–68°C/10^{-1} mbar) to yield 14.8 g (63%, 77.0 mmol, rel. **5b**) of **7a**.

IR (NaCl, cm^{-1}): $\nu_{CH} = 3045$ (s), 2969 (s), 2937 (s), 2852 (s), 2817 (s), 2781 (s); $\nu_{SiH} = 2135$ (vs), 2081 (m); $\nu_{C=C} = 1586$ (s). ^{1}H-NMR ($CDCl_3$): δ 2.35 (s, 6 H, $NC\mathit{H}_3$), 4.73 (d, $^3J_{HH} = 3.2$ Hz, 2 H, $Si\mathit{H}$), 3.67 (s, 2 H, $C\mathit{H}_2$), 6.13 (dd, $^2J_{HH} = 4.4$ Hz, $^3J_{HH} = 19.5$ Hz, 1 H, $C_2\mathit{H}_3$), 6.28 (dd, $^2J_{HH} = 4.4$ Hz, $^3J_{HH} = 14.1$ Hz, 1 H, $C_2\mathit{H}_3$), 6.4–6.6 (m, 1 H, $C_2\mathit{H}_3$), 7.2–7.3 (m, 1 H, $C_6\mathit{H}_4$), 7.4–7.5 (m, 2 H, $C_6\mathit{H}_4$), 7.8–7.9 (m, 1 H, $C_6\mathit{H}_4$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 46.3 ($N\mathit{C}H_3$), 61.9 ($\mathit{C}H_2$), 126.6, 126.9, 129.4, 133.2, 133.5, 136.9, 139.5, 145.7 (C_2H_3 and C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ -46.2. EI MS *m*/*e* (rel. int.): M^+, 191 (36); $M^+ - CH_3$, 176 (57); $M^+ - C_2H_3$, 164 (64); $M - CH_3{-}C_2H_4$, 148 (98); $(C_6H_4CH_2)Si(C_2H_3)^+$, 145 (100). Anal. Calc. for $C_{11}H_{17}NSi$ (191.34): C, 69.05; H, 8.95. Found: C, 68.98; H, 9.04%.

*3.8. Synthesis of [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(R)SiH (**7**) from **3***

A solution of 16.0 g (62 mmol) [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)$SiCl_2$ (**3d**) in 300 ml of diethyl ether or 30.0 g (124 mmol) [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(CH_3)-SiCl (**3e**) in 500 ml of diethyl ether is added dropwise to a suspension of 2.6 g (68.4 mmol) $LiAlH_4$ in 500 ml of diethyl ether at 0°C. The reaction mixture is slowly warmed to 25°C and then refluxed for 1 h. All volatile materials are removed at 0°C and the residue obtained extracted with a total of 500 ml of *n*-pentane. Filtration through a pad of Celite and following distillation under vacuum produced the compounds [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(R)SiH (**7a**: R = H; **7b**: R = CH_3) as colorless oils.

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[1] Hindered rotation of the $^iC_3H_7$ units at 25°C.

[2] Due to the hindered rotation of the $^iC_3H_7$ units at 25°C two resonance signals for the methyl carbon atoms are observed.

*3.8.1. Data for [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)SiH_2 (**7a**)*

Yield: 6.7 g (35.3 mmol, 57%, rel. **3d**). For spectroscopic and analytical data see Section 3.7.

*3.8.2. Data for [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(CH_3)SiH (**7b**)*

