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Steering S−H and N−H Bond Activation by a Stable N-Heterocyclic Silylene: Different Addition of H_2S, NH_3, and Organoamines on a Silicon(II) Ligand versus Its Si(II)→$Ni(CO)_3$ Complex

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Abstract: The strikingly different behavior of the ylide-like, N-heterocyclic silylene LSi: (**5**: L = $CH[(C{=}CH_2)CMe(NAr)_2]$; Ar = 2,6-$^iPrC_6H_3$) versus its LSi→$Ni(CO)_3$ complex **13** to activate E−H bonds (E = S, N) of small molecules is reported. Remarkably, conversion of **5** with hydrogen sulfide leads exclusively to the first isolable silathioformamide, L′Si(=S)H (**16**: L′ = $CH[C(Me)NAr]_2$; Ar = 2,6-$^iPrC_6H_3$) with a donor-supported Si=S double bond and four-coordinate silicon. The latter result demonstrates the unusual ambivalent reactivity of **5** by combining two modes of reactivity involving S−H bond activation and subsequent 1,4- and 1,1-addition, respectively. In addition, **5** can serve as a ligand with well-balanced σ-donor and π-acceptor capabilities toward transition metals. This has been demonstrated by the isolable [Ni^0(arene)] complexes **12a**−**e** (arene = $Me_nC_6H_{6-n}$, $n = 0-3$), which are ideal precursors for the formation of the corresponding $Ni(CO)_3$ complex **13**. The latter activates a S−H bond in hydrogen sulfide, too, but the presence of the $Ni(CO)_3$ moiety governs the formation of the complex **17**, bearing an unprecedented β-diketiminate silicon(II) thiol ligand: L′Si(SH): (L′ = $CH[C(Me)NAr]_2$; Ar = 2,6-$^iPrC_6H_3$). Likewise, the Si(II)→$Ni(CO)_3$ coordination in **13** steers exclusively 1,4-addition of ammonia, isopropylamine, and phenylhydrazine onto the silylene ligand **5**, leading to the corresponding β-diketiminate silicon(II) amide or hydrazide complexes L′Si(NHR)→$Ni(CO)_3$ (**23a**−**c**: R = H, ^{i}Pr, N(H)Ph). IR measurements reveal that the carbonyl stretching frequencies of the $Ni(CO)_3$ moiety in **23a**−**c** are shifted to even lower wavenumbers in comparison to those of NHCs or phosphines. In other words, the β-diketiminate silicon(II) amide ligands in **23a**−**c** represent the strongest donors in the series of N-heterocyclic silylenes reported as yet.

Introduction

The first stable N-heterocyclic silylene (NHSi)[1] was reported only 3 years after Arduengo et al. published their initial communication on an isolable N-heterocyclic carbene (NHC).[2] Even though derivatives of both classes have been utilized as ligands in transition-metal complexes from an early stage, their chemistry has developed quite differently. In particular, NHCs have been shown to be extremely fruitful ligands for the synthesis of homogeneous transition-metal catalysts.[3a−c] Thus, NHCs are well-established and indispensable ligands for the stabilization of, for example, low-coordinate metal centers and low-valent main group compounds,[4,5] and they have also found numerous applications in catalysis and materials synthesis.[6,7] NHSis are also known to form complexes with various transition metals, but the inherent reactivity of the metal−silicon bond has prevented any application to date. Some recently reported, catalytically active silylene complexes[8] feature either NHSi[8a,d] or terminal silylene ligands.[8c−f]

Catalytic systems in which the ligands participate directly in a given reaction hold a great deal of potential. The ability of main-group compounds to activate key substrates such as hydrogen and ammonia under mild conditions has only been realized very recently.[9] This has been achieved with systems which exhibit cooperating Lewis acid and Lewis base sites. The

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(1) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33–34.
(2) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
(3) (a) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3741–3747. (b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759. (c) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760–3765.
(4) (a) Wang, Y.; Xie, Y.; Wie, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069–1071. (b) Wang, Y.; Xie, Y.; Wie, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971.
(5) (a) Ghadwal, R.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683–5686.
(6) Filippou, A. C.; Chernov, O.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5687–5690.
(7) (a) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676. (b) Samojlowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708–3742.
(8) (a) Fuerstner, A.; Krause, H.; Lehmann, C. W. *Chem. Commun.* **2001**, 2372–2373. (b) Klei, S. R.; Tilley, T. D.; Bergmann, R. G. *Organometallics* **2002**, *21*, 4648–4661. (c) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640–13641. (d) Zhang, M.; Liu, X.; Shi, C.; Ding, Y.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1755–1758. (e) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 9226–9227. (f) Calimano, E.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 11161–11173.
(9) Kenward, L. A.; Piers, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 38–41.

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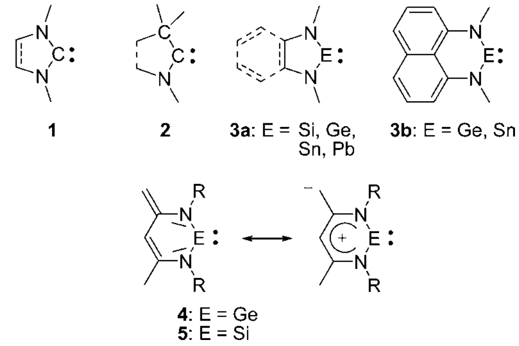


Figure 1. NHCs and some heavier homologues of group 14 elements. Dashed lines represent structural variations of known compounds, e.g. saturated and unsaturated NHCs (**1**) or cyclic and acyclic alkyl(amino)carbenes (**2**). R = 2,6-^{i}PrC$_6$H$_3$.

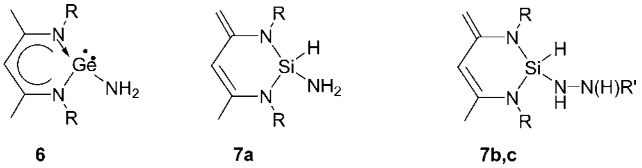
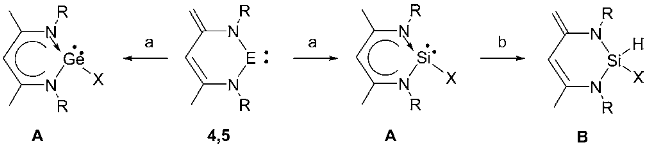


Figure 2. 1,4- and 1,1-addition products of germylene **4** and silylene **5** with ammonia (**6**, **7a**), hydrazine (**7b**), and methylhydrazine (**7c**): **7b**, R′ = H; **7c**, R′ = CH$_3$; R = 2,6-^{i}Pr$_2$C$_6$H$_3$.

