Organometallics **2008,** *27,* 6579–6586

Ring Opening of Organosilicon-Substituted Benzoxazolinone: A Convenient Route to Chelating Ureato and Carbamido Ligands

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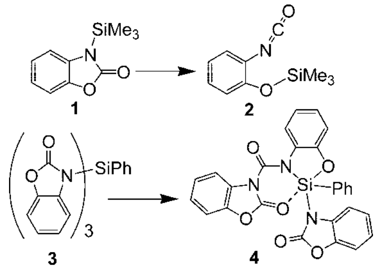
Received August 18, 2008

N-Silylated benzoxazolin-2-one reacts with N−H and C−H acidic heterocycles (benzoxazolinone, 3,5-dimethylpyrazole, *N*-methylimidazole) under benzoxazolinone ring cleavage and formation of *ortho*-siloxyphenyl-substituted ureas and carbamides, respectively. These products were shown to serve as sources for tridentate (O′NO) and (N′NO) chelating ligands.

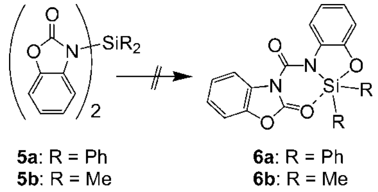
Introduction

Benzoxazolin-2-one, upon *N*-silylation (**1**), was reported to undergo rearrangement to 2-siloxyphenylisocyanate **2** at elevated temperatures (Scheme 1, top).[1] In one of our recent studies we have shown that ring cleavage of a silylated benzoxazolin-2-one, **3**, accompanied by addition of a second equivalent of Si-bound benzoxazolinone, may furthermore lead to the formation of a novel tridentate ureato ligand (compound **4**, Scheme 1, bottom).[2] In general, tridentate (O′NO) chelators are of interest in both main group and transition metal coordination chemistry, e.g., in coordination compounds of group 14,[3] group 15,[4] and various transition metals.[5] A special feature of the (O′NO) chelator in **4** is the presence of the exocyclic amide carbonyl, which can serve as an electronic buffer by delocalization of charge out to the periphery of the ligand as and when required. The strategy applied to the synthesis of **4** clearly has a less desirable design issue in that one out of three benzoxazolinone moieties of **3** remains unused as a superfluous Si-bound benzoxazolinyl substituent in **4**. This tempted us to further explore this reaction in order to find suitable templates for full atom-efficient conversion of benzoxazolinone into tridentate chelating ligands.

Scheme 1



Scheme 2



Results and Discussion

Replacing the extraneous third benzoxazolinonyl group in **3** by an alternative sacrificial substituent appears as an obvious starting point. Hence, benzoxazolinone derivatives **5a** and **5b** (Scheme 2) were prepared from benzoxazolinone and the respective diorganodichlorosilane in a straightforward manner. Unexpectedly, neither of these compounds appear disposed to rearrangement to provide the desired silacycles **6a** and **6b**, respectively, upon heating. Whereas the formation of **4** was found to occur in toluene under reflux (bp 110 °C) within a few minutes, **5a** and **5b** appear inert under these conditions. Even increased temperatures (xylene, reflux; bp 137−140 °C) did not lead to any detectable transformation within several hours (monitored by ^{29}Si NMR spectroscopy).

One possible key to the significantly altered reactivity of **5a** and **5b** was found in their solid state structures, which were determined by X-ray diffraction analyses (Tables 1 and 4). In **3**, one Si−N bond was found to be displaced from the benzoxazolinone plane,[2] a response to steric pressures around

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[1] Kricheldorf, H. R. *Liebigs Ann. Chem.* **1973**, *771−772*, 772.

[2] Wagler, J.; Hill, A. F. *Organometallics* **2007**, *26*, 3630.

[3] For examples for Si, Ge, and Sn complexes of (O′NO) ligands see: (a) Wagler, J. *Organometallics* **2007**, *26*, 155. (b) Driess, M.; Muresan, N.; Merz, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6738. (c) Seiler, O.; Burschka, C.; Metz, S.; Penka, M.; Tacke, R. *Chem.−Eur. J.* **2005**, *11*, 7379. (d) Driess, M.; Dona, N.; Merz, K. *Chem.−Eur. J.* **2004**, *10*, 5971. (e) Beltrán, H. I.; Zamudio-Rivera, L. S.; Mancilla, T.; Santillan, R.; Farfán, N. *Chem.−Eur. J.* **2003**, *9*, 2291. (f) Bencini, A.; Ciofini, I.; Gianassi, E.; Daul, C. A.; Doclo, K. *Inorg. Chem.* **1998**, *37*, 3719. (g) Dakternieks, D.; Baul, T. S. B.; Dutta, S.; Tiekink, E. R. T. *Organometallics* **1998**, *17*, 3058.

[4] For examples for P, As, and Sb complexes of (O′NO) ligands see: (a) Timosheva, N. V.; Chandrasekaran, A.; Holmes, R. R. *Inorg. Chem.* **2004**, *43*, 7403. (b) Arduengo, A. J., III; Lattman, M.; Dias, H. V. R.; Calabrese, J. C.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 1799. (c) Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 627. (d) di Bianca, F.; Rivarola, E.; Spek, A. L.; Meinema, H. A.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *63*, 293.

[5] For examples for transition metal complexes of (O′NO) ligands see: (a) Ebel, M.; Rehder, D. *Inorg. Chem.* **2006**, *45*, 7083. (b) Goshe, A. J.; Steele, I. M.; Bosnich, B. *J. Am. Chem. Soc.* **2003**, *125*, 444. (c) Dhar, S.; Senapati, D.; Das, P. K.; Chattopadhyay, P.; Nethaji, M.; Chakravarty, A. R. *J. Am. Chem. Soc.* **2003**, *125*, 12118. (d) Smith, K. I.; Borer, L. L.; Olmstead, M. M. *Inorg. Chem.* **2003**, *42*, 7410. (e) Blum, S. A.; Bergman, R. G.; Ellman, J. A. *J. Org. Chem.* **2003**, *68*, 150. (f) Brown, J. C.; Wardeska, J. G. *Inorg. Chem.* **1982**, *21*, 1530.