Yield: 14.3 g (70.0 mmol, 54%, rel. **3d**). B.p. 63°C/ 10^{-1} mbar. IR (NaCl, cm^{-1}): $\nu_{CH} = 3043$(s), 2997 (s), 2965 (s), 2937 (s), 2851 (s), 2817 (vs), 2773 (vs); $\nu_{SiH} = 2133$ (vs), 2094 (m); $\nu_{C=C} = 1586$ (m). ^{1}H-NMR ($CDCl_3$): δ 0.55 (d, $^3J_{HH} = 3.6$ Hz, 3 H, SiCH_3), 2.29 (s, 6 H, NCH_3), 3.59 (s, 1 H, CH_2), 3.61 (s, 1 H, CH_2), 4.75 (dq, $^3J_{HH} = 2.6$ Hz, $^3J_{HH} = 3.6$ Hz, 1 H, SiH), 5.96 (dd, $^2J_{HH} = 4.2$ Hz, $^3J_{HH} = 19.9$ Hz, 1 H, C_2H_3), 6.19 (dd, $^2J_{HH} = 4.2$ Hz, $^3J_{HH} = 14.4$ Hz, 1 H, C_2H_3), 6.49 (ddd, $^3J_{HHSi} = 2.6$ Hz, $^3J_{HH} = 14.4$ Hz, $^3J_{HH} = 19.9$ Hz, 1 H, C_2H_3), 7.3–7.4 (m, 3 H, C_6H_4), 7.7–7.8 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −4.4 (SiCH_3), 44.5 (NCH_3), 64.6 (CH_2), 126.5 (C_6H_4), 128.3 (C_6H_4), 129.1 (C_6H_4), 132.4 (C_6H_4), 136.0 (C_6H_4), 136.2 (C_2H_3), 137.8 (C_6H_4), 145.8 (C_2H_3). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −31.9. EI MS *m/e* (rel. int.): M^+, 205 (13); $M^+ - CH_3$, 190 (53); $M^+ - C_2H_3$, 178 (14); $M^+ - CH_3{-}C_2H_4$, 162 (100); $M^+ - 3CH_3$, 160 (61); $(C_6H_4CH_2)Si(C_2H_3)^+$, 145 (77). Anal. Calc. for $C_{12}H_{19}NSi$ (205.37): C, 70.16; H, 9.32. Found: C, 69.83; H, 9.24%.

*3.9. General procedure for the synthesis of compounds **8a–d** and **9a–c***

20.0 mmol HC≡CR (R = C_6H_5: 2.04 g; R = $Si(CH_3)_3$: 1.96 g) in 50 ml of diethyl ether are lithiated using equimolar amounts of a 2.5 M ^{n}BuLi solution in *n*-hexane at 0°C. The obtained LiC≡CR reagents are warmed to 25°C and then slowly added to 20.0 mmol of [$C_6H_4CH_2N(CH_3)_2$-2](CH_3)(R)SiCl (**3b**: R = CH_3, 4.56 g; **3e**: R = $H_2C{=}CH$, 4.79 g; synthesis of compounds **8a–d**) or 10.0 mmol of [$C_6H_4CH_2N(CH_3)_2$-2](R)$SiCl_2$ (**3c**: R = CH_3, 2.48 g; **3d**: R = $H_2C{=}CH$, 2.60 g; synthesis of compounds **9a–c**) at −30°C. The reaction mixture is allowed to warm to 25°C. After addition of 200 ml of *n*-pentane the suspension is filtered through a pad of Celite. While compounds **8a** and **9a** can further be purified by crystallization from concentrated diethyl ether/*n*-pentane (1:1) solution at −30°C, compounds **8b–d**, **9b** and **9c** are best purified by vacuum distillation.

*3.9.1. Data for [$C_6H_4CH_2N(CH_3)_2$-2]$(CH_3)_2$Si(C≡CC_6H_5) (**8a**)*

Yield: 5.0 g (17 mmol, 85%, rel. **3b**). IR (KBr, cm^{-1}): $\nu_{C\equiv C} = 2160$ (vs). ^{1}H-NMR ($CDCl_3$): δ 0.61 (s, 6 H, SiCH_3), 2.25 (s, 6 H, NCH_3), 3.70 (s, 2 H, CH_2), 7.3–7.4 (m, 6 H, C_6H_4, C_6H_5), 7.5–7.6 (m, 2 H, C_6H_4, C_6H_5), 7.8–7.9 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 0.5 (SiCH_3), 44.8 (NCH_3), 64.5 (CH_2), 94.2 (SiC≡C), 105.6 (SiC≡C), 123.0, 127.9, 128.5, 128.8, 129.0, 129.7, 132.0, 136.6, 137.5, 146.0 (C_6H_4, C_6H_5). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −24.2. EI MS *m/e* (rel. int.): M^+, 293 (34); $M^+ - CH_3$, 278 (32); $M^+ - N(CH_3)_2$, 250 (100); $M^+ - N(CH_3)_2{-}CH_3$, 235 (23); $M^+ - C_2C_6H_5$, 191 (6); $M^+ - C_2C_6H_5{-}CH_3$, 176 (68); $HC_2C_6H_5^+$, 102 (12). Anal. Calc. for $C_{19}H_{23}NSi$ (293.48): C, 77.76; H, 7.90. Found: C, 77.94; H, 8.13%.