Scheme 1. Reaction Pathways of Germylene **4** and Silylene **5** with HX[a]



[a] Legend: (a) 1,4-addition of HX to **4**, **5**; (b) isomerization to 1,1-addition product. **4**, **5**: E = Si, Ge; R = 2,6-^{i}Pr$_2$C$_6$H$_3$.

activation usually proceeds via a heterolytic bond cleavage by main-group elements in low oxidation states. In some cases, the increased contribution of triplet character in the electronic ground state might also be of importance as shown for diarylstannylenes, a digermyne, and a distannyne studied by Power et al.[10] Stephan et al. were able to show that hydrogen can be activated and even cleaved heterolytically by combining an electron-poor borane (Lewis acid) with a bulky phosphine, amine or carbene (Lewis base) that do not form stable adducts (so-called "frustrated Lewis acid/base pairs").[11] In fact, such systems can serve as active catalysts for the hydrogenation of imines.[12] While NHCs **1**[13] with two nitrogen donors next to the carbon(II) center are inert toward ammonia and hydrogen (Figure 1), related alkyl(amino)carbenes **2**,[14] which are better σ-donors and π-acceptors than carbenes of type **1**, do add hydrogen and ammonia readily in a 1,1-mode via the heterolytic cleavage of the H−H or N−H bond, respectively.[15] The chemistry of the heavier carbene analogues of group 14 elements—silylenes, germylenes, stannylenes, and plumbylenes—has been a prominent topic in main-group chemistry for decades.[16] The five- and six-membered NHC analogues of group 14 elements **3a**,**b**[17] cannot be employed for hydrogen or ammonia activation, even though they are more Lewis acidic and have a smaller singlet−triplet gap compared to the corresponding carbenes. On the other hand, germylene **4**[18] and silylene **5**,[19] which feature a modified β-diketiminate backbone, can undergo facile addition of ammonia (**4**, **5**) and hydrazines (**5**) to give the 1,4- and 1,1-insertion products **6** and **7a**−**c**[20,21] (Figure 2), respectively.

This can be explained by the significant electron-withdrawing effect of the butadiene backbone allowing for the necessary simultaneous interaction of the substrate with the reactant′s lone pair and formally empty valence p orbital, as represented by their resonance structures (Figure 1). Thus, addition of electrophiles onto the germylene **4** leads exclusively to the 1,4-adducts **A** as final products (Scheme 1).[22]

In contrast, the 1,4-adducts **A** are only the primary products from the addition of small HX molecules (X = OSO$_2$CF$_3$, halide) or related organic halides onto silylene **5**, which subsequently undergoes isomerization to give the thermodynamically favored 1,1-adduct **B** (Scheme 1).

Accordingly, the reaction of silylene **5** with other eletrophiles such as trimethylsilyl triflate yields the β-diketiminate silicon(II) triflate **8** as the kinetic product via 1,4-addition (Scheme 2).[19]

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(10) (a) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 12268–12269. (b) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233. (c) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettinger, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042–6044. (d) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2009**, *131*, 16272–16282.

(11) (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126. (b) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881. (c) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7428–7432. (d) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433–7437. (e) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136.

(12) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050–8053.

(13) (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172. (b) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445–3478.

(14) (a) Lavallo, V.; Canac, Y.; Praesang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705–5709. (b) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670–8671.

(15) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439–441.

(16) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511, and references cited therein.

(17) For example: (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belykov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692. (b) Denk, M.; Green, J.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405–2410. (c) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485–1489. (d) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245–252. (e) Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1888–1891. (f) Braunschweig, H.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1922–1928. (g) Hahn, E.; Heitmann, D.; Pape, T. *Eur. J. Inorg. Chem.* **2008**, 1039–1041. (h) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162–11167. (i) Avent, A. G.; Drost, C.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2090–2096.

(18) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 4349–4352.

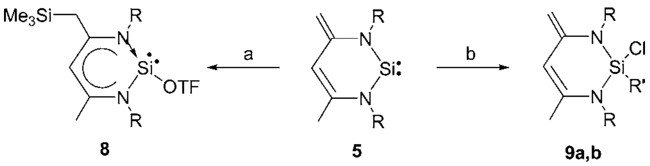
(19) Driess, M.; Yao, S.; Brym, M.; van Wuellen, C.; Lentz, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628–9629.

(20) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, *48*, 798–800.

(21) (a) Jana, A.; Schultzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601. (b) Jana, A.; Roesky, H. W.; Schultzke, C.; Samuel, P. P. *Organometallics* **2009**, *28*, 6574–6577.

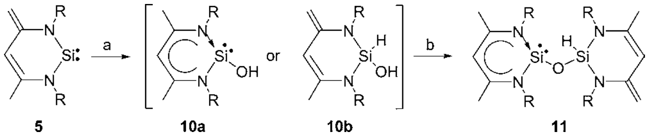
(22) (a) Jana, A.; Nekoueishahraki, B.; Roesky, H. W.; Schulzke, C. *Organometallics* **2009**, *28*, 3763–3766. (b) Yao, S.; van Wuellen, C.; Driess, M. *Chem. Commun.* **2008**, 5393–5395.

Scheme 2. Conversion of Silylene **5**[a]



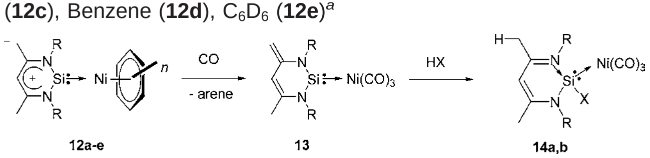
[a] 1,4-Addition: (a) Me_3SiOTf. 1,1-Addition: (b) CH_2Cl_2, $R' = CH_2Cl$; (b) $HSiCl_3$, $R' = SiHCl_2$. $R = 2,6\text{-}^iPr_2C_6H_3$.

Scheme 3. Synthesis of Siloxysilylene **11** via the Intermediates **10a**,**b**[a]



[a] Legend: (a) H_2O; (b) **5**. $R = 2,6\text{-}^iPr_2C_6H_3$.

Scheme 4. Nickel(0) Complexes of Silylene **5**, Including η^6-Coordinated Arenes: Toluene (**12a**), *p*-Xylene (**12b**), Mesitylene (**12c**), Benzene (**12d**), C_6D_6 (**12e**)[a]



[a] **14a,b**: X = OH, OTf. $R = 2,6\text{-}^iPr_2C_6H_3$.