10.1021/om800796z CCC: $40.75

Table 1. Crystal Data and Experimental Parameters[a] for Crystal Structure Analyses of 5a, 5b, 7a, and 8b

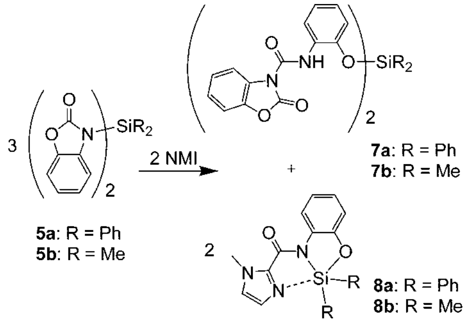
	5a (CCDC-698683)	**5b** (CCDC-698682)	**7a** (CCDC-698680)	**8b** (CCDC-698679)
empirical formula	$C_{26}H_{18}N_2O_4Si$	$C_{16}H_{14}N_2O_4Si$	$C_{40}H_{28}N_4O_8Si$	$C_{13}H_{15}N_3O_2Si$
formula mass, g mol^{-1}	450.51	326.38	720.75	273.37
collection T, K	110(2)	110(2)	100(2)	100(2)
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a, Å	9.6245(1)	7.3257(2)	9.8419(1)	7.2892(1)
b, Å	14.0115(2)	13.6736(4)	12.6734(3)	9.8847(2)
c, Å	16.1647(2)	14.8738(4)	13.8628(2)	18.3983(4)
α, deg	90	90	85.201(1)	90
β, deg	100.990(1)	90	75.716(1)	98.578(1)
γ, deg	90	90	87.212(1)	90
V, Å^3	2139.89(4)	1489.89(7)	1669.08(5)	1310.80(4)
Z	4	4	2	4
ρ_{calcd}, Mg/m^3	1.398	1.455	1.434	1.385
F(000)	936	680	748	576
θ_{max}, deg	38.0	30.0	32.0	35.0
no. of collected rflns	89 802	20 136	50 990	44 579
no. of indep rflns/R_{int}	11 652/0.0628	2481/0.0476	11 508/0.0455	5762/0.0541
no. of rflns ($I > 2\sigma(I)$)	8816	2190	8889	4758
params	298	210	486	175
GOF	1.061	1.060	1.054	1.053
R1, wR2 ($I > 2\sigma(I)$)	0.0423, 0.1109	0.0345, 0.0834	0.0433, 0.1082	0.0352, 0.0953
R1, wR2 (all data)	0.0646, 0.1191	0.0439, 0.0873	0.0643, 0.1156	0.0481, 0.1011
max., min. res electron dens, e Å^{-3}	0.587, −0.306	0.300, −0.276	0.445, −0.313	0.484, −0.274

[a] All measurements performed using Mo Kα radiation ($\lambda = 0.71073$ Å).

silicon that quite possibly contributes to an activation of the Si−N bond. In contrast, the Si−N bonds in **5a** and **5b** are essentially coplanar with the benzoxazolinyl rings.

Hypervalency in silicon chemistry typically results in bond activation through a combination of increased steric pressures and bond polarization, thus promoting bond cleavage and rearrangement reactions.[6] In our previous report[2] we have shown that the coordination of *N*-methylimidazole (NMI) to a neutral (but pentacoordinate) benzoxazolinone-substituted silane, **4**, is possible and, moreover, causes a significant Si−N bond lengthening with respect to the Si-bound benzoxazolinone. Accordingly, in order to weaken the Si−N bonds of **5a** and **5b**, NMI was added to xylene solutions of **5a** and **5b**, which were then heated under reflux. Although there was no NMR spectroscopic evidence for NMI−Si coordination at the silicon atoms of **5a** and **5b** at ambient temperature, ^{29}Si NMR spectra of the reaction mixtures revealed the formation of silicon compounds bearing pentacoordinate silicon centers after 8 h under reflux in the presence of NMI. In addition to the ^{29}Si NMR signals of the starting materials (δ **5a**: −22.5, **5b**: +5.7) and the signals of the reaction products bearing a pentacoordinate silicon atom (δ −82.2 and −59.2, respectively) a further signal appeared that indicated the formation of a new compound bearing a tetracoordinate Si atom (δ −32.9 and −0.2, respectively). The unexpected course of the reaction became obvious when crystals suitable for X-ray analyses were separated from the above reaction mixtures. From the reaction of **5a** crystals of compound **7a** formed (Scheme 3, Figure 1, Table 1). The reaction of **5b** afforded a solid that consisted of a white powder and some crystals of **8b** (Scheme 3, Figure 2, Table 1).

Scheme 3



The molecular structure of **7a** in the solid state exhibits the potentially tridentate ligand moiety comprising two coupled benzoxazolinone units (which was found to act as a tridentate chelator in **4**) attached twice to the silicon atom via the phenoxy group only. (Hence, the ^{29}Si NMR signal at δ −32.9 can be attributed to the formation of **7a**.) The amide nitrogen atoms remain protonated (the positions of the amide hydrogen atoms at N2 and N4 were located from residual electron density). The origin of the benzoxazolinone molecules, which were a prerequisite to generate this ligand at **7a**, becomes clear when the formation of **8b** is considered.

Unexpectedly, NMI is found to serve the role of reagent in addition to catalyzing Si−N bond activation; that is, a C−C bond was formed between the carbon atom in the 2-position of the NMI molecule and the carbonyl carbon atom of a former benzoxazolinone moiety. The overall reaction can be regarded as a combination of the steps depicted in Scheme 4. Upon addition of the NMI nitrogen atom (position 3) to the isocyanate carbon atom (step 1), the positive charge of the resulting imidazolium cation is distributed over ring positions 1, 2, and 3 as shown by López and Méndez.[7] Hence, intramolecular deprotonation of this cation in ring position 2 by the carbamido nitrogen atom (step 2) enables the formation of an *N*-carbazoyl N-heterocyclic carbene, the carbazoyl moiety of which may then migrate to the nucleophilic carbene carbon atom (step 3). Upon

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(6) For examples for Si−X bond activation by Si-hypercoordination see: (a) Yamamura, M.; Kano, N.; Kawashima, T. *Tetrahedron Lett.* **2007**, *48*, 4033. (b) Wagler, J.; Roewer, G. *Z. Naturforsch. B* **2006**, *61*, 1406. (c) Gostevskii, B.; Kalikhman, I.; Tessier, C. A.; Panzner, M. J.; Youngs, W. J.; Kost, D. *Organometallics* **2005**, *24*, 5786. (d) Wagler, J.; Doert, T.; Roewer, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2441. (e) Bassindale, A. R.; Taylor, P. G.; Lane, T. H.; Alvarez, K. E. *Polym. Prepr.* **2004**, *45*, 568. (f) Richter, I.; Penka, M.; Tacke, R. *Organometallics* **2002**, *21*, 3050. (g) Riedel, R.; Kroke, E.; Greiner, A.; Gabriel, A. O.; Ruwisch, L.; Nicolich, J.; Kroll, P. *Chem. Mater.* **1998**, *10*, 2964. (h) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed.* **1996**, *35*, 1420. (i) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 6429.