*3.9.2. Data for [$C_6H_4CH_2N(CH_3)_2$-2]$(CH_3)_2$Si[C≡C$Si(CH_3)_3$] (**8b**)*

Yield: 3.90 g (13.5 mmol, 67%, rel. **3b**). B.p. 98°C/ 10^{-1} mbar. IR (NaCl, cm^{-1}): $\nu_{C\equiv C} = 2102$ (vw). ^{1}H-NMR ($CDCl_3$): δ 0.26 (s, 9 H, SiCH_3), 0.51 (s, 6 H, SiCH_3), 2.24 (s, 6 H, NCH_3), 3.66 (s, 2 H, CH_2), 7.3–7.5 (m, 3 H, C_6H_4), 7.8–7.9 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −0.1 (SiCH_3), 0.5 (SiCH_3), 44.9 (NCH_3), 64.5 (CH_2), 114.5 (C≡C), 114.8 (C≡C), 126.4, 128.6, 129.4, 135.3, 135.9, 145.8 (C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −24.4 [$Si(CH_3)_3$], −30.6 [$Si(CH_3)_2$]. EI MS *m/e* (rel. int.): M^+, 289 (1); $M^+ - CH_3$, 274 (17); $M - N(CH_3)_2$, 246 (57); $M^+ - Si(CH_3)_3$, 216 (11); $M^+ - Si(CH_3)_3{-}CH_3$, 201 (9); $M^+ - C_2Si(CH_3)_3{-}CH_3$, 176 (100). Anal. Calc. for $C_{16}H_{27}NSi_2$ (289.57): C, 66.37; H, 9.40. Found: C, 66.16; H, 9.43%.

*3.9.3. Data for [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(CH_3)Si(C≡CC_6H_5) (**8c**)*

Yield: 4.90 g (16.1 mmol, 80%, rel. **3e**). B.p. 210°C/ 10^{-1} mbar (ball tube distillation). IR (NaCl, cm^{-1}): $\nu_{C\equiv C} = 2155$ (vs); $\nu_{C=C} = 1587$ (s). ^{1}H-NMR ($CDCl_3$): δ 0.80 (s, 3 H, SiCH_3), 2.32 (s, 6 H, NCH_3), 3.75 (s, 2 H, CH_2), 6.2–6.3 (m, 2 H, C_2H_3), 6.4–6.6 (m, 1 H, C_2H_3), 7.4–7.5 (m, 6 H, C_6H_4, C_6H_5), 7.6–7.7 (m, 2 H, C_6H_4, C_6H_5), 8.1–8.2 (m, 1 H, C_6H_4) $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −1.2 (SiCH_3), 44.9 (NCH_3), 64.5 (CH_2), 93.2 (SiC≡C), 106.3 (SiC≡C), 123.4, 126.5, 128.1, 128.3, 128.5, 129.5, 131.8, 132.9, 134.1, 135.5, 136.7, 145.9 (C_2H_3, C_6H_4, C_6H_5). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −36.5. EI MS *m/e* (rel. int.): M^+, 305 (12); $M^+ - CH_3$, 290 (33); $M^+ - N(CH_3)_2$, 262 (100); $M^+ - N(CH_3)_2{-}C_2H_3$, 234 (31); $M^+ - C_2C_6H_5{-}CH_3$, 188 (87). Anal. Calc. for $C_{20}H_{23}NSi$ (305.49): C, 78.63; H, 7.59. Found: C, 77.41; H, 7.68%.