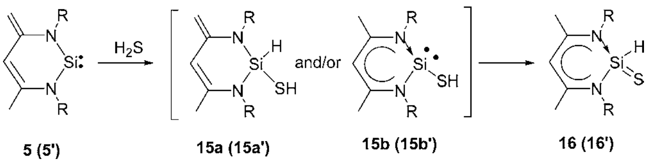
Remarkably, halocarbons or chlorosilanes such as dichloromethane and trichlorosilane allow for the isolation of the corresponding 1,1-insertion products **9a**,**b** (Scheme 2).[23]

The addition of water onto the silylene **5** deserves particular attention, because the process affords the donor-stabilized siloxysilylene (mixed-valent disiloxane) **11** (Scheme 3).[24] Although the mechanism is still unknown, we reason that the conversion could either proceed via 1,4-addition to give the elusive hydroxosilylene **10a** or via 1,1-addition to give the silanol **10b**.

We have also shown recently that the silylene **5** can also serve as a stabilizing ligand for the Ni(arene) complexes **12**,[25] which can be easily transformed into the more robust $Ni(CO)_3$ complex **13** (Scheme 4).[26] Strikingly, the silylene ligand **5** in the latter is still capable of activating H−X bonds of HX substrates (X = OTf, OH) to give merely the *β*-diketiminate silicon(II) nickel(0) complexes **14a**,**b**; that is, the presence of the $Ni(CO)_3$ moiety steers the progress of the reaction in a way that 1,4-addition is now thermodynamically preferred.

Interestingly, it is possible to tune the *σ*-donor and *π*-acceptor abilities of the new silicon(II) ligands generated in the coordination sphere of nickel(0) over a wide range.[26] The possibility to control 1,4- over 1,1-addition by Ni^0 coordination to the Si(II) atom inspired us to extend our studies to the activation of N−H- and S−H-containing substrates, which results in 1,4-addition. The latter conversions would allow access for the first time to unique *β*-diketiminate silicon(II) amines and thiols in the coordination sphere of Ni(0). At first, we report the unexpected facile formation of the first isolable N-donor-stabilized silathioformamide **16** from addition of H_2S onto **5**. Furthermore, we describe the remarkable reactivity of the $Ni(CO)_3$ complex **13** toward H_2S, NH_3, *i*$PrNH_2$, and $H_2N-NH(Ph)$, which demonstrates the particular steering role of the silylene ligand **5** in the $Si(II) \rightarrow Ni(CO)_3$ moiety.

Scheme 5. Formation of the Silathioformamide **16** via the Proposed Intermediates **15a**,**b**[a]



[a] $R = 2,6\text{-}^iPr_2C_6H_3$. Model systems **5′**, **15a′**, **15b′**, and **16′** with R = Ph.

Results

The reaction of silylene **5** with 1 equiv of H_2S gas at low temperature resulted in the surprisingly simple formation of the donor-stabilized silathioformamide **16** (Scheme 5).

Analogous to the reaction of silylene **5** with water (Scheme 3), two possible intermediates might be envisaged. The silathioformamide **16** could result from an 1,1-insertion of the silicon(II) center into an S−H bond to give the proposed intermediate **15a** followed by migration of an H atom to the exocyclic methylene group. A second reasonable reaction path could proceed via the donor-stabilized amino(mercapto)silylene **15b** with subsequent protonation of the silicon(II) lone pair.

The intramolecular stabilization of the intermediate by hydrogen migration is obviously faster than the reaction with another 1 equiv of silylene **5**, as has been observed in the case of the hydrolysis (Scheme 3). The acidity of the SH proton, which is several magnitudes higher (pK_a values in aqueous solution: H_2O, 16; H_2S, 7) compared to OH, could play a key role in the intramolecular stabilization of **15a**,**b**. DFT calculations (B3LYP with 6-31G(d) basis set; see the Supporting Information) of the respective model systems (Scheme 5) in which the bulky aryl groups R at nitrogen were replaced by phenyl groups revealed that the postulated intermediates **15a′** ($E_{rel} = 0$ kcal mol^{-1}) and **15b′** ($E_{rel} = -0.2$ kcal mol^{-1}) are practically isoenergetic, while its tautomer **16′** is favored by −23 kcal mol^{-1}. Attempts to observe an intermediate by monitoring the conversion of **5** with H_2S at −78 °C in an NMR tube by means of ^1H NMR spectroscopy were unsuccessful. Since the formation of **16** is still very fast under the latter conditions in solution, we monitored the heterogeneous reaction of solid **5** with gaseous H_2S at ambient temperature by means of solid-state MAS ^{29}Si NMR spectroscopy. After a sample of silylene **5** had been in contact with an approximately 20-fold excess of gaseous H_2S for 3 days, only the resonances of silylene **5** and silathioformamide **16** in the ratio of 4:6 (^1H NMR) could be observed (see the Supporting Information and Experimental Section for further details). It is astonishing that the tautomerization reaction of the initial products to give **16** is remarkably fast even without a solvent.

Although stable species containing a Si=S double bond are already known (silanethiones),[27,28] compound **16** is the first isolable silathioformamide to be stabilized by intramolecular donor stabilization. Its composition has been proven by elemental analysis, and the structure is evident from ^1H and ^{29}Si NMR spectroscopy. In the ^1H NMR spectrum the characteristic signals of the exocyclic methylene and methyl groups of precursor **5**

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(23) Xiong, Y.; Yao, S.; Driess, M. *Organometallics* **2009**, *28*, 1927–1933.
(24) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268–7269.
(25) Meltzer, A.; Praesang, C.; Milsmann, C.; Driess, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3170–3173.
(26) Meltzer, A.; Praesang, C.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7232–7233.