(7) López, P.; Méndez, F. *Org. Lett.* **2004**, *6*, 1781.

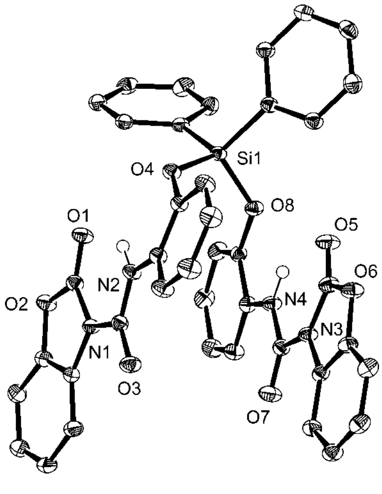


Figure 1. Molecular structure of **7a** (50% displacement ellipsoids, C-bound H atoms omitted, heteroatoms labeled).

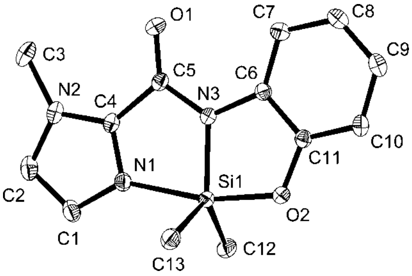
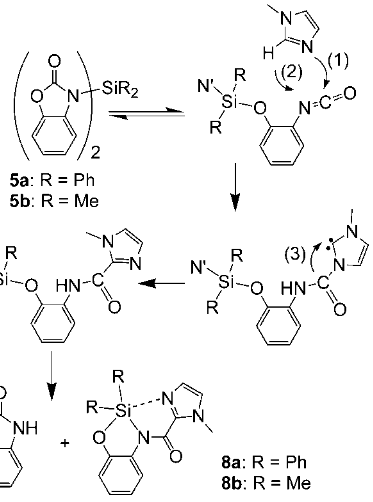


Figure 2. Molecular structure of **8b** (50% displacement ellipsoids, H atoms omitted).

formation of a tridentate ligand, the sequence of proton transfer, chelate formation, and extrusion of a benzoxazolinone molecule as leaving group appears most plausible. In place of NMI, benzoxazolinone may now act as both an N-H acidic compound and as an N-nucleophile precursor that is capable of adding to 2-siloxyphenylisocyanates under formation of compounds such as **7a**. This latter hypothesis was finally probed using **5b** plus 2 equiv of benzoxazolinone as starting materials (in xylene under reflux, NMI was also added as a catalyst to deprotonate the benzoxazolinone). Indeed, this reaction gave rise to the deliberate synthesis of **7b** in good yield.

The ease of formation of **7b** from silylated benzoxazolinone **5b** and benzoxazolinone coupled with the formation of the novel tridentate (N′NO) ligand system of **8b** from a silylated benzoxazolinone plus NMI under C−C bond formation suggested to us that *N*-trimethylsilylated benzoxazolinone **1** might itself serve as a potential precursor to tridentate ligands via benzoxazolinone ring cleavage. Thus, **1** was prepared from the reaction of benzoxazolinone with an excess of chlorotrimethylsilane and triethylamine. The crude product was obtained as a colorless oil and used as such. (Compound **1** formed some single crystals upon mixing with NMI; thus the solid state structure of **1** was determined by X-ray diffraction analysis, Table 2). In the reactions depicted in Scheme 5 compound **1** was mixed with a stochiometric (**9a**, **9c**) or excess (**9b**) amount of the N- and C-nucleophile precursor, respectively, and heated to 190 °C for 1 h (**9a**), 2 h (**9c**), or 10 h (**9b**). The reactions to **9a** and **9c** were aparently complete within the time given above (as concluded from ^{29}Si NMR spectra of the crude product). In the case of **9b** the ^{29}Si NMR spectrum of the crude product mixture indicated ca. 80% conversion within 10 h. Whereas **9a** and **9c** were isolated directly as solids, **9b** provided an oily product mixture that could upon crystallization from a mixture of dichloromethane and methanol provide crystals of **10b**. Compounds **9a**, **9c**, and **10b** were characterized by single-crystal X-ray diffraction analysis (Table 2).

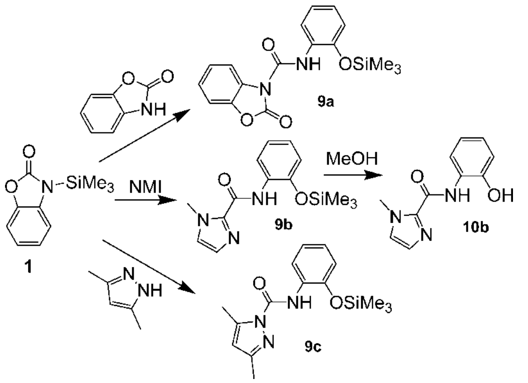
Scheme 4



5a: R = Ph
5b: R = Me

8a: R = Ph
8b: R = Me

Scheme 5



Whereas the carbamido ligand **10b** appeared to be stable after desilylation, the ureas **10a** and **10c** (desilylated **9a** and **9c**, respectively) could not be prepared by treatment of the silylated ligands **9a** and **9c**, respectively, with methanol: Decomposition of the free ligand acids was observed spectroscopically (NMR) and by isolation of decomposition products benzoxazolinone and 3,5-dimethylpyrazole, respectively. It would thus appear that the *ortho*-hydroxyl function promotes protolysis/solvolysis of these ureas.

In a test reaction ligand **10b** was shown to be a suitable chelator for tetra- and hexacoordinate Ni^{2+} cations (formation of **11b** and **12b**, Scheme 6, Table 3). Thus, solvolysis of **9a** was also carried out prior to the immediate addition of Ni(II)-acetate and ammonia (to trap *in situ* generated ligand **10a**). In spite of the presence of the transition metal reagent and a supporting base the ligand system decomposed readily to provide benzoxazolinone with the ultimate formation of dibenzoxazolinonyltetraamminnickel(II) (**13**) in quantitative yield (Scheme 7). The solid state structure of **13** was determined crystallographically (Table 3). Hence, even in the presence of a ligand trap and a supporting base urea **10a** decomposes rapidly.

As the ligand systems of compounds **9a** and **9c** were found to be stable as *O*-trimethylsilylated derivative and the ligand system of **9a** was known to be also stable as a tridentate chelator in silicon complexes (compound **4**), an attempt was made to at least transfer the ureato ligand of **9c** onto another silicon atom.