*3.9.4. Data for [$C_6H_4CH_2N(CH_3)_2$-2]($H_2C{=}CH$)(CH_3)Si[C≡C$Si(CH_3)_3$] (**8d**)*

Yield: 4.20 g (13.9 mmol, 70%, rel. **3e**). B.p. 102°C/ 5×10^{-2} mbar. IR (NaCl, cm^{-1}): $\nu_{C\equiv C} = 2102$ (vw); $\nu_{C=C} = 1587$ (s). ^{1}H-NMR ($CDCl_3$): δ 0.36 (s, 9 H, SiCH_3), 0.66 (s, 3 H, SiCH_3), 2.28 (s, 6 H, NCH_3), 3.69 (s, 2 H, CH_2), 6.10 (dd, $^2J_{HH} = 4.3$ Hz, $^3J_{HH} = 19.6$ Hz, 1 H, C_2H_3), 6.21 (dd, $^2J_{HH} = 4.3$ Hz, $^3J_{HH} = 14.6$ Hz, 1 H, C_2H_3), 6.48 (dd, $^3J_{HH} = 14.6$ Hz, $^3J_{HH} = 19.6$ Hz, 1 H, C_2H_3), 7.3–7.4 (m, 3 H, C_6H_4), 7.9–8.0 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −1.3 (SiCH_3), −0.1 (SiCH_3), 44.8 (NCH_3), 64.4 (CH_2), 112.5 (C≡C), 114.9 (*C*≡C), 126.4, 128.4, 129.5, 132.9, 133.9, 136.6, 136.8, 145.9 (C_2H_3, C_6H_4) $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −24.3 [*Si*(CH_3)$_3$], −37.8 (*Si*CH_3). EI MS *m*/*e* (rel. int.): M^+, 301 (10); $M^+ - CH_3$, 286 (28); $M^+ - N(CH_3)_2$, 258 (100); $M^+ - N(CH_3)_2{-}C_2H_3$, 230 (12); $M^+ - C_2Si(CH_3)_3{-}CH_3$, 188 (95). Anal. Calc. for $C_{17}H_{27}NSi_2$ (301.58): C, 67.71; H, 9.02. Found: C, 67.86; H, 8.73%.

3.9.5. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](CH_3)Si(C{\equiv}CC_6H_5)_2$ ***(9a)***

Yield: 2.4 g (6.3 mmol, 63%, rel. **3c**). M.p. 69°C. IR (NaCl, cm^{-1}): $\nu_{C\equiv C} = 2160$ (vs). ^1H-NMR ($CDCl_3$): δ 0.79 (s, 3 H, $SiCH_3$), 2.28 (s, 6 H, NCH_3), 3.77 (s, 2 H, CH_2), 7.3–7.4 (m, 9 H, C_6H_4, C_6H_5), 7.5–7.6 (m, 4 H, C_6H_4, C_6H_5), 8.3–8.4 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 1.9 ($SiCH_3$), 44.7 (NCH_3), 64.2 (CH_2), 92.7 (SiC≡*C*), 104.8 (Si*C*≡C), 123.3, 126.7, 128.0, 128.1, 128.4, 129.9, 131.9, 132.6, 137.3, 146.4 (C_6H_4, C_6H_5). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −50.6. EI MS *m*/*e* (rel. int.): M^+, 379 (41); $M^+ - CH_3$, 364 (32); $M^+ - N(CH_3)_2$, 335 (20); $M^+ - 3CH_3$, 334 (24); $M^+ - C_2C_6H_5$, 278 (29); $M^+ - C_2C_6H_5{-}CH_3$, 263 (46); $M^+ - C_2C_6H_5{-}N(CH_3)_2$, 234 (70); $M^+ - C_2C_6H_5{-}N(CH_3)_2{-}CH_3$, 219 (34); $M^+ - 2C_2C_6H_5$, 177 (21); $M^+ - 2C_2C_6H_5{-}CH_3$, 162 (19); $SiC_2C_6H_5^+$, 129 (21); $HC_2C_6H_5^+$, 102 (17); $C_6H_5CH_2^+$, 91 (16); $C_6H_5^+$, 77 (9); $CH_2N(CH_3)_2^+$, 58 (100). Anal. Calc. for $C_{26}H_{25}NSi$ (379.58): C, 82.27; H, 6.64. Found: C, 81.92; H, 6.41%.