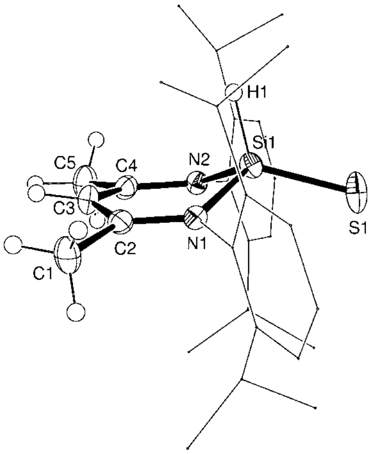

Figure 3. Molecular structure of **16** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1, C3, C5, and Si1. Selected bond distances (pm) and angles (deg) of **16**: Si1−S1, 198.54(9); Si1−N1, 181.0(2); Si1−N2, 180.0(2); N1−C2, 133.4(3); N2−C4, 134.6(3); C1−C2, 149.8(3); C2−C3, 139.3(3); C3−C4, 138.4(3); C4−C5, 150.2(3); N1−Si1−N2, 97.63(9); S1−Si1−N1, 116.90(7).

are replaced by a single resonance at δ 1.91 ppm corresponding to six protons. Additionally, the proton of the Si−H group resonates as a singlet at δ 6.09 with ^{29}Si satellites ($^1J_{\mathrm{SiH}} = 255$ Hz). The ^{29}Si chemical shift of **16** (δ −16.8 ppm) is in the range for tetracoordinate silicon and is comparable to that of related donor-stabilized compounds with a Si═S bond (chemical shift range +23.3 to −41.3 ppm).[27] The structure of **16** was confirmed by single crystal X-ray diffraction analysis (Figure 3). The Si═S distance of 198.5 pm is between those of related donor-stabilized silanethiones (201 pm)[27] versus unsupported ones (195−196 pm)[28] but significantly shorter than Si−S single bonds (ca. 214 pm).[29]

We have already reported some Ni^0 complexes of silylene **5** in order to investigate its capability to add small molecules containing E−H bonds and to compare the σ-donor/π-acceptor properties of the resulting silicon(II)−nickel complexes with related NHSi−Ni^0 complexes that are known in the literature.[25,26,30]

Isolable (η^6-arene)−Ni^0 complexes are very rare,[31] and the surprising stability of compounds **12a**−**e** can be explained by increased back-bonding from the electron-rich metal atom to the electron-deficient silicon center, facilitated by the electronic influence of the butadiene backbone.[26] A comparison of the X-ray crystallographic data of "free" silylene **5** with those of complex **12a** and the newly reported complexes **12c**,**d** (Figure 4) reveals only small changes within the ligand moieties. Common features are, for example, the short Si−N (**5**, 173.5 pm; **12a**,**c**,**d**, 173−174 pm) and N−C$_{\mathrm{ring}}$ distances (**5**, 141.6 pm; **12a**,**c**,**d**, 140.8−141.2 pm), acute N−Si−N angles (**5**, 99.3°; **12a**,**c**,**d**, 99.3 and 100°), and the virtually planar six-membered SiC$_3$N$_2$ ring skeleton. Accordingly, the Ni and Si centers of **12a**,**c**,**d** are positioned almost within the mean plane of the C$_3$N$_2$ ligand backbone (**12c**: C$_3$N$_2$−Si, 10 pm; C$_3$N$_2$−Ni, 23 pm).

Silylene complex **12a** turned out to be an ideal starting material for the preparation of complex **13** (Scheme 4), which was utilized to synthesize several β-diketiminate silicon(II) ligands with variable donor strengths.[26] Interestingly, this has been realized while the silicon center remains coordinated to the Ni(CO)$_3$ moiety. Because of this, the silicon lone pair cannot participate in any reaction directly and the corresponding substrates were compelled to react at the Lewis basic methylene group and the Lewis acidic silicon center instead.

In other words, **13** is still capable of reacting with H$_2$S even in the presence of the Ni(CO)$_3$ moiety. Thus, the resulting compound **17** was obtained by reaction of **13** with stochiometric amounts of H$_2$S and isolated after crystallization from toluene in 27% yield (Scheme 6). A small amount (ca. 5%) of the side product **16** was detected by ^{1}H NMR spectroscopy in the crude reaction mixture. Similar to the reaction with water, H$_2$S adds in a 1,4-fashion to the silylene center and the ligand backbone. Apparently, a possible second 1,4-addition between product **17** and another 1 equiv of complex **13** is prevented for steric reasons.

The reactivity of transition-metal−silylene complexes toward Brønsted acids has been studied quite extensively over the last few decades.[32] The resonance structures of complexes of type **18** (Scheme 6) offer a good description of the electronic polarization (ylide-like character) of the Si(II)−metal bond, which generally undergoes a 1,2-addtion if reacted with substrates of sufficient acidity. The corresponding products, silyl metal hydrides **19**, have been isolated and characterized, even from the reaction of an NHSi molybdenum complex with water to give **22**.[33] The direct and stepwise rupture of the Si−metal bond has also been observed. In these cases, the silylene ligands were converted to alkoxysilanes **20** and dialkoxysilanes **21**, respectively.

The ^{1}H and ^{13}C NMR spectra of complex **17** reflect its higher symmetry compared to the starting material **13**; the SH resonance was detected at 1.30 ppm as a somewhat broadened singlet. Single crystals suitable for X-ray analysis were obtained from toluene at −20 °C.

Intriguingly, despite the high thiophilicity of nickel, H$_2$S reacts with **13** exclusively by 1,4-addition to the silylene ligand. A comparison of the structural data of complex **17** (Figure 5) with those of complex **14a** (Scheme 4) indicates a weaker interaction of the ligand backbone with the silicon center, probably due to the lower electronegativity of sulfur as compared to oxygen. Thus, the N−Si bonds are longer (**17**, 184.2 pm;**14a**, 180.7 pm) and the N−C$_{\mathrm{ring}}$ bonds are slightly shorter (**17**, 134.7 pm; **14a**, 135.8 pm). The Si−SH distance of 219.0 pm represents clearly

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(27) (a) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016–1018. (b) So, C.-W.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Jones, P. G. *Dalton Trans.* **2007**, 5241–5244. (c) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *Chem. Asian J.* **2009**, *3*, 113–118. (d) Yao, S.; Xiong, Y.; Driess, M. *Chem. Eur. J.* **2009**, in press, DOI: 10.1002/chem.200902467.

(28) (a) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578–11579. (b) Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 16914–16920.

(29) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 1, pp 228−233.

(30) (a) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *Organometallics* **1998**, *17*, 5599–5601. (b) Schmedake, T. A.; Haaf, M.; Paradise, B. J.; Powell, D.; West, R. *Organometallics* **2000**, *19*, 3263–3265. (c) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, *686*, 321–331.

(31) (a) Nickel, T.; Goddard, R.; Krueger, C.; Poerschke, K.-R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 879–882. (b) Hoon, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802–13803.

(32) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493–506.

(33) Petri, S. H. A.; Eikenberg, D.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *Organometallics* **1999**, *18*, 2615–2618.