Table 2. Crystal Data and Experimental Parameters[a] for Crystal Structure Analyses of 1, 9a, 9c, and 10b

	1 (CCDC-698686)	**9a** (CCDC-698684)	**9c** (CCDC-698688)	**10b**(CCDC-698685)
empirical formula	$C_{10}H_{13}NO_2Si$	$C_{17}H_{18}N_2O_4Si$	$C_{15}H_{21}N_3O_2Si$	$C_{11}H_{11}N_3O_2$
formula mass, g mol^{-1}	207.30	342.42	303.44	217.23
collection T, K	100(2)	100(2)	150(2)	100(2)
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$Pbca$	$C2/c$	$P2_1/c$	$P2_1/c$
a, Å	12.1828(2)	23.1498(7)	12.0673(2)	12.2364(6)
b, Å	9.7269(2)	6.4984(2)	12.6067(2)	13.4662(6)
c, Å	18.0635(3)	24.0295(7)	10.8886(2)	6.1023(3)
β, deg	90	114.710(1)	90.118(1)	97.017(2)
V, Å^3	2140.54(7)	3283.92(17)	1656.47(5)	997.99(8)
Z	8	8	4	4
ρ_{calcd}, Mg/m^3	1.287	1.385	1.213	1.446
F(000)	880	1440	648	456
θ_{max}, deg	31.0	30.0	30.0	30.0
no. of collected rflns	32 496	28 428	21 696	16 019
no. of indep rflns/R_{int}	3394/0.0368	4759/0.0613	4804/0.0480	2912/0.0481
no. of rflns ($I > 2\sigma(I)$)	2842	3690	3679	2301
params	130	224	194	154
GOF	1.046	1.060	1.041	1.058
R1, wR2 ($I > 2\ \sigma(I)$)	0.0341, 0.0909	0.0424, 0.1029	0.0400, 0.0993	0.0418, 0.0983
R1, wR2 (all data)	0.0449, 0.0950	0.0635, 0.1105	0.0604, 0.1061	0.0600, 0.1045
max., min. res electron dens, e Å^{-3}	0.356, −0.287	0.376, −0.323	0.307, −0.216	0.292, −0.212

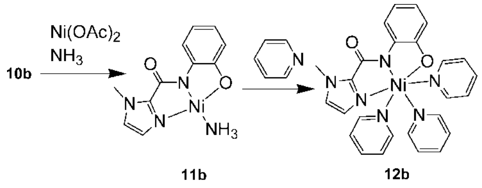
[a] All measurements performed using Mo Kα radiation ($\lambda = 0.71073$ Å).

Table 3. Crystal Data and Experimental Parameters[a] for Crystal Structure Analyses of 11b·$(H_2O)_{0.5}$, 12b·$(H_2O)_{1.75}$, 13, and 14c

	11b·$(H_2O)_{0.5}$ (CCDC-698690)	**12b**·$(H_2O)_{1.75}$ (CCDC-698681)	**13** (CCDC-698687)	**14c** (CCDC-698689)
empirical formula	$C_{11}H_{13}N_4NiO_{2.5}$	$C_{26}H_{27.5}N_6NiO_{3.75}$	$C_{14}H_{20}N_6NiO_4$	$C_{24}H_{21}N_3O_2Si$
formula mass, g mol^{-1}	299.96	542.75	395.07	411.53
collection T, K	100(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	17.4537(7)	9.4184(1)	6.9600(1)	15.0974(3)
b, Å	16.9011(5)	14.4888(2)	12.4871(3)	11.6399(3)
c, Å	9.6894(4)	18.2332(3)	9.3214(2)	23.4817(5)
β, deg	123.441(2)	93.932(1)	104.732(2)	103.043(1)
V, Å^3	2385.07(15)	2482.27(6)	783.49(3)	4020.03(16)
Z	8	4	2	8
ρ_{calcd}, Mg/m^3	1.671	1.452	1.675	1.360
F(000)	1240	1134	412	1728
θ_{max}, deg	33.0	30.0	32.0	32.0
no. of collected rflns	15 323	51 421	19 002	60 249
no. of indep rflns/R_{int}	4491/0.0297	7237/0.0388	2716/0.0526	13 843/0.0546
no. of rflns ($I > 2\sigma(I)$)	3859	6071	2221	10 985
params	185	351	115	541
GOF	1.077	1.055	1.057	1.049
R1, wR2 ($I > 2\sigma(I)$)	0.0304, 0.0796	0.0305, 0.0737	0.0318, 0.0736	0.0398, 0.0977
R1, wR2 (all data)	0.0383, 0.0827	0.0409, 0.0774	0.0466, 0.0781	0.0565, 0.1036
max., min. res electron dens, e Å^{-3}	0.592, −0.660	0.342, −0.520	0.465, −0.499	0.408, −0.294

[a] All measurements performed using Mo Kα radiation ($\lambda = 0.71073$ Å).

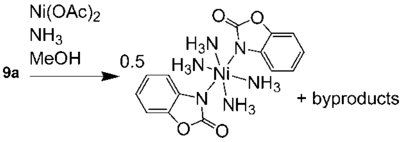
Scheme 6



Transsilylation reactions are a well-known tool for the synthesis of higher-coordinate silicon complexes.[8] Hence, in a combined salt elimination/transsilylation reaction (Scheme 8, Figure 3, Table 3) the novel tridentate (N′NO) ligand system of **9c** was successfully transferred onto a diphenylsilicon moiety, delivering compound **14c** in moderate yields.

Together with complex **8b**, **14c** contributes to the still scarcely explored class of organosilicon complexes bearing a tridentate (N′NO) ligand system.[9] Although **8b** and **14c** appear structurally related to compound **15**,[9a] Scheme 9 (the dianionic tridentate N′NO-chelator is setting up two five-membered rings about the silicon atom), the N(imine)−N(amide)−O donor sequence of the ligands of **8b** and **14c** versus the N(amide)−N(imine)−O

Scheme 7



Scheme 8

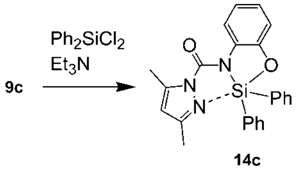


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Table 4. Selected Interatomic Distances [Å] and Angles [deg] of 1, 5a, 5b, and 3 (in order of increasing length or angle for columns Si−N, Si−O, Si−C, and Si−N−C(@ C=O), whereas the angles of the last column correspond to the previous one)

compound	Si−N	Si−O	Si−C	Si−N−C(@ C=O)	Si−N−C(@ aryl)
1	1.801(1)	3.111(1)	1.849(1)	120.32(7)	132.22(7)
			1.850(1)		
			1.851(1)		
5a	1.769(1)	3.053(1)	1.850(1)	119.48(5)	132.71(5)
	1.771(1)	3.219(1)	1.858(1)	125.34(6)	127.33(5)
5b	1.770(2)	3.083(2)	1.837(2)	120.16(13)	132.65(13)
	1.790(2)	3.092(2)	1.840(2)	120.49(14)	132.05(14)
3	1.746(2)	3.022(2)	1.834(2)	117.75(14)	131.06(14)
	1.752(2)	3.082(2)			132.42(15)
	1.752(2)	3.209(2)		125.91(15)	127.05(14)

donor sequence of **15** results in distinctive structural features of note (selected bond lengths, referring to Scheme 9 bottom right, are given in Table 5). In particular, striking differences can be found for the Si−N bond lengths. The different electronic properties of the ligand systems of **8b** and **14c** versus **15** further cause significant differences in the colors of the above complexes (**8b** and **14c** are colorless, whereas **15** is red).

