Decamethylsilicocene Chemistry: Reaction with Carbon−Nitrogen Triple-Bond Species

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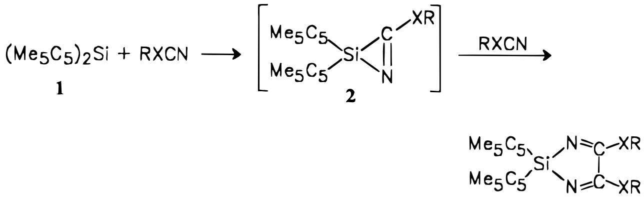
Reaction of decamethylsilicocene, $(Me_5C_5)_2Si$ (**1**), with MeSCN, 2,4-$Me_2C_6H_3OCN$, Me_2NCN, BrCN, and Me_3SiCN is described. In all reactions, the formal oxidation state of the silicon atom changes from +2 in **1** to +4 in the products, and the hapticity of the pentamethylcyclopentadienyl ligands changes from η^5 to η^1. Under mild conditions (−78 °C or room temperature) **1** reacts with 2 equiv of MeSCN, 2,4-$Me_2C_6H_3OCN$, and Me_2NCN under C−C bond formation to the respective diazasilole derivatives **3**−**5**. Reaction of **1** with BrCN at −78 °C affords the silyl cyanide **7**; at room temperature, a mixture of the silyl cyanide **7** and of the silyl isocyanide **8** is formed. Reaction of **1** with Me_3SiCN leads to the silyl cyanide **10**. In the reactions described, the product formation presumably proceeds via [2 + 1] cycloaddition compounds of the azasilirene type as reactive intermediates. All products are characterized by NMR (^1H, ^{13}C, ^{29}Si) spectroscopy, IR spectroscopy, mass spectrometry, and microanalytical data. The structures of **3**, **4**, and **10** were determined by X-ray crystallography.

Introduction

Reaction of silylenes (silanediyls)—transient or stable—with organic compounds that contain a carbon−nitrogen triple bond are rarely investigated. Only three attempts have been reported.[1] The silanediyls investigated [$(Me_3C)_2Si^{1a,b}$ and $(2\text{-}(Me_2NCH_2)C_6H_4)_2Si^{1c}$] were generated by photochemically or thermally induced processes. In the reactions with organic nitriles, the products obtained were the result of the formation of highly reactive intermediates of the azasilirene type, which were stabilized in different ways.

Decamethylsilicocene (**1**) was the first stable silicon(II) compound described in the literature.[2] It allows chemical reactions under ordinary conditions in a normal temperature range. The chemistry of **1** has already been investigated in some detail.[3] As a result of these investigations, **1** is regarded as a hypercoordinated, nucleophilic silylene, which reacts preferentially with electrophilic substrates and under oxidation of the Si atom from the formal +2 to the +4 oxidation state.

Scheme 1



X	S	N	O
R	Me	Me_2	2,4-$Me_2C_6H_3$
	3	**4**	**5**

Compounds containing a C≡N triple bond are classified as electrophilic substrates. In this context, we have investigated the reaction of **1** with different organic C≡N triple-bond species of the type RXCN [RX = MeS, Me_2N, ArO (Ar = 2,4-$Me_2C_6H_3$)] and RCN (R = Br, $SiMe_3$).

Results and Discussion

Carbon−carbon bond formation was observed in the reaction of decamethylsilicocene (**1**) with substrates of the type RXCN [RX = MeS, Me_2N, ArO (Ar = 2,4-$Me_2C_6H_3$)]. Room-temperature reaction of **1** with methyl thiocyanate in toluene as solvent afforded the 1,3-diaza-2-silole **3** in reasonable yield (see Scheme 1). The formation of **3** was independent of the stoichiometry of the reactants. Compound **3** was obtained as yellow crystals, which were soluble in all common organic solvents.

In a similar fashion, decamethylsilicocene (**1**) reacted with dimethylcyanamide and with 2,4-dimethylphenyl cyanate. Under very mild conditions (−78 °C) the 1,3-diaza-2-silole derivatives **4** and **5** were formed as colorless crystals, which showed physical properties similar to those of **3** (see Scheme 1).

The compounds **3**−**5** were characterized by spectroscopic (NMR, IR, MS) and in the case of **3** and **4** by microanalytical data and by an X-ray diffraction analy-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

[1] (a) Weidenbruch, M.; Schäfer, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1986**, *314*, 25. (b) Weidenbruch, M.; Flintjer, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 95. (c) Belzner, J.; Ihmels, H.; Noltemeyer, M. *Tetrahedron Lett.* **1995**, *36*, 8187.