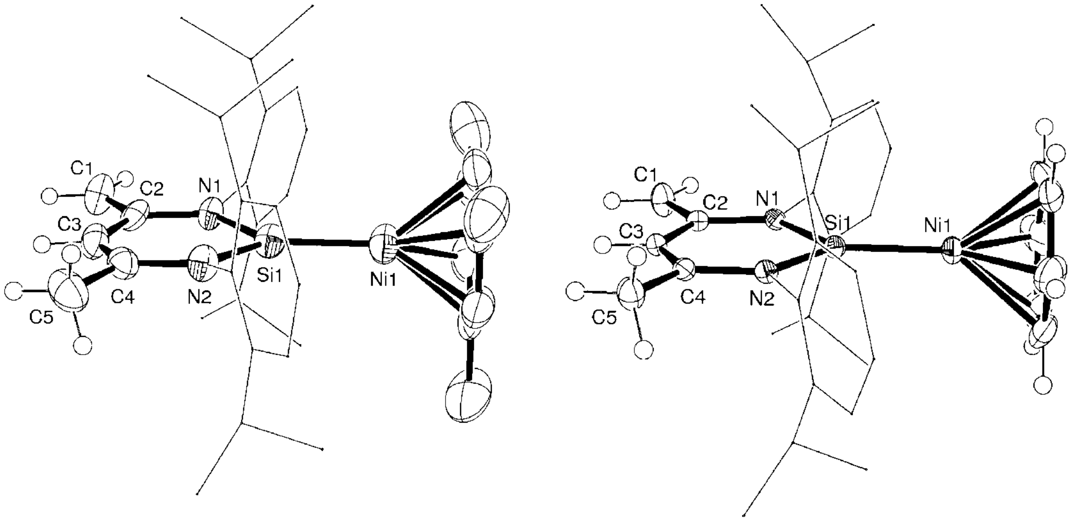
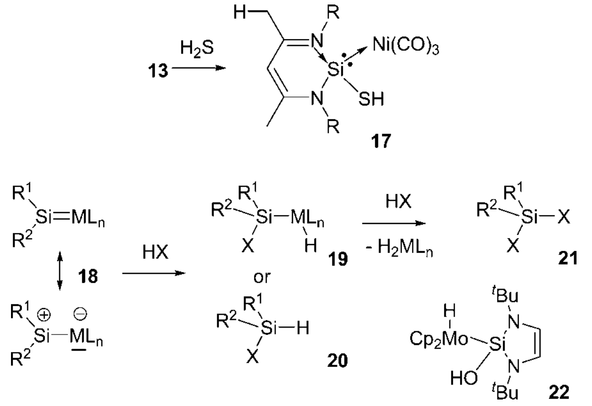


Figure 4. Molecular structures of **12c** (left) and **12d** (right) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1−C5 and C31A−C36A (**12d**). Selected bond distances (pm) and angles (deg) of **12c**: Si1−Ni1, 206.0(1); Si1−N1, 173.5(3); Si1−N2, 174.0(2); C1−C2, 136.7(4); C2−C3, 143.0(4); C3−C4, 134.2(4); C4−C5, 150.4(4); Ni1−C(mesitylene, average), 213.1; Ni1−C(mesitylene, centroid), 160.7; N1−Si1−N2, 99.3(1); N1−Si1−Ni1, 129.73(9); N2−Si1−Ni1, 130.9(1). Selected bond distances (pm) and angles (deg) of **12d**: Si1−Ni1, 206.47(6); C1−C2, 139.9(3); C2−C3, 140.8(3); C3−C4, 138.4(3); C4−C5, 143.6(3); Ni1−C(benzene, average), 212.2; Ni1−C(benzene, centroid), 160.4; N1−Si1−N2, 99.31(9); N1−Si1−Ni1, 129.08(7); N2−Si1−Ni1, 131.61(7).

Scheme 6. 1,4-Addition of H_2S to **13** vs Common Reactivity of Transition-Metal−Silylene Complexes toward Brønsted Acids HX[a]



[a] $R^{1,2}$ = H, alkyl, Cl, H; R = 2,6-$^iPr_2C_6H_3$.

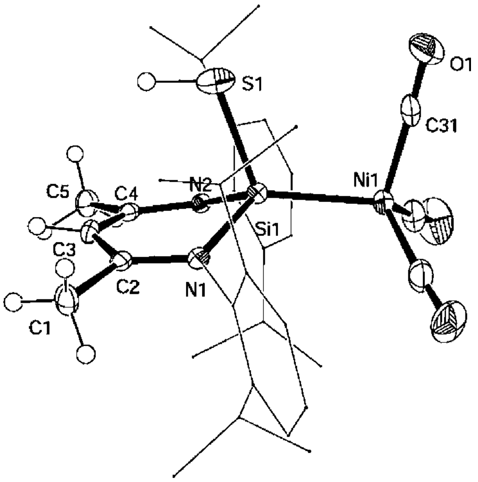


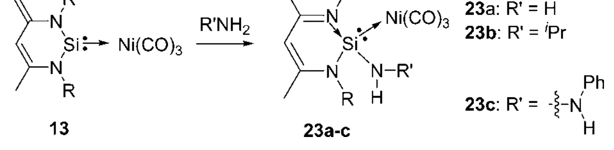
Figure 5. Molecular structure of **17** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1, C3, and S1. Selected bond distances (pm) and angles (deg) of **17**: Si1−Ni1, 224.66(6); Si1−S1, 219.01(9); Si1−N1, 184.0(2); Si1−N2, 184.4(2); N1−C2, 134.6(3); C1−C2, 150.2(4); C2−C3, 138.6(3); C3−C4, 138.9(3); C4−C5, 150.2(4); C4−N2, 134.7(3); Ni1−C(average), 178.5; C−O(average), 114.1; N1−Si1−N2, 95.67(9); N1−Si1−Ni1, 120.88(7); Ni1−Si1−S1, 113.50(3); N1−Si1−S1, 100.35(7).

a single bond, about 10 pm (5%) longer than the partial Si═S double bond in **16** (198.5 pm).

Considering the pK_a values of trifluoromethanesulfonic acid, H_2S, and water (in aqueous solution: −15, 7, and 16, respectively) it is not surprising that the exocyclic methylene group of **13** is also able to abstract a proton from H_2S. Amines and phosphines are primarily bases (and thus correspondingly very weak acids), and the activation of N−H bonds by transition-metal complexes is in competition with their suitability to simply act as a ligand and coordinate to the metal center with their lone pairs. It is therefore interesting to learn that **13** is also capable of activating amines without rupture of the Si−metal bond or ligand exchange at the Ni^0 center. Moreover, the impact of a wider range of substituents on the donor/acceptor capabilities of β-diketiminate silicon(II) ligands in complexes of type **14** could be studied.