Concluding Remarks

In conclusion, *N*-silylated benzoxazolin-2-one has been shown to serve as a suitable starting material for the construction of tridentate ligand systems via benzoxazolinone ring-opening processes. Thus, organosilicon substitution of benzoxazolin-2-one has been shown to be a valuable tool for moderating the reactivity of this heterocycle with respect to ring-opening reactions and templated ligand syntheses. Lewis acidic silicon centers have recently been reported to serve as a starting point for the *in situ* or templated generation of a tridentate ligand,[10] while silicon substitution of chelating ligands may also promote ring closure and hence deactivation of tridentate ligands as shown for benzimidazoline formation.[9c] Thus, the common perspective of organosilicon species as protecting groups is only part of the story. The results herein demonstrate quite the reverse, i.e., reactions that are facilitated by the special properties of silyl substituents.

In addition to our previously reported templated ligand synthesis,[2] which represents a benzoxazolinone dimerization, the fusion of two different N−H acidic heterocycles (one of them being benzoxazolin-2-one) has now been demonstrated. Weakly C−H acidic heterocycles such as *N*-methylimidazole may undergo similar reactions with *N*-silylated benzoxazolinone to yield carbamido ligand systems via C−C bond formation. The above reactions were shown to also proceed without a templating bi- or trifunctional silane attached to the benzoxazolinone N atom; that is, it transpires that even trimethylsilylated benzoxazolinone is capable of accessing the desired ligand systems, albeit at somewhat higher temperatures.

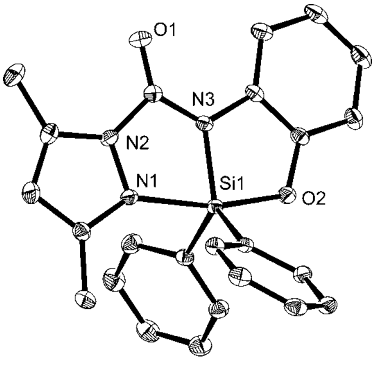


Figure 3. Molecular structure of one of the two crystallographically independent molecules in the crystal structure of **14c** (50% displacement ellipsoids, H atoms omitted, heteroatoms labeled).

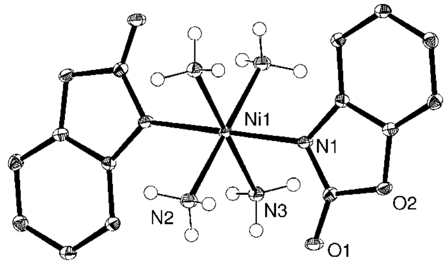


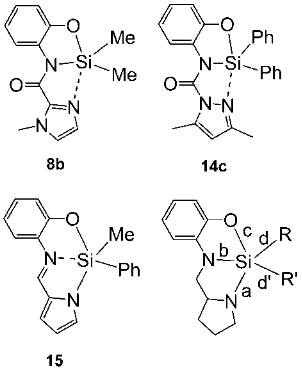
Figure 4. Molecular structure of **13** (50% displacement ellipsoids, C-bound H atoms omitted, heteroatoms labeled). Selected bond lengths [Å] and angles [deg]: Ni1−N1 2.132(1), Ni1−N2 2.126(1), Ni1−N3 2.132(1), N1−Ni1−N2 88.89(5), N1−Ni1−N3 88.93(5), N2−Ni1−N3 90.25(5), N1−Ni1−N2* 91.11(5), N1−Ni1−N3* 91.07(5), N2−Ni1−N3* 89.75(5).

Table 5. Selected Bond Lengths [Å] of Compounds 8b, 14c, and 15[a]

bond	8b	14c	15
a	2.039(1)	2.017(1)	1.923(2)
		2.079(1)	1.915(2)
b	1.838(1)	1.828(1)	1.897(1)
		1.812(1)	1.896(1)
c	1.774(1)	1.747(1)	1.776(1)
		1.751(1)	1.765(1)
d,d′	1.865(1)	1.885(1)	1.867(2)
	1.865(1)	1.887(1)	1.885(2)
		1.872(1)	1.860(2)
		1.878(1)	1.883(2)

[a] The crystal structures of **14c** and **15** comprise two crystallographically independent but similar molecules, the bond lengths of the first molecule are given first.

Scheme 9



The novel ligands prepared were shown to act as tridentate chelators in silicon(IV) and nickel(II) compounds and may serve as a novel pool of starting materials for the preparation of further main group and transition metal complexes where O′NO and N′NO chelating systems are required. Applicable ligand transfer routes (transsilylation, salt elimination) will have to be explored for each ligand system in further studies, as initial attempts to isolate the urea-related ligands rendered them unstable with respect to solvolysis reactions. In contrast, the NMI-derived carbamido ligand acid **10b** was successfully isolated upon desilylation.

Discussion of Structural Features of New Compounds

In addition to our previously reported *N*-silylated benzoxazolinone derivative **3**[2] and the two diorganosilicon benzoxazolinone compounds **5a** and **5b** the solid state structure of **1** complements the series of X-ray crystallographically characterized *N*-mono-, -di-, and -triorganosilicon-substituted benzoxazolinones. This series allows comparison of the bonding parameters of the above compounds (Table 4). To the best of our knowledge, these provide the only structural data currently available for *N*-silylated benzoxazolin-2-ones.[11] In general, the steric demand of the benzo group causes a (more or less) widened angle Si−N−C(@ aryl) ranging between 127.0° and 132.7°, with the corresponding angles Si−N−C(@ C=O) being noticeably smaller (ranging between 117.8° and 125.9°). The variability of the latter is accompanied by variable Si−O separations ranging between 3.02 and 3.22 Å without any discernible systematic influence of the Si substitution pattern. Whereas the above parameters appear quite arbitrary, a sytematic bond shortening of Si−N bonds is observed with increasing number of Si-bound benzoxazolinonyl substituents. The influence of the number of Si−N bonds on the Si−C bond lengths is less pronounced and close to the limit of significance.