[2] (a) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blohm, A.; Gleiter, R.; Hyla-Kryspin, I. *Chem. Ber.* **1989**, *122*, 1629. (b) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

[3] (a) Jutzi, P.; Eikenberg, D.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 753. (b) Jutzi, P.; Eikenberg, D.; Bunte, E.-A.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 1930. (c) Jutzi, P.; Bunte, E.-A.; Holtmann, U.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1993**, *446*, 139. (d) Jutzi, P.; Bunte, E.-A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605. (e) Jutzi, P. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P., Eds.; Royal Society of Chemistry: Cambridge, England, 1991. (f) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 893. (g) Jutzi, P.; Möhrke, A.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1518. (h) Jutzi, P.; Möhrke, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 762. (i) Jutzi, P.; Holtmann, U.; Bögge, H.; Müller, A. *J. Chem. Soc., Chem. Commun.* **1988**, 305. (j) Jutzi, P.; Kanne, D.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1986**, *121*, 1299.

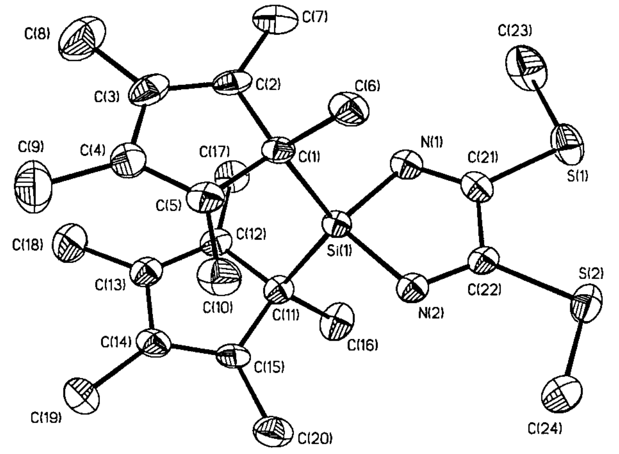


Figure 1. Molecular structure of **3**.

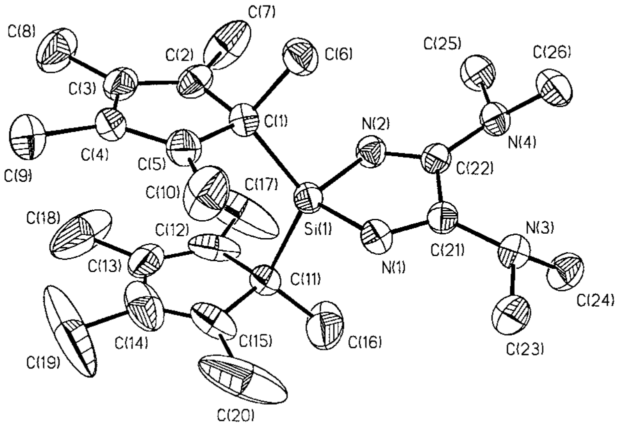


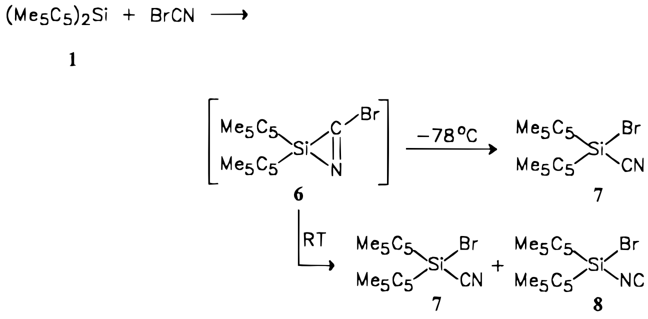
Figure 2. Molecular structure of **4**.

sis (Figures 1 and Figure 2; vide infra). The 1,3-diazasilole framework underlying the compounds **3**−**5** has already been described in the literature.[4]

For the above reaction of **1** with substrates of the type RXCN we propose the following pathway (see Scheme 1): At first, a highly reactive azasilirene type intermediate **2** is formed by a [2 + 1] cycloaddition process. This intermediate reacts with a further substrate molecule regiospecifically under ring opening at the silicon−carbon bond and under C−C bond and Si−N bond formation to give the corresponding 1,3-diaza-2-silole derivative.

In the literature, highly reactive azasilirenes have already been postulated as intermediates in the reaction of transient silanediyls with nitriles. The products obtained have been the result of quite different ways of stabilization: Weidenbruch et al.[1a,b] observed in the reaction of the transient silylene (Me$_3$C)$_2$Si with nitriles the formation of 1,4- or 1,3-diaza-2,5-disilacyclohexadiene derivatives. The products obtained were the result of a σ-dimerization of the azasilirene intermediates. Belzner et al.[1c] discussed in the reaction of the transient silylene Ar$_2$Si (Ar = 2-(Me$_2$NCH$_2$)C$_6$H$_4$) with substrates of the type RC≡N (R = Me, SiMe$_3$, CMe$_3$) the formation of azasilirenes, which were stabilized either by insertion of a further silylene into the Si−C or Si−N bond under formation of 1-aza-2,3-disilacyclobutene derivatives or by rearrangement to the formal oxidative addition products. It is worth mentioning that a stable phosphasilirene derivative has been obtained by Weidenbruch et al.[5] in the reaction of a silylene with a phosphaalkyne, and only recently the first stable azasilirene has been isolated by Okazaki and co-workers.[6]

Scheme 2



The reaction sequence as described in Scheme 1 is unprecedented in silylene chemistry. The steric requirements of the pentamethylcyclopentadienyl ligands might prevent a further insertion of **1** into the Si−C or Si−N bond of **2** or a σ-dimerization process of **2**.