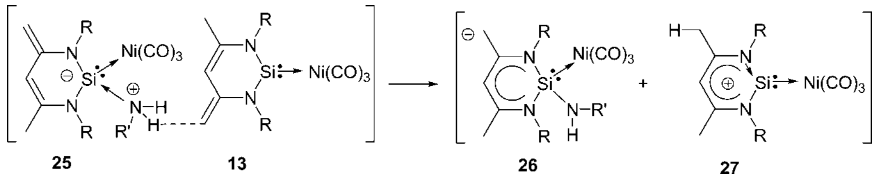
In fact, reactions of complex **13** with ammonia, isopropylamine, and phenylhydrazine in toluene yield the corresponding β-diketiminate Si^{II}−$Ni(CO)_3$ complexes **23a**−**c** (Scheme 7). No significant byproduct except for small amounts (ca. 5%) of the H_2O adduct **14a** were detected by ^1H NMR in the crude reaction mixtures. The ^1H and ^{13}C NMR spectra of **23a**−**c** are consistent with their expected C_s symmetry, with mirror planes perpendicular to the silylene ligand backbone. The NH protons are observed at δ 1.52 (**23a**), 1.49 (**23b**), and 3.98, 4.95 (**23c**) ppm

Scheme 7. Reaction of Complex **13** with Amines and a Hydrazine[a]



[a] R = 2,6-$^iPr_2C_6H_3$.

Scheme 8. Proposed Intermediates during the Formation of **23a**–**c** with Simultaneous Activation of Amines $R'NH_2$[a]



[a] R = 2,6-$^{i}Pr_2C_6H_3$.

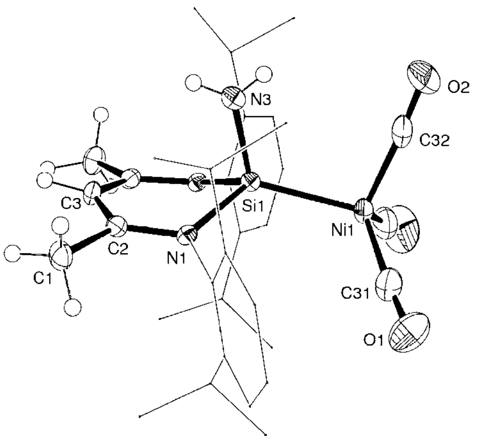


Figure 6. Molecular structure of **23a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1, C3, and N3. Selected bond distances (pm) and angles (deg) of **23a**: Si1–Ni1, 225.5(1); Si1–N1, 185.2(2); Si1–N2, 171.1(4); N1–C2, 134.0(4); C1–C2, 150.8(4); C2–C3, 138.8(3); Ni1–C(average), 178.6; C–O(average), 114.0; N1–Si1–N1, 94.06(9); N1–Si1–Ni1, 120.98(8); N3–Si1–Ni1, 100.5(2); N1–Si1–N3, 100.5(2).

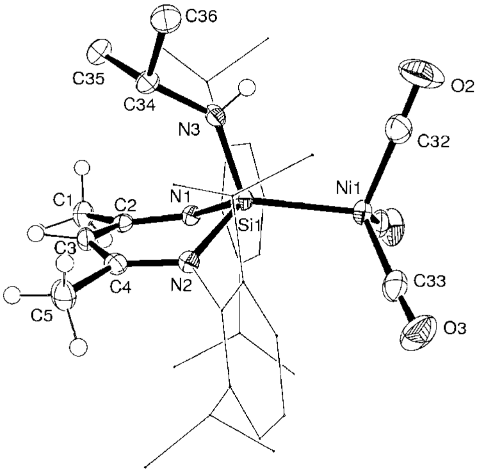


Figure 7. Molecular structure of **23b** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1, C3, C5, and N3. Selected bond distances (pm) and angles (deg) of **23b**: Si1–Ni1, 225.52(6); Si1–N1, 186.2(1); Si1–N2, 183.8(1); Si1–N3, 173.0(2); N1–C2, 133.7(2); C1–C2, 150.0(2); C2–C3, 139.4(2); C3–C4, 138.6(2); C4–C5, 150.6(3); N2–C4, 134.3(2); Ni1–C(average), 178.3; C–O(average), 113.7; N1–Si1–N2, 94.11(6); N1–Si1–Ni1, 117.76(5); N3–Si1–Ni1, 114.83(6); N1–Si1–N3, 104.11(7).

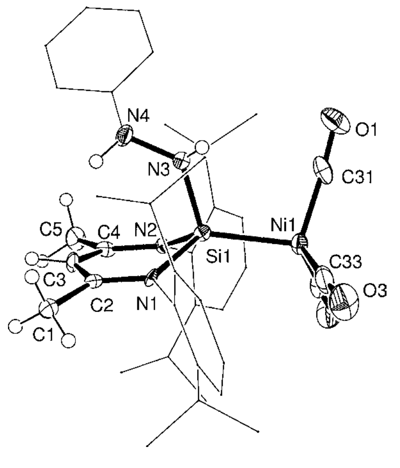


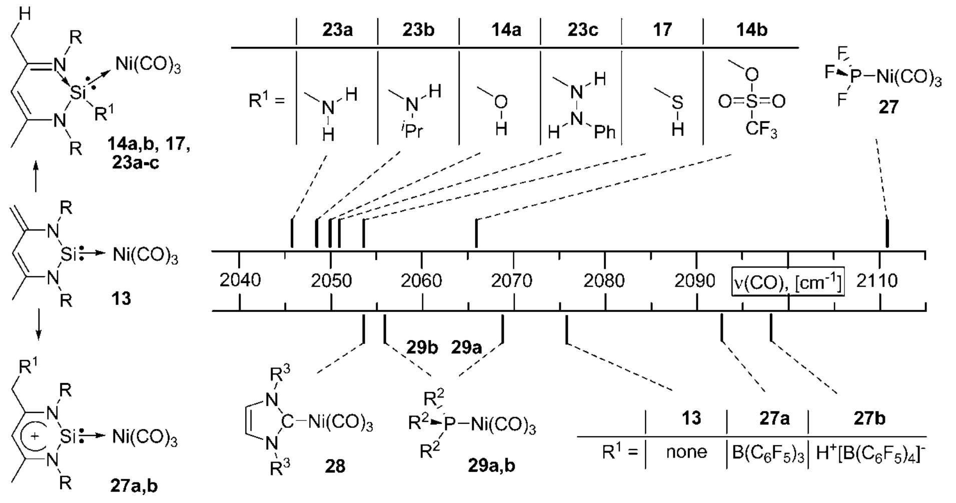
Figure 8. Molecular structure of **23c** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except those of C1, C3, C5, N3, and N4. Selected bond distances (pm) and angles (deg) of **23c**: Si1–Ni1, 223.6(1); Si1–N1, 185.4(4); Si1–N2, 181.9(4); Si1–N3, 174.8(5); N1–C2, 133.2(5); C1–C2, 150.9(7); C2–C3, 139.8(6); C3–C4, 137.9(7); C4–C5, 151.0(6); N2–C4, 135.1(5); N3–N4, 141.5(6); Ni1–C(average), 177.4; C–O(average), 115.1; N1–Si1–N2, 94.8(2); N1–Si1–Ni1, 120.3(1); N3–Si1–Ni1, 111.0(2); N1–Si1–N3, 102.7(7); Si1–N3–N4, 129.4(3).

as singlets corresponding to one or two protons (**23a**), respectively. The ^{29}Si NMR chemical shifts exhibit a upfield shift of δ 110–116 ppm in comparison to complex **13** (δ 142.1), which is consistent with the increase of the coordination number at the silicon centers from 3 to 4 and comparable to the same effect observed for **14a**,**b**.