In contrast to **1**, compound **13** (Figure 4) represents an *N*-transition-metal-substituted benzoxazolin-2-one (to date the only example of a crystallographically characterized *N*-transition metal-substituted benzoxazolin-2-one.[11]) So far, in addition to the above silylated benzoxazolinones, only a crystal structure of a single *N*-aluminated benzoxazolinone was reported in the literature.[12] The Ni atom of **13** is situated on a crystallographically imposed center of inversion. Hence, 180° angles arise for the axial atomic arrangements within this nearly octahedral complex. The remaining angles of the Ni coordination sphere are close to orthogonal (ranging between 88.9° and 91.1°), and even more surprisingly, the Si−N bonds adjust to very similar lengths, although highly disparate ligands are involved (sp^2 nitrogen of the anionic benzoxazolinonide ligand versus sp^3 nitrogen of the neutral ammonia ligand). As for the *N*-silylated benzoxazolinones, the sterically demanding benzene ring causes a widening of the angle Ni1−N1−C(@ aryl) (130.83(9)°), whereas the corresponding angle Ni1−N1−C(@ C=O) is significantly smaller (123.22(9)°).

Experimental Section

Unless otherwise stated, syntheses were carried out under an inert atmosphere of dry and purified dinitrogen using standard Schlenk techniques and dry solvents. ^{1}H, ^{13}C, ^{29}Si NMR spectra (solution) were recorded on Varian Inova 300 and Varian Inova 500 spectrometers at 25 °C using $SiMe_4$ as an internal standard. Elemental microanalytical data were provided by the Research School of Chemistry analytical service. Single-crystal X-ray structural analyses were performed on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved with direct methods (SHELXS-97) and refined with full-matrix least-squares methods (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in idealized positions and refined isotropically except N- and O-bound hydrogen atoms of compounds **7a**, **9a**, **9c**, **10b**, and **11b**, which were located by analysis of residual electron density maps and refined isotropically without any restraints. (Bond length restraints were applied to the O−H bonds in the water of crystallization in the structure of **12b**.)

Synthesis of 5a. To a solution of benzoxazolin-2-one (2.00 g, 14.8 mmol) and triethylamine (1.80 g, 17.8 mmol) in dry THF (30 mL) was added dropwise dichlorodiphenylsilane (1.90 g, 7.51 mmol) at room temperature, whereupon triethylammonium chloride precipitated. The mixture was briefly heated to 50 °C (ca. 15 min), allowed to cool to ambient temperature, and stored at room temperature overnight. The $[Et_3NH]Cl$ precipitate was then filtered off, washed with THF (15 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure and the residue dissolved in dry dichloromethane (5 mL). Upon addition of diethyl ether (5 mL) to the dichloromethane solution, crystallization of **5a** commenced. After 1 day a further 5 mL portion of diethyl ether was added to induce further crystallization. After a further day the supernatant was decanted from the colorless crystals, which were washed with diethyl ether (7 mL) and dried in a vacuum. Yield: 2.55 g (3.54 mmol, 48%). Mp: 164−170 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 6.07 (d, 2 H, 8.5 Hz), 6.80 (m, 2 H), 7.03 (m, 2 H), 7.17 (d, 2 H, 8.5 Hz), 7.5−8.0 (mm, 10 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ_C 110.0, 112.5, 123.2, 123.7, 126.2(i), 128.8(o/m), 132.4, 132.7(p), 136.5(o/m), 145.2, 157.5. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} −22.4. Anal. Found: C, 69.29; H, 4.22; N, 6.01. Calcd for $C_{26}H_{18}N_2O_4Si$: C, 69.32; H, 4.03; N, 6.22.

Synthesis of 5b. To a solution of benzoxazolin-2-one (3.00 g, 22.2 mmol) and triethylamine (2.60 g, 25.7 mmol) in dry THF (50 mL) was added dropwise dichlorodimethylsilane (1.45 g, 11.2 mmol) at room temperature, whereupon triethylammonium chloride precipitated. The mixture was briefly heated to 50 °C (15 min), allowed to cool to ambient temperature, and stored at 8 °C for 2 h. The $[Et_3NH]Cl$ precipitate was then filtered off, washed with THF (20 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure and the residue recrystallized from dry toluene (10 mL). After 1 day the supernatant was decanted from the colorless crystals, which were washed with toluene (4 mL) and dried in a vacuum. Yield: 3.0 g (9.2 mmol, 83%). Mp: 124−126 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 1.15 (s, 6 H, CH_3), 7.0 −7.2 (m, 8 H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ_C −1.5 (CH_3), 110.1, 111.5, 123.4, 124.1, 131.7, 144.7, 157.0. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} 5.7. Anal. Found: C, 58.66; H, 4.63; N, 8.35. Calcd for $C_{16}H_{14}N_2O_4Si$: C, 58.88; H, 4.32; N, 8.58.

Synthesis of 7a. To a solution of **5a** (0.57 g, 1.3 mmol) in xylenes (5 mL) was added *N*-methylimidazole (0.1 mL), and the solution was heated with stirring under reflux for 10 h. From the resultant solution the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (1 mL) and diethyl ether (1 mL). From this solution at ambient temperature **7a** formed colorless crystals, which were separated from the mother liquor by decantation and dried under vacuum. Yield: 0.15 g (0.21 mmol, 48%, Scheme 3). Mp: 178−180 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 6.80−7.00 (mm, 6 H), 7.20−7.50 (mm, 12 H), 7.85−8.15

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(10) Metz, S.; Burschka, C.; Platte, D.; Tacke, R. *Angew. Chem., Int. Ed.* **2007**, *46*, 7006.

(11) According to a Cambridge Structure Data Base search, ConQuest version 1.10, copyright CCDC 2008.

(12) Bird, C. M.; Breheny, C.; Davidson, M. G.; Edwards, A. J.; Llewellyn, S. C.; Raithby, P. R.; Snaith, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1483.

(mm, 8 H), 10.30 (s, 2 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C 109.8, 115.7, 119.2, 121.4, 122.7, 124.6, 124.9, 125.0, 127.8, 127.9, 128.1, 129.7, 131.4, 135.3, 141.7, 143.9, 146.9, 152.5. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} −33.0. Anal. Found: C, 66.24; H, 4.08; N, 7.82. Calcd for $C_{40}H_{28}N_4O_8Si$: C, 66.66; H, 3.92; N, 7.77.