Contrary to the above described reaction sequences of decamethylsilicocene (**1**) with substrates of the type RXC≡N, simple formal oxidative addition products were observed in the reaction of **1** with bromocyanogen and with trimethylsilyl cyanide. The product formation was independent of the stoichiometry of the reactants. Compound **1** reacted with bromocyanogen already under mild conditions. The products obtained depend on the reaction temperature. At −78 °C the silyl cyanide **7**, at room temperature a mixture of the silyl cyanide **7** and of the silyl isocyanide **8** in a ratio of about 1:1 (according to the integrals of the ^{29}Si NMR signals), was formed (see Scheme 2). The compounds **7** and **8** were characterized by spectroscopic (NMR, IR, MS) data and in the case of **7** by microanalytical data. Purification of **8** by crystallization or sublimation was unsucessful.

It is well-known that silyl cyanides like Me$_3$SiCN or Et$_3$SiCN are in equilibrium with the respective isocyanides.[7] In contrast, no such an equilibrium could be observed in the case of **7** and **8**. Thus, heating a solution of **7** in toluene at 100 °C over a period of 4 d did not lead to any formation of the respective isocyanide **8**. Furthermore, in NMR investigations (^{13}C, ^{29}Si) of **7**, in a temperature range between −80 and 80 °C, only the signals of the silyl cyanide **7** could be observed. Presumably the steric demand of the Cp* ligands prevents the formation of a six-menbered intermediate necessary for the equilibrium process.[7]

In the reaction of **1** with BrCN we postulate a pathway which includes the azasilirene type intermediate **6** (see Scheme 2). Reaction at low temperature favors the Si−N bond splitting in the rearrangement process; at room temperature, Si−N or Si−C bond splitting has to be considered. As a consequence of the formation of **7** and **8** in the reaction of **1** with BrCN, we

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[4] Derkach, N. Ya.; Smetankina, N. P. *Zh. Obshch. Khim.* **1966**, *36* (11), 2001.

[5] Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776.

[6] Okazaki, R. Presented at the 29th Organosilicon Symposium, Northwestern University, Evanston, IL, 1996.

[7] (a) Hertler, W. R.; Dixon, D. A.; Matthews, E. W.; Davidson, F.; Kitson, F. G. *J. Am. Chem. Soc.* **1987**, *109*, 6532. (b) Seckar, J. A.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 501. (c) Booth, M. R.; Frankiss, S. G. *Spectrochim. Acta* **1970**, *26a*, 859.

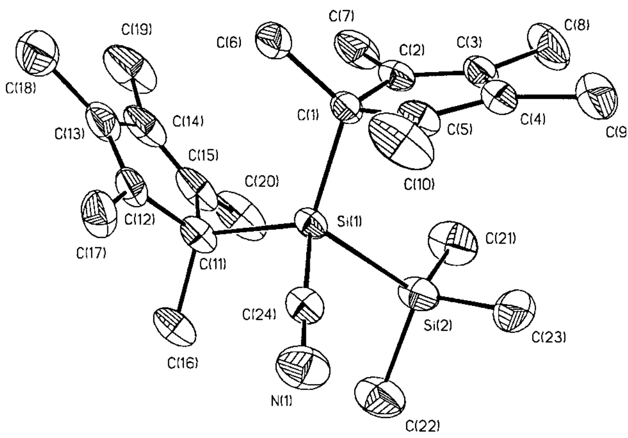
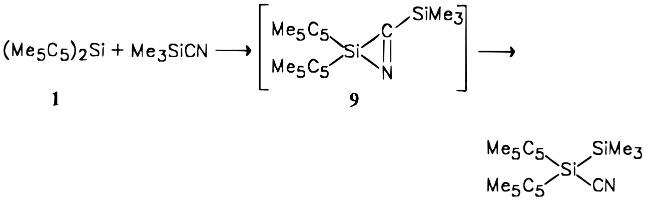


Figure 3. Molecular structure of **10**.