The mechanism is still unknown but the surprising effortlessness of the 1,4-additions of amines to **13** could be explained by the initial formation of an acid–base pair such as compound **25** (Scheme 8). The latter would cause an increased acidity of the N–H protons as well as an increase in basicity of the exocyclic methylene group. A second molecule of complex **13** could then assist to deprotonate the amine ligand; however, this process might also occur simultaneously. This would yield two complexes: the anionic, strongly basic intermediate **26**, which could easily be converted into the observed product by deprotonation of another acid–base pair **25**, and the cationic, Lewis acidic complex **27**, which has already been isolated and characterized.[26] The resultant complexes **23a**–**c** could then result through (back) protonation of **26** with **27**.

Single crystals suitable for X-ray analysis were obtained in toluene (**23a**) (Figure 6) and hexane (**23b**,**c**) (Figures 7 and 8). In all three cases, an N–H bond clearly reacted by 1,4-addition to the ligand moiety. Similar to the case for the complexes **14a**,**b** and **17**, the silicon centers of **23a**–**c** are coordinated in a distorted-tetrahedral fashion and the Si atom is out of the mean plane of the ligand backbone by 64–74 pm. The increased valence p character of all Si–N bonds can be derived from the somewhat acute N–Si–N angles of 94–95° (ligand backbone) and 101–104° (ligand N–exocyclic N). At the same time, the larger Ni–Si–N angles (111–124°) point to an increasing s character of the Si–Ni bond. The amine and hydrazine groups act as strong donors toward the silicon center, in accordance with the rather short Si–N distances (**23a**–**c**: Si–N, 171.2,

Chart 1. Comparison of $Ni(CO)_3$ Carbonyl Stretching Frequencies (A1 Mode) of Novel Complexes with Those of Analogous Phosphine and NHC Systems and from Ref 26[a]



[a] R = 2,6-$^iPr_2C_6H_3$. **28**: R^3 = 2,4,6-$Me_3C_6H_2$. **29a**: R^2 = Ph. **29b**: R^2 = ^tBu.

173.0, and 176.8 pm; N−Si(backbone), 180.7, 185.0 (average), 183.7 (average) pm) and IR spectroscopic data (vide infra).

IR Spectroscopy

Carbonyl stretching frequencies are a convenient probe to judge the σ-donor/π-acceptor capabilities of a wide range of ligands L in transition metal complexes of the general formula $LM(CO)_n$. We have shown recently[26] that these properties of complex **13** can be tuned over a wide range by either addition of a Lewis acid to the exocyclic methylene group or 1,4-addition of water or triflic acid to the ligand while the silylene ligand is coordinated to a $Ni(CO)_3$ moiety (complexes **27a**,**b** (Chart 1) and **14a**,**b** (Scheme 4), respectively). The cationic and quasi-cationic ligands of complexes **27a**,**b** are quite similar to the moderate σ-donor and good π-acceptor PF_3 with regard to their impact on the carbonyl stretching frequencies of the $Ni(CO)_3$ metal complex fragment (Chart 1). Complexes **13** and **14b** are more similar to triphenylphosphine, a frequently used ligand in transition-metal chemistry. All other silicon(II) ligands in the complexes **14a**, **17**, and **23a**−**c** are similar to trialkylphosphines and NHCs: e.g. tri-*tert*-butylphosphine, **29b**; *N*,*N*′-dimesityl-substituted NHC, **28** (see Chart 1).[34]

Varying the terminal substituents at nitrogen or interchanging from saturated to unsaturated NHC frameworks has little effect on the corresponding CO wavenumbers of the $Ni(CO)_3$ moiety.[34] The variances observed for $Ni(CO)_3$ complexes with ligands derived from silylene **5** are remarkable and cover a range of 52 cm^{-1}, which is nearly as large as the difference between trialkylphosphines and PF_3 (55 cm^{-1}).

Summary

The ylide-like silylene **5** undergoes a facile reaction with H_2S to form the first isolable N-donor-stabilized silathioformamide **16** with a Si═S moiety and tetracoordinate silicon. DFT calculations of the model system **16′**, in which the bulky aryl groups at nitrogen are replaced by phenyl, revealed that this form is favored by 23 kcal mol^{-1} over the two possible tautomers with a tetravalent Si(H)SH or divalent:Si(SH) subunit. Remarkably, the silylene ligand **5** is able to stabilize otherwise quite elusive Ni^0(arene) complexes, **6a**−**e**, thanks to its ability to act as a good σ-donor and π-acceptor simultaneously. The latter are ideal precursors for the facile synthesis of the $Ni(CO)_3$ complex **13**. Remarkably, the silylene ligand in **13** is still capable of activating S−H and N−H bonds of several substrates in the presence of the $Ni(CO)_3$ moiety without breaking of or addition across the Si−Ni bond. Instead, addition proceeds exclusively in a 1,4-fashion across the silylene ligand to yield unprecedented β-diketiminate silicon(II)−thiol, −amide, and −hydrazide ligands with striking σ-donor/π-acceptor capabilities comparable to those of phosphines and NHCs.