Compound **8a** was spectroscopically detected ($^{29}Si\{^1H\}$ NMR) in the above crude product mixture (see **7a**) ($CDCl_3$, δ_{Si} −82.2).

Synthesis of 7b. To a solution of **5b** (0.36 g, 1.1 mmol) and benzoxazolinone (0.30 g, 2.2 mol) in xylenes was added *N*-methylimidazole (5 drops), and the mixture was heated under reflux for 2 h and then allowed to cool. On standing at room temperature for 14 days a solid product separated from the solution, which was filtered off, washed with xylenes (1 mL), and dried in a vacuum. Yield: 0.42 g (0.70 mmol, 64%). Mp: 170−171 °C. ^1H NMR ($CDCl_3$, 25 °C): δ_H 0.64 (s, 6 H, CH_3), 6.90−7.40 (mm, 12 H), 8.10−8.30 (mm, 4 H), 10.52 (s, 2 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C −2.3 (CH_3), 109.9, 115.7, 118.2, 120.1, 122.6, 124.4, 124.7, 125.1, 127.9, 128.4, 141.7, 143.4, 146.6, 152.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} −0.2. Anal. Found: C, 60.17; H, 4.35; N, 9.39. Calcd for $C_{30}H_{24}N_4O_8Si$: C, 60.39; H, 4.05; N, 9.39.

Some crystals of compound **8b** were manually separated from the product mixture, which crystallized at room temperature after heating compound **5b** (0.73 g) and *N*-methylimidazole (0.1 mL) in xylenes for 8 h, removal of solvent in a vacuum, followed by addition of dichloromethane (1 mL) and diethyl ether (1 mL). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, crude product mixture): δ_{Si} −59.2. Anal. Found (for separated crystals): C, 57.53; H, 6.14; N, 14.68. Calcd for $C_{13}H_{15}N_3O_2Si$: C, 57.12; H, 5.53; N, 15.37.

Synthesis of 9a. Chlorotrimethylsilane (0.45 g, 4.15 mmol) was added to a THF solution (20 mL) of benzoxazolinone (1.00 g, 7.41 mmol) and triethylamine (1.0 g, 9.9 mmol) at ambient temperature, whereupon triethylammonium chloride precipitated. The $[Et_3NH]Cl$ precipitate was filtered, washed with THF (3 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure to yield a solid mixture of benzoxazolinone and its *N*-trimethylsilyl derivative **1**. This crude mixture was heated to 190 °C. This temperature was maintained for 1 h before the product was allowed to cool to room temperature. To the solid product was added hexane (2 mL), the solid was ground to a fine powder, and the suspension was stored at 8 °C for 1 h. Then the solid product was filtered, washed with hexane (3 mL), and dried in a vacuum. Yield: 0.94 g (2.75 mmol, 66%). Mp: 130 °C. ^1H NMR ($CDCl_3$, 25 °C): δ_H 0.38 (s, 9 H, CH_3), 6.85−6.95 (m, 1 H), 6.95−7.05 (m, 2 H), 7.20−7.30 (m, 3 H), 8.10−8.20 (m, 1 H), 8.25−8.35 (m, 1 H), 10.57 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C 0.28 (CH_3), 109.9, 115.7, 117.8, 120.0, 121.7, 124.3, 124.7, 125.0, 127.9, 128.7, 141.8, 144.7, 146.8, 152.8. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} 23.2. Anal. Found: C, 59.52; H, 5.05; N, 8.35. Calcd for $C_{17}H_{18}N_2O_4Si$: C, 59.63; H, 5.30; N, 8.18.

Synthesis of 9c. Chlorotrimethylsilane (4.50 g, 41.5 mmol) was added to a THF solution (100 mL) of benzoxazolinone (5.00 g, 37.0 mmol) and triethylamine (5.00 g, 49.5 mmol) at 0 °C, whereupon triethylammonium chloride precipitated. After 1 h at 0 °C the $[Et_3NH]Cl$ precipitate was filtered off, washed with THF (40 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure to yield **1** as an oil. 3,5-Dimethylpyrazole (3.50 g, 36.5 mmol) was added to this oil, and the mixture was heated to 190 °C for 2 h before being allowed to cool to room temperature. To the solid product diethyl ether (2.5 mL) and pentane (2.5 mL) were added, the solid was ground to a fine powder, and the suspension was stored at 8 °C for 4 h. The solid product was then filtered off, washed with a mixture of diethyl ether (2 mL) and pentane (8 mL), and dried in a vacuum. From this crude product traces of dimethylpyrazole were removed by vacuum sublimation at 140 °C. The product obtained was then recrystallized from hexane (20 mL). **9c** formed colorless crystals, which were, following storage at 8 °C overnight, separated from the solvent by decantation, washed with hexane (5 mL), and dried in a vacuum. Yield: 6.30 g (20.8 mmol, 57%). Mp: 88−89 °C. ^1H NMR ($CDCl_3$, 25 °C): δ_H 0.36 (s, 9 H, Si-CH_3), 2.23 (s, 3 H, pzCH_3), 2.61 (s, 3 H, pzCH_3), 5.94 (s, 1 H, pyrazole), 6.80−7.05 (mm, 3 H), 8.25−8.30 (m, 1 H), 9.93 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C 0.23 (Si-CH_3), 13.6, 14.0 (pzCH_3), 110.0, 118.0, 118.9, 121.9, 123.4, 129.4, 143.5, 144.4, 148.3, 150.1. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_{Si} 22.9. Anal. Found: C, 59.34; H, 6.76; N, 13.82. Calcd for $C_{15}H_{21}N_3O_2Si$: C, 59.37; H, 6.98; N, 13.85.