Scheme 3



1 **9** **10**

exclude a simple oxidative addition process, as postulated in the reaction of **1** with Br_2 or I_2.[3e]

More drastic conditions were necessary to initiate the reaction of decamethylsilicocene (**1**) with trimethylsilyl cyanide. After heating of a solution of **1** in toluene with excess Me_3SiCN for 3 d at 100 °C, the silyl cyanide **10** was isolated as colorless crystals in good yield (see Scheme 3). Compound **10** was characterized by NMR and IR spectroscopic, mass spectrometric, and microanalytical data as well as by an X-ray diffraction analysis (Figure 3; vide infra).

As pointed out in Scheme 3, we favor a reaction mechanism with the azasilirene type intermediate **9**. Silyl group migration and Si−N bond splitting leads to the final product **10**. A comparable pathway has been described by Belzner et al.[1c] for the reaction of the transient silylene Ar_2Si ($Ar = 2\text{-}(Me_2NCH_2)C_6H_4$) with trimethylsilyl cyanide. Similar rearrangement processes are well-known in the chemistry of silacyclopropenes.[8]

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of 3

Bond Lengths			
Si1−N1	1.777(3)	Si1−N2	1.778(3)
Si1−C1	1.897(3)	Si1−C11	1.892(4)
N1−C21	1.270(4)	N2−C22	1.277(4)
S1−C21	1.753(3)	S2−C22	1.748(3)
S1−C23	1.793(4)	S2−C24	1.790(4)
C21−C22	1.533(4)		
Bond Angles			
N1−Si1−N2	96.9(1)	C1−Si1−C11	120.6(1)
N1−Si1−C1	107.5(1)	N1−Si1−C11	110.9(1)
N2−Si1−C1	109.3(1)	N2−Si1−C11	109.0(1)
Si1−N1−C21	105.3(2)	Si1−N2−C22	105.2(2)
N1−C21−C22	116.4(3)	N2−C22−C21	116.0(3)
N1−C21−S1	126.4(2)	N2−C22−S2	126.1(2)
C21−S1−C23	99.9(2)	C22−S2−C24	99.9(2)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 4

Bond Lengths			
Si1−N1	1.757(3)	Si1−N2	1.760(3)
Si1−C1	1.907(3)	Si1−C11	1.908(3)
N1−C21	1.293(4)	N2−C22	1.293(4)
N3−C21	1.384(4)	N4−C22	1.381(4)
N3−C23	1.460(4)	N3−C24	1.471(4)
N4−C25	1.459(4)	N4−C26	1.457(4)
C21−C22	1.548(4)		
Bond Angles			
N1−Si1−N2	97.78(14)	C1−Si1−C11	120.00(14)
N1−Si1−C1	111.5(2)	N1−Si1−C11	106.7(2)
N2−Si1−C1	106.8(2)	N2−Si1−C11	111.8(2)
Si1−N1−C21	105.5(2)	Si1−N2−C22	105.3(2)
N1−C21−C22	114.5(3)	N2−C22−C21	114.8(2)
N1−C21−N3	122.8(3)	N2−C22−N4	122.5(3)
C21−N3−C23	114.6(2)	C21−N3−C24	117.8(2)
C22−N4−C25	115.7(2)	C22−N4−C26	119.8(2)
C23−N3−C24	113.1(3)	C25−N4−C26	113.1(3)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) of 10

Bond Lengths			
Si1−C1	1.937(2)	Si1−C11	1.943(2)
Si1−Si2	2.384(1)	Si1−C24	1.898(2)
Si2−C21	1.868(2)	Si2−C22	1.873(2)
Si2−C23	1.869(2)	C24−N1	1.141(2)
Bond Angles			
C1−Si1−C11	117.35(8)	C24−Si1−Si2	95.45(7)
C24−Si1−C1	116.00(8)	C24−Si1−C11	99.97(8)
Si2−Si1−C1	112.18(6)	Si2−Si1−C11	118.20(7)
Si1−C24−N1	171.7(2)	Si1−Si2−C21	117.26(9)
Si1−Si2−C22	107.32(8)	Si1−Si2−C23	107.33(8)
C21−Si2−C22	109.92(11)	C21−Si2−C23	108.30(11)
C22−Si2−C23	106.15(12)		

Structural Data for 3, 4, and 10. Single-crystal X-ray diffraction analyses have been performed with **3**, **4**, and **10**. The molecular structures are presented in Figures 1−3. Bond lengths and bond angles are displayed in Tables 1−3. Crystallographic data are given in Table 4.

Common to the structures of **3**, **4**, and **10** is the presence of two Si-bonded planar σ-pentamethylcyclopentadienyl (Cp*) ligands. In **3** and **4**, these ligands adopt a parallel, nearly sandwichlike orientation, whereas in **10** these ligands are turned away from each other. This conformational change has drastic consequences on the respective (Cp*)CSiC(Cp*) angle. Whereas in **3** and **4** as in other compounds with sandwichlike-orientated Cp* ligands[3a,c] this angle is enlarged [up to 122.6° in the product of the reaction of **1** with CO_2[3a]], the angle in **10** is in the normal range for an sp^3-hybridized silicon atom. It must be concluded that the steric demand of two σ-bonded Cp* ligands is more pronounced in case of a parallel orientation of the Cp* ring planes. The observed conformational change does not dramatically effect the corresponding Si−C(Cp*) bond lengths. In both situations, rather long Si−C(Cp*) bonds are found; they are in a range 1.90−1.94 Å.