Experimental Section

General Considerations. All experiments and manipulations were carried out under a dry and oxygen-free atmosphere of nitrogen using standard Schlenk techniques or in an MBraun inert-atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The complexes LSi−Ni(η^6-toluene) (**12a**), LSi−Ni(η^6-*p*-xylene) (**12b**), and LSi-Ni(η^6-mesitylene) (**12c**)[25] and the starting material LSi-$Ni(CO)_3$ (**13**) as well as L′Si(OH)−$Ni(CO)_3$ (**14a**), L′Si(OTf)−$Ni(CO)_3$ (**14b**), $[(C_6F_5)_4B][L'Si-Ni(CO)_3]$ (**27b**), and $(C_6F_5)_3B-LSi-Ni(CO)_3$ (**27a**)[26] (L′ = HC[C(Me)NAr]$_2$; Ar = 2,6-$^iPr_2C_6H_3$) were prepared according to literature procedures.[25] Solution NMR spectra were recorded with Bruker AM200 and AM400 spectrometers and referenced to the residual solvent signals as internal standard. Solid-state $^{29}Si\{^1H\}$ MAS cross-polarization (CP) measurements were carried out on a Bruker Avance II spectrometer at an external magnetic field of 9.4 T using a standard Bruker 4 mm double-resonance H-X MAS probe operating at a ^{29}Si resonance frequency of 79.4 MHz. The spectra were recorded with a cross-polarization time of 2 ms, and composite pulse ^1H decoupling was applied during the acquisition. A total of 5000 transients were recorded with a relaxation delay of 2 s under MAS conditions with a rotation frequency of 10 kHz. The spectra were referenced to TMS (tetramethylsilane) using TKS (tetrakis(trimethylsilyl)silane) as a secondary reference.

Single-Crystal X-ray Structure Determinations. Crystals were each mounted on a glass capillary in perfluorinated oil and measured under a cold N_2 flow. The data for compounds **12c**,**d**, **16**, **17**, and **23a**−**c** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo Kα radiation, λ = 0.710 73 Å). The structures were

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(34) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.

solved by direct methods and refined on F^2 with the SHELX-97[35] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Synthesis of LSi−Ni(η^6-C_6H_6) (12d). The synthesis of **12d** follows the same protocol as the synthesis of the related LSi−Ni(η^6-arene) complexes.[25] A solution of silylene **5** (500 mg, 1.12 mmol) in benzene (10 mL) was added to a suspension of $[Ni(cod)_2]$ (206 mg, 0.75 mmol) in benzene (10 mL) at −60 °C. The reaction mixture was slowly warmed to room temperature overnight. All volatiles were removed in vacuo, and *n*-hexane (15 mL) was added. Filtration and cooling to −20 °C gave 252 mg of complex **12d** (39%) as red crystals. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.18, 1.37, 1.40, 1.44 (each d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.43 (s, 3H, CH_3), 3.30 (s, 1H, CHH'), 3.40, 3.54 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 3.91 (s, 1H, CHH'), 5.37 (s, 1H, γ-*H*), 6.9−7.3 (m, 12H, H_{aryl}) ppm. ^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ 22.2 (CH_3), 24.1, 24.3, 25.1, 25.5 ($CH(CH_3)_2$), 28.6, 28.7 ($CH(CH_3)_2$), 81.2 (CH_2), 95.1 (t, $^1J_{CD}$ = 26 Hz, η^6-C_6D_6), 105.3 (γ-*C*), 123.5, 124.0, 127.5, 127.6, 138.5, 138.9 (C_{aryl}), 140.4 ($NCCH_3$), 148.0, 148.2 (C_{aryl}), 148.7 ($NCCH_2$) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6, 25 °C): δ 100.4 (C_6D_6 complex). IR (KBr, cm^{-1}): ν 465 (w), 531 (w), 610 (w), 677 (w), 746 (w), 760 (w), 802 (w), 918 (w), 980 (w), 1057 (w), 1072 (w), 1103 (w), 1176 (w), 1203 (w), 1252 (w), 1321 (w), 1356 (m), 1383 (m), 1443 (w), 1464 (w), 1550 (w), 1640 (w), 2866 (w), 2926 (w), 2960 (m), 3062 (w). EI MS (70 eV): *m/z* (%) 580 (1) [M^+], 502 (3) [$M^+ - C_6H_6$], 444 (5) [$M^+ - Ni(C_6H_6)$], 429 (100) [$M^+ - Ni(C_6H_6) - CH_3$], 414 (7) [$M^+ - Ni(C_6H_6) - 2CH_3$], 401 (12) [$M^+ - Ni(C_6H_6)$-^{i}Pr]. Anal. Calcd for $C_{35}H_{46}N_2SiNi$: C, 72.3;, H, 7.3; N, 4.8. Found: C, 72.2;, H, 8.0; N, 4.7.

Synthesis of L′Si(S)H (16). A 22 mL portion of H_2S (0.93 mmol) was slowly added to a solution of silylene **5** (344 mg, 0.77 mmol) in 15 mL of toluene at −78 °C. The reaction mixture was warmed to ambient temperature and then kept at −30 °C for 2 days. All volatile components were removed under vacuum, and the slightly yellow residue was dissolved in toluene. Cooling to −30 °C overnight yielded X-ray-quality crystals of silathioformamide **16** (199 mg, 54%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.17, 1.27, 1.34, 1.43 (each d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.91 (s, 6H, CH_3), 2.95, 8.38 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 5.58 (s, 1H, γ-*H*), 6.09 (s, $^1J_{SiH}$ = 255 Hz, 1H, S*H*), 7.1−7.4 (m, 6H, H_{aryl}). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 25 °C): δ 23.8 ppm, 24.3, 24.7, 25.0 ($CH(CH_3)_2$), 25.9 (CH_3), 29.2, 29.2 ($CH(CH_3)_2$), 100.4 (γ-*C*); 124.6, 125.1, 128.0, 136.3, 145.2, 145.2 (C_{aryl}), 171.4 ($NCCH_3$). ^{29}Si NMR (79.5 MHz, $CDCl_3$, 25 °C): δ −16.8 ppm. IR (KBr, cm^{-1}): ν 2962 (s), 2927 (m), 2865 (m), 2127 (m, Si−H), 1544 (s), 1370 (s), 669 (m, Si═S). EI MS (70 eV): *m/z* (%) 478 (10) $[M]^+$, 463 (100) $[M - CH_3]^+$, 435 (11) $[M - C_3H_7]^+$, 403 (7) $[M - C_3H_7 - S]^+$. Anal. Calcd for $C_{32}H_{42}N_2O_3SSiNi$: C, 72.75; H, 8.84; N, 5.85. Found: C, 72.64; H, 8.90; N, 5.73.

Heterogeneous Reaction of Solid Silylene 5 with Gaseous H_2S. A 100 mg portion of silylene **5** (0,225 mmol) was placed in a Schlenk tube with a Teflon-coated magnetic stirbar. The reaction vessel was evacuated to 1×10^{-2} mbar and then filled with H_2S to standard pressure (approximately 100 mL, 4.5 mmol). The mixture was stirred for 3 days, and then the hydrogen sulfide was replaced by