Synthesis of 10b. Chlorotrimethylsilane (4.50 g, 41.5 mmol) was added to a THF solution (100 mL) of benzoxazolinone (5.00 g, 37.0 mmol) and triethylamine (5.0 g, 49.5 mmol) at 0 °C, whereupon triethylammonium chloride precipitated. After 1 h at 0 °C the precipitate was filtered off, washed with THF (40 mL), and discarded. From the combined filtrate and washings the solvent was removed under reduced pressure to yield **1** as an oil. *N*-Methylimidazole (4.00 g, 48.8 mmol) was added to this oil, whereupon colorless crystals of **1** formed. After separation of a crystal of **1** for X-ray diffraction analysis the above mixture was heated to 190 °C. This temperature was maintained for 10 h before the product was allowed to cool to room temperature. The oily material was dissolved in dichloromethane (10 mL), and dry methanol (2.5 mL) was added. Within 1 day crystals of **10b** formed. The mixture was then stored at 8 °C for 1 h, and the crystals were filtered off, washed with methanol (20 mL), and dried in a vacuum (4.15 g). From the filtrate further product of comparable purity to the initial crop was obtained upon storage at −20 °C (0.75 g). Combined yield: 4.90 g (22.6 mmol, 61%). Mp: 180−182 °C. ^1H NMR ($CDCl_3$, 25 °C): δ_H 4.13 (s, 3 H, N-CH_3), 6.84−7.06 (mm, 3 H), 7.08 (s, 1 H), 7.20 (s, 1 H), 7.82 (dd, 1 H, 1.5 Hz, 8.1 Hz), 9.54 (s, 1 H, OH), 10.66 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ_C 36.3 (N-CH_3), 117.1, 120.1, 121.2, 125.7, 126.0, 126.4, 127.3, 138.7 (br), 147.6, 157.0. Anal. Found: C, 60.74; H, 5.15; N, 19.31. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82, H, 5.10; N, 19.34.

Synthesis of 11b (anaerobic anhydrous conditions not required). Nickel(II)-acetate tetrahydrate (0.20 g, 0.80 mmol) was dissolved in mixture of 25% aqueous ammonia (3 mL) and methanol (15 mL) and stirred at ambient temperature, whereupon solid ligand **10b** (0.17 g, 0.78 mmol) was added. Within a few minutes, a clear yellow-brown solution formed. Tetrahydrofuran (10 mL) was added, and the solution was opened to the atmosphere to allow for slow evaporation of solvents. When the solution had concentrated to an approximate final volume of 8 mL, the dark red crystalline product was separated by decantation, washed with methanol (2 mL), and dried in air. Yield: 0.14 g. **11b**·$(H_2O)_{0.5}$ (0.47 mmol, 60%). Anal. Found: C, 44.37; H, 4.61; N, 18.81. Calcd for $C_{11}H_{13}N_4O_{2.5}Ni$: C, 44.05; H, 4.37; N, 18.68. The crystal structure of the hemihydrate **11b**·$(H_2O)_{0.5}$ (Table 3) was determined.

Synthesis of 12b (anaerobic anhydrous conditions not required). The hemihydrate of **11b** (0.040 g, 0.13 mmol) was dissolved in a mixture of acetonitrile (3 mL) and pyridine (0.6 mL). A small amount of green precipitate formed, which was filtered off and discarded. Upon storage of the brown filtrate (open to air), some milligrams of brown crystals of **12b**·$(H_2O)_{1.75}$ formed, which were separated manually and dried on filter paper. Anal. Found: C, 57.44; H, 4.86; N, 15.24. Calcd for $C_{26}H_{27.5}N_6O_{3.75}Ni$: C, 57.54; H, 5.11; N, 15.48.

Synthesis of 13. In an attempt to trap *in situ* the desilylated compound **9a** in the presence of ammoniacal nickel acetate, complex **13** formed. To a solution of **9a** (0.18 g, 0.53 mmol) in dichloromethane (3 mL) was added dry methanol (2.5 mL) followed by the addition of a freshly prepared solution of Ni(II)-acetate tetrahydrate (0.13 g, 0.53 mmol) in methanol (2 mL) and 25% aqueous ammonia (0.6 mL). The product solution was exposed to ambient air to allow for slow evaporation of ca. 50% of the solvent over 1 day, whereupon the remaining supernatant was decanted from the mauve crystalline product, which was washed with methanol (0.5 mL) and dried in air. Yield: 0.10 g (0.25 mmol, 96%). Anal. Found: C, 42.82; H, 5.19; N, 21.17. Calcd for $C_{14}H_{20}N_6O_4Ni$: C, 42.56; H, 5.10; N, 21.27.

Synthesis of 14c. The ligand precursor **9c** (0.30 g, 0.99 mmol) was dissolved in THF (5 mL) and treated with triethylamine (0.20 g, 2.0 mmol) and dichlorodiphenylsilane (0.26 g, 1.0 mmol), whereupon a small amount of white precipitate formed. The mixture was briefly heated to reflux, then cooled 0 °C. The $[Et_3NH]Cl$ precipitate was filtered off and washed with THF (1 mL). From the filtrate and combined washings the solvent was removed under reduced pressure to yield a colorless oil, which was then dissolved in dichloromethane (0.3 mL) and diethyl ether (0.6 mL). As there was no indication of the formation of solid product even upon storage at 8 °C, a ^{29}Si NMR spectrum was recorded (in $CDCl_3$) which confirmed the formation of products bearing only tetracoordinate silicon atoms (δ_{Si} 22.9, 5.8, and −10.9 were observed). Another ^{29}Si NMR spectrum of the same reaction mixture, recorded two months later, indicated the formation of the pentacoordinate silicon complex in good yield [δ_{Si} 31.7 ($ClSiMe_3$) and −79.9 (**14c**)]. Thus, the solvent was allowed to evaporate (solution exposed to air), whereupon crystals of **14c** formed, which were separated from the remaining solution by decantation, washed with ethanol (ca. 0.2 mL), and dried in air. Yield: 0.20 g (0.49 mmol, 50%). ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 1.48 (s, 3 H, $pzCH_3$), 2.80 (s, 3 H, $pzCH_3$), 6.08 (s, 1 H, pzCH), 6.70−7.00 (mm, 3 H), 7.20−7.40 (mm, 5 H), 7.50−7.65 (mm, 5 H) 8.2 (m, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ_C 0.23 (Si-CH_3), 12.6, 12.8 ($pzCH_3$), 112.3, 112.9, 116.2, 118.1, 124.4, 127.9, 129.2, 130.0, 133.9, 138.2, 142.6, 147.9, 149.3, 151.0. ^{29}Si{^{1}H} NMR ($CDCl_3$, 25 °C): δ_{Si} −79.9.

Acknowledgment. This work was supported by a fellowship within the Post-Doctoral Programme of the German Academic Exchange Service (DAAD) and by the Australian Research Council (DP0771497). Furthermore, we thank a referee for suggesting the initial steps of the reaction pathway depicted in Scheme 4.

Supporting Information Available: Crystallographic data for **1**, **5a**, **5b**, **7a**, **8b**, **9a**, **9c**, **10b**, **11b**·$(H_2O)_{0.5}$, **12b**·$(H_2O)_{1.75}$, **13**, and **14c** in CIF format as well as a PDF document containing ORTEP drawings of **1**, **5a**, **5b**, **9a**, **9c**, **10b**, **11b**, and **12b** are available free of charge via the Internet at http://pubs.acs.org.

OM800796Z