The structures of **3** and **4** show planar 1,3-diaza-2-silole ring systems with quite similar bond lengths and bond angles. Under exclusion of the Cp* ligands, **3** and **4** possess C_{2v} and C_2 symmetry, respectively. In both cases, the discussed σ-$Cp^*{}_2Si$ effect leads to a pronounced ring strain as documented by rather small bond angles within the SiN_2C_2 framework [N1Si1N2 = 96.9(1)°, Si1N1C21 = 105.3(2)°, N1C21C22 = 116.4(3)° for **3**; N1Si1N2 = 97.8(1)°, Si1N1C21 = 105.5(2)°,

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[8] (a) Ishikawa, M.; Sagisawa, H.; Fuchikami, T.; Kumada, M.; Yamabe, T.; Kawakami, H.; Fukui, K.; Ueki, Y.; Shizuka, H. *J. Am. Chem. Soc.* **1982**, *104*, 2872. (b) Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* **1980**, *190*, 117.

Table 4. Crystallographic Data[a]

	compd		
	3	**4**	**10**
empirical formula	$C_{24}H_{36}N_2S_2Si$	$C_{26}H_{42}N_4Si$	$C_{24}H_{39}NSi_2$
cryst size, mm^3	0.40 × 0.80 × 1.00	0.80 × 0.80 × 0.30	1.10 × 0.60 × 0.30
fw	444.80	438.73	397.74
cryst syst	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P\bar{1}$
lattice params			
a, Å	38.730(10)	15.44(2)	8.729(3)
b, Å	9.165(3)	10.99(2))	8.844(4)
c, Å	14.816(4)	15.76(2))	18.006(5)
α, deg	90	90	77.37(3)
β, deg	106.64(2)	104.76(11)	77.61(3)
γ, deg	90	90	65.61(3)
V, $Å^3$	5039(2)	2586(6)	1223.2(8)
Z	8	4	2
d_{calc}, g/cm^3	1.173	1.127	1.080
diffractometer	Siemens $P2_1$	Siemens $P2_1$	Siemens $P2_1$
$F(000)$	1920	960	436
m(Mo Kα), mm^{-1}	0.261	0.110	0.154
temp, °C	−100	−100	−100
$2\theta_{max}$, deg	3.0−55.0	4.56−50.10	4.68−60.12
no. data collcd	5800	4743	7614
no.of params refined	263	294	257
no. obsd data [$F > 4s(F)$]	3819	3458	5096
residuals: R_F, wR_{F^2} for obsd data	0.049	0.0687, 0.1924	0.0525, 0.1346
largest peak in final diff map, e/$Å^3$	0.47	0.6	0.4
abs corr	XABS	none	none

[a] X-ray structure determination details: A single crystal was coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173 K for data collection. The crystallographic programs used for structure solution and refinement were from SHELXTL PLUS and SHELXL-93. The structures were solved by using direct methods and was (were) refined by using full-matrix least squares on F for all observed reflections for **3** and on F^2 for all unique reflections for **4** and **10**, with anisotropic thermal parameters for all non-hydrgen atoms. Hydrogen atoms were included at the calculated positions with $U(H) = 1.2U_{eq}$ for CH and CH_2 groups and $U(H) = 1.5U_{eq}$ for CH_3 groups for **4** and **10**, with fixed $U(H)$ of 0.08 $Å^2$ for **3**.

N1C21C22 = 114.5(3)° for **4**]. Rather long Si−N distances (1.778(3) Å for **3**, 1.760(3) Å for **4**) are noteworthy, too. For comparison, in the six-membered ring system of 2,2,4,5,5,6-hexa-*tert*-butyl-1,3-diaza-2,5-disilacyclohexa-3,6-diene, the Si−N distances are 1.712(2) Å and the NSiN angle is 110.8(2)°.[1a]

As already pointed out, the Cp* rings in **10** are twisted to each other; the torsion angle [expressed by the dihedral angle (C6C1SiC11C16)] is 138.1°, and the angle between their best planes is 57.1°. Nearly the same geometry was observed in the product of the reaction of **1** with 4-methylcatechol.[3c] All other bis(pentamethylcyclopentadienyl) compounds of main group elements characterized so far crystallize with nearly parallel ring systems.[9] There is a good accord in bond angles and bond lengths with the corresponding data for the silyl cyanide $Ar_2Si(SiMe_3)CN$ ($Ar = 2\text{-}(Me_2NCH_2)C_6H_4$).[1c]

Conclusion

It has been demonstrated that decamethylsilicocene (**1**) reacts with different types of C≡N triple-bond species. This is the first time that the reaction of a silicon(II) compound (transient or stable) with organic compounds like RSCN, ROCN, R_2NCN, and BrCN is described.