3.9.6. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si(C{\equiv}CC_6H_5)_2$ ***(9b)***

Yield: 2.5 g (6.5 mmol, 65%, rel. **3d**). B.p. 190°C/5 × 10^{-2} mbar (ball tube distillation). IR (NaCl, cm^{-1}): $\nu_{CH} = 3047$ (s), 2947 (vs), 2850 (s), 2812 (s), 2773 (s); $\nu_{C\equiv C} = 2156$ (vs); $\nu_{C=C} = 1588$ (s). ^1H-NMR ($CDCl_3$): δ 2.33 (s, 6 H, NCH_3), 3.81 (s, 2 H, CH_2), 6.2–6.3 (m, 2 H, C_2H_3), 6.4–6.5 (m, 1 H, C_2H_3), 7.2–7.5 (m, 9 H, C_6H_4, C_6H_5), 7.5–7.7 (m, 4 H, C_6H_4, C_6H_5), 8.3–8.4 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 44.7 (NCH_3), 63.9 (CH_2), 91.4 (SiC≡*C*), 105.6 (Si*C*≡C), 123.3, 126.8, 127.8, 128.2, 128.5, 130.1, 131.6, 131.8, 132.0, 133.7, 135.3, 146.4 (C_2H_3, C_6H_4, C_6H_5). EI MS *m*/*e* (rel. int.): M^+, 391 (13); $M^+ - CH_3$, 376 (11); $M^+ - C_2H_3$, 364 (10); $M^+ - CH_3{-}C_2H_3$, 348 (19); $M^+ - C_2C_6H_5$, 290 (47); $M^+ - C_2C_6H_5{-}N(CH_3)_2$, 247 (100); $HC_2C_6H_5^+$, 102 (47); $CH_2N(CH_3)_2^+$, 58 (21). Anal. Calc. for $C_{27}H_{25}NSi$ (391.59): C, 82.82; H, 6.44. Found: C, 82.82; H, 6.04%.

3.9.7. Data for $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si[C{\equiv}CSi(CH_3)_3]_2$ ***(9c)***

Yield: 1.85 g (4.8 mmol, 48%, rel. **3d**). B.p. 190°C/5 × 10^{-2} mbar (ball tube distillation). IR (NaCl, cm^{-1}): $\nu_{CH} = 3047$ (s), 2953 (vs), 2893 (m), 2774 (s), 2721 (s), 2697 (s); $\nu_{C\equiv C} = 2105$ (vw); $\nu_{C=C} = 1587$ (m). ^1H-NMR ($CDCl_3$): δ 0.27 (s, 18 H, $SiCH_3$), 2.20 (s, 6 H, NCH_3), 3.67 (s, 2 H, CH_2), 6.1–6.2 (m, 3 H, C_2H_3), 7.2–7.3 (m, 1 H, C_6H_4), 7.3–7.4 (m, 2 H, C_6H_4), 8.1–8.2 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ −0.2 ($SiCH_3$), 44.4 (NCH_3), 63.6 (CH_2), 110.1 (*C*≡C), 114.3 (C≡*C*), 126.6, 127.5, 129.9, 133.9, 135.1, 136.8, 137.8, 146.3 (C_2H_3, C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ −18.7 (*Si*CH_3), −62.3 [*Si*(C_2H_3)]. EI MS *m*/*e* (rel. int.): M^+, 384 (18); $M^+ - CH_3$, 369 (23); $M^+ - CH_3{-}C_2H_3$, 342 (32); $M^+ - Si(CH_3)_3$, 311 (25); $M^+ - C_2Si(CH_3)_3$, 287 (31); $M^+ - HC_2Si(CH_3)_3{-}CH_3$, 270 (100); $M^+ - C_2Si(CH_3)_3{-}C_2H_3$, 260 (14); $M^+ - C_2Si(CH_3)_3{-}3CH_3$, 242 (18). Anal. Calc. for $C_{21}H_{33}NSi_3$ (383.75): C, 65.73; H, 8.67. Found: C, 65.61; H, 8.51%.

3.10. Synthesis of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si\{NH[C_6H_2(CH_3)_3\text{-}2,4,6]\}_2$ ***(10)***

A total of 1.30 g (5.0 mmol) of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (**3d**) dissolved in 50 ml of diethyl ether are slowly added to a solution of 10.0 mmol $LiNH[C_6H_2(CH_3)_3\text{-}2,4,6]$ (obtained from the reaction of 4.0 ml 2.5 M ^{n}BuLi in *n*-hexane and 1.35 g (10.0 mmol) $NH_2[C_6H_2(CH_3)_3\text{-}2,4,6]$ in 3.0 ml of diethyl ether) at −70°C. The reaction mixture is warmed to 25°C for 12 h and then filtered through a pad of Celite. After removal of all volatile materials at 25°C the orange residue is crystallized from *n*-pentane at −30°C to obtain compound **10** as orange crystals.