In all reactions described, a change of hapticity of the pentamethylcyclopentadienyl ligands from η^5 in **1** to η^1 in the products and also a change of the oxidation state of silicon from +II to +IV is observed.

Different reaction pathways leading to different types of products have been observed. The pathways depend on the further substituents at the C≡N unit. With compounds of the type RXCN (RX = RS, RO, R_2N) the formation of diazasilole derivatives takes place, independent of substrate stoichiometry. The postulated azasilirene intermediates are attacked regiospecifically by a further substrate molecule. This reaction type is unprecedented in silicon(II) chemistry. The steric requirements of the Cp* ligands might prevent other routes of product formation. With compounds like BrCN and Me_3SiCN reaction in a 1:1 stoichiometry is observed, in which the respective azasilirene intermediate rearranges to the final product. The different reaction pathways observed can be explained with the quite different nucleophilicity of the substrates.[10] Stronger nucleophiles as present in the RXCN (RX = RS, RO, R_2N) type molecules are able to attack the transient azasilirenes under Si−C bond splitting and under Si−N and C−C bond formation; with the weaker nucleophiles BrCN and Me_3SiCN such an attack is prevented and the stabilization of the azasilirene intermediate takes place by rearrangement processes.

The C−C bond formation in the reaction of **1** with compounds of the type RXCN is of preparative interest, especially if very mild reaction conditions are required.

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(9) See for example the following. (a) For $(Me_5C_5)_2BF$, see: Jutzi, P.; Hursthouse, M.; Howes, A. J. *Chem. Ber.* **1987**, *120*, 565. (b) For $(Me_5C_5)_2SiCl_2$ and $(Me_5C_5)_2SiF_2$, see ref 2j. (c) For $(Me_5C_5)_2S$, see: Bard, A. J.; Cowly, A. H.; Leland, J. K.; Thomas, G. J. N.; Norman, N. C.; Jutzi, P.; Morley, C. P.; Schlüter, E. *J. Chem. Soc., Dalton Trans.* **1985**, 1303.

(10) The ionization energies serve as a measure of the intrinsic nucleophilicity. For the energies of the nitrogen lone pairs (obtained from the PE spectra), see the following. (a) For MeSCN (12.8 eV): Bock, H.; Hirabayashi, T.; Mohmand, S. *Chem. Ber.* **1982**, *115*, 492. (b) For Me_2NCN (12.5 eV): Stafast, H.; Bock, H. *Chem. Ber.* **1974**, *107*, 1182. (c) For BrCN (13.5 eV): Heilbronner, E.; Hornung, V.; Muszkat, K. A. *Helv. Chim. Acta* **1970**, *53*, 347.

Experimental Section

General Considerations. Standard Schlenk techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods and distilled under argon prior to use. The reagents MeSCN, $\mathrm{Me_2NCN}$, 2,4-$\mathrm{Me_2C_6H_3OCN}$, BrCN, and $\mathrm{Me_3SiCN}$ were procured commercially and used without further purification.

Physical Measurements. IR spectra were obtained from KBr pellets or from solution in hexane using a Mattson Perkin Polaris FTIR spectrophotometer. Mass spectra (EI) were run on a Varian 311 A mass spectrometer (70 eV, 300 μA emission), and NMR spectra were obtained using a Bruker AM 300 spectrometer (^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz; ^{29}Si, 59.60 MHz). NMR spectra were referenced to the residual protic impurities of the deuteriated solvents $\mathrm{C_6D_6}$ or toluene-d_8. Elemental analyses were performed by the Microanalytical Laboratory of the University of Bielefeld. Melting points (uncorrected) were measured using a Büchi 510 melting point apparatus in sealed capillary tubes.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-bis(thiomethyl)-1,3-diaza-2-silole (3). A 0.8 mL (11.78 mmol) amount of MeSCN was added to a solution of 1.17 g (3.93 mmol) of **1** in 12 mL of toluene at room temperature. The reaction mixture was stirred for 3 h at this temperature. Volatiles were removed under reduced pressure, and the pale yellow residue was crystallized twice in *n*-hexane. **3** (mp: 130 °C) was obtained as yellow crystals (0.95 g, 54% yield). ^{1}H ($\mathrm{C_6D_6}$; δ): 0.69, 1.77, 2.06 (s, 6H:12H:12H, $\mathrm{C_5}(\mathit{CH_3})_5$); 2.29 (s, 6H, $\mathrm{S}\mathit{CH_3}$). ^{13}C ($\mathrm{C_6D_6}$; δ): 12.0 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 13.4 ($\mathrm{S}\mathit{C}\mathrm{H_3}$); 136.5 ($\mathit{C}_5(\mathrm{CH_3})_5$); 173.4 ($-\mathrm{N}{=}\mathit{C}\mathrm{S}$). ^{29}Si($\mathrm{C_6D_6}$; δ): 22.6. Anal. Calcd for $\mathrm{C_{24}H_{36}N_2S_2Si}$: C, 64.86; H, 8.11; N, 6.31. Found: C, 64.04; H, 8.42; N, 5.93.[11] MS (*m*/*z*): 444 ($\mathrm{M^+}$). IR (KBr): ν(N=C) 1605 cm^{-1}; ν(C−S) 595 cm^{-1}; ν(Si−N) 565 cm^{-1}.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-bis(dimethylamino)-1,3-diaza-2-silole (4). A solution of 0.42 g (6.00 mmol) of $\mathrm{Me_2NCN}$ in 10 mL of toluene was added at −78 °C to a solution of 0.89 g (2.99 mmol) of **1** in 15 mL of toluene over a period of 5 min. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm up slowly to room temperature. The solvent was removed in vacuo and the colorless residue dissolved in 10 mL of toluene. Cooling this solution to −60 °C yielded **4** (mp: 140 °C) as colorless crystals (0.7 g, 53% yield). ^{1}H ($\mathrm{C_6D_6}$; δ): 0.89, 1.87, 2.23 (s, 6H:12H:12H, $\mathrm{C_5}(\mathit{CH_3})_5$); 2.73 (s, 12H, $\mathrm{N}(\mathit{CH_3})_2$). ^{13}C ($\mathrm{C_6D_6}$; δ): 11.9, 12.4, 16.2 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 39.7 ($\mathrm{N}(\mathit{C}\mathrm{H_3})_2$); 53.0 (allyl, $\mathit{C}_5(\mathrm{CH_3})_5$); 135.2, 137.8 ($\mathit{C}_5(\mathrm{CH_3})_5$); 166.0 ($-\mathrm{N}{=}\mathit{C}\mathrm{N}$). ^{29}Si ($\mathrm{C_6D_6}$; δ): 14.3. Anal. Calcd for $\mathrm{C_{26}H_{42}N_4Si}$: C, 71.17; H, 9.64; N, 12.77. Found: C, 70.75; H, 9.70; N, 12.60. MS (*m*/*z*): 438 ($\mathrm{M^+}$). IR (KBr): ν(N=C) 1634 cm^{-1}; ν(C−N) 1570 cm^{-1}; ν(Si−N) 547 cm^{-1}.

Synthesis of 2,2-Bis(pentamethylcyclopentadienyl)-4,5-bis(2,4-dimethylphenoxy)-1,3-diaza-2-silole (5). A solution of 0.98 g (6.66 mmol) of 2,4-$\mathrm{Me_2C_6H_3OCN}$ in 10 mL of toluene was added to a solution of 0.95 g (3.19 mmol) of **1** in 20 mL of toluene at −78 °C over a period of 5 min. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm slowly to room temperature. The mixture was reduced to dryness in vacuo, and the orange residue was crystallized twice in *n*-hexane. **5** (mp: 147−149 °C) was obtained as colorless crystals (0.80 g, 42% yield). ^{1}H ($\mathrm{C_6D_6}$; δ): 0.98, 1.66, 1.89 (s, 6H:12H:12H, $\mathrm{C_5}(\mathit{CH_3})_5$); 2.02, 2.38 (s, 6H:6H, $\mathrm{C_6}(\mathit{CH_3})_2\mathrm{H_3}$); 6.85 (s, 2H, $\mathrm{C_6(CH_3)_2}\mathit{H}_3$); 6.87, 7.36 (d, ^3J = 7.98 Hz, 2H:2H, $\mathrm{C_6(CH_3)_2}\mathit{H}_3$). ^{13}C ($\mathrm{C_6D_6}$; δ): 11.7, 16.0 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 16.4, 20.7 ($\mathrm{C_6}(\mathit{CH_3})_2\mathrm{H_3}$); 52.5 (allyl, $\mathit{C}_5(\mathrm{CH_3})_5$); 121.7, 129.6, 132.0, 135.1 ($\mathit{C}_6(\mathrm{CH_3})_2\mathit{H}_3$); 136.4 ($\mathit{C}_5(\mathrm{CH_3})_5$); 150.3 ($\mathrm{O}\mathit{C}_6(\mathrm{CH_3})_2\mathit{H}_3$); 160.6 ($-\mathrm{N}{=}\mathit{C}\mathrm{O}$). ^{29}Si ($\mathrm{C_6D_6}$): δ 12.8. MS (*m*/*z*): 592 ($\mathrm{M^+}$). IR (*n*-hexane): ν(N=C) 1625 cm^{-1}; ν(C−O) 1195 cm^{-1}; ν(Si−N) 551 cm^{-1}.

Synthesis of Bis(pentamethylcyclopentadienyl)bromocyanosilane (7). A solution of 0.31 g (2.92 mmol) of BrCN in 10 mL of toluene was added to a solution of 0.85 g (2.85 mmol) of **1** in 15 mL of toluene at −78 °C over a period of 5 min. The yellow reaction mixture was stirred 1 h at −78 °C and then allowed to warm slowly to room temperature. The solvent was removed under reduced pressure, and the yellow residue was recrystallized in *n*-hexane. **7** was isolated as colorless crystals (0.94 g, 82% yield). ^{1}H ($\mathrm{C_6D_6}$; δ): 1.58 (s, 30H, $\mathrm{C_5}(\mathit{CH_3})_5$). ^{1}H (toluene-$d_8$; −40 °C; δ): 1.20, 1.51, 1.77, 1.90 (s, 6H:12H:6H:6H, $\mathrm{C_5}(\mathit{CH_3})_5$). ^{13}C ($\mathrm{C_6D_6}$; δ): 13.2 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 123.0 ($\mathit{C}$N); 138.6 ($\mathit{C}_5(\mathrm{CH_3})_5$). ^{29}Si ($\mathrm{C_6D_6}$; δ): −8.9. Anal. Calcd for $\mathrm{C_{21}H_{30}BrNSi}$: C, 62.38; H, 7.42. Found: C, 61.77; H, 7.32.[11] MS (*m*/*z*): 405/403 ($\mathrm{M^+}$); 270/268 ($\mathrm{M^+ - C_5(CH_3)_5}$). IR (KBr): ν(CN) 2186 cm^{-1}; ν(Si−Br) 406 cm^{-1}.

Reaction at room temperature affords a product mixture of the silyl cyanide **7** and of the silyl isocyanide **8** in a ratio of about 1:1 in 82% yield.

Spectroscopic Data for Bis(pentamethylcyclopentadienyl)bromo(isocyano)silane (8). ^{1}H ($\mathrm{C_6D_6}$; δ): 1.58 (s, 30H, $\mathrm{C_5}(\mathit{CH_3})_5$). ^{13}C ($\mathrm{C_6D_6}$; δ): 11.8 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 138.6 ($\mathit{C}_5(\mathrm{CH_3})_5$); 194.7 (N$\mathit{C}$). ^{29}Si ($\mathrm{C_6D_6}$; δ): −9.1. MS (*m*/*z*): 405/403 ($\mathrm{M^+}$); 379/377 ($\mathrm{M^+ - NC}$); 270/268 ($\mathrm{M^+ - C_5(CH_3)_5}$); 163 ($\mathrm{SiC_5(CH_3)_5}$). IR (KBr): ν(NC) 2084 cm^{-1}.

Synthesis of Bis(pentamethylcyclopentadienyl)cyano(trimethylsilyl)silane (10). A solution of 1.08 g (3.62 mmol) of **1** and 0.72 g (7.25 mmol) of $\mathrm{(CH_3)_3SiCN}$ in 15 mL of toluene was heated to 100 °C for 3 d. Volatiles were removed, and the yellow residue was crystallized in *n*-hexane. **10** (mp: 109 °C) was obtained as colorless crystals (0.8 g, 55% yield). ^{1}H ($\mathrm{C_6D_6}$; δ): 0.18 (s, 9H, $(\mathit{CH_3})_3\mathrm{Si}$); 1.15, 1.65, 1.91 (s, 6H:12H:12H, $\mathrm{C_5}(\mathit{CH_3})_5$). ^{13}C ($\mathrm{C_6D_6}$; δ): 1.2 ($(\mathit{C}\mathrm{H_3})_3\mathrm{Si}$); 11.6, 12.4, 12.9, 18.3 ($\mathrm{C_5}(\mathit{C}\mathrm{H_3})_5$); 54.9 (allyl, $\mathit{C}_5(\mathrm{CH_3})_5$) 126.6 ($\mathit{C}$N); 136.4, 137.4, 138.5, 140.6 ($\mathit{C}_5(\mathrm{CH_3})_5$). ^{29}Si ($\mathrm{C_6D_6}$; δ): −13.4 ($\mathrm{Si}{-}\mathit{Si}(\mathrm{CH_3})_3$); −26.9 ($\mathit{Si}{-}\mathrm{Si(CH_3)_3}$). Anal. Calcd for $\mathrm{C_{24}H_{39}NSi_2}$: C, 72.47; H, 9.88; N, 3.52. Found: C, 72.19; H, 10.01; N, 3.57. MS (*m*/*z*): 397 ($\mathrm{M^+}$). IR (KBr): ν(CN) 2165 cm^{-1}; ν(Si−Si) 491 cm^{-1}.

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **3**, **4**, and **10** (20 pages). Ordering information is given on any current masthead page.

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(11) NMR investigations indicated the presence of low volatility organic compounds.