Yield: 2.0 g (4.37 mmol, 88%, rel. **3d**). M.p. 172°C. IR (KBr, cm^{-1}): $\nu_{NH} = 3175$ (br); $\nu_{CH} = 3044$ (s), 3006 (m), 2978 (s), 2942 (vs), 2856 (s), 2818 (s), 2773 (s); $\nu_{C=C} = 1594$ (m). ^1H-NMR ($CDCl_3$): δ 2.18 (s, 12 H, *o*-CH_3), 2.22 (s, 6 H, NCH_3), 2.27 (s, 6 H, *p*-CH_3), 3.38 (s, 2 H, CH_2), 4.51 (br, 2 H, NH), 6.1–6.4 (m, 3 H, C_2H_3), 6.81 (s, 4 H, C_6H_2), 7.1–7.2 (m, 1 H, C_6H_4), 7.2–7.4 (m, 2 H, C_6H_4), 7.8–8.0 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 20.1 (*o*-CH_3), 20.4 (*p*-CH_3), 44.9 (NCH_3), 64.7 (CH_2), 126.6, 128.8, 128.9, 130.0, 130.3, 130.8, 135.6, 135.7, 135.8, 138.6, 140.7, 143.5 (C_2H_3, C_6H_2, C_6H_4). EI MS *m*/*e* (rel. int.): M^+, 457 (8); $M^+ - N(CH_3)_2$, 413 (8); $M^+ - C_6H_2(CH_3)_3$, 338 (100). Anal. Calc. for $C_{29}H_{39}N_3Si$ (457.72): C, 76.09; H, 8.59. Found: C, 76.17; H, 8.76%.

3.11. Synthesis of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)Si[P(C_6H_5)_2]_2$ ***(11)***

A solution of 2.9 g (15.4 mmol) $PH(C_6H_5)_2$ in 50 ml of THF is reacted with equimolar amounts of a 1.6 M CH_3Li solution in diethyl ether at −30°C. The reddish colored reaction mixture is gently warmed to 25°C. Afterwards it is added dropwise to a solution of 2.0 g (7.7 mmol) of $[C_6H_4CH_2N(CH_3)_2\text{-}2](H_2C{=}CH)SiCl_2$ (**3d**) in 50 ml of THF. After warming overnight to 25°C the solvents were removed under vacuum and the obtained brown slurry is treated with 100 ml of dichloromethane. The suspension obtained is filtered through a pad of Celite. After cooling to $-30°C$ compound **11** is obtained as an off-white solid.

Yield: 1.85 g (3.3 mmol, 43%, rel. **3d**). M.p. 112°C. IR (KBr, cm^{-1}): $\nu_{C=C} = 1593$ (m). ^1H-NMR ($CDCl_3$): δ 2.07 (s, 6 H, NCH_3), 3.21 (s, 2 H, CH_2), 5.81 (dd, $^2J_{HH} = 3.2$ Hz, $^3J_{HH} = 19.8$ Hz, 1 H, C_2H_3), 6.10 (dd, $^2J_{HH} = 3.2$ Hz, $^3J_{HH} = 14.5$ Hz, 1 H, C_2H_3), 6.3–6.5 (m, 1 H, C_2H_3), 7.1–7.7 (m, 24 H, C_6H_4, C_6H_5). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 44.9 (NCH_3), 63.6 (CH_2), 125–138 (C_2H_3, C_6H_4, C_6H_5), 144.0 (C_6H_4). $^{29}Si\{^1H\}$-NMR ($CDCl_3$): δ -14.0 (t, $^1J_{PSi} = 49.3$ Hz). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ -58.5 (s). EI MS m/e (rel. int.): M^+, 560 (56); $M^+ - CH_3$, 544 (7); $M^+ - P(C_6H_5)_2$, 374 (100); $P(C_6H_5)_2$, 185 (29). Anal. Calc. for $C_{35}H_{35}NP_2Si$ (559.70): C, 75.11; H, 6.30. Found: C, 74.25; H, 6.40%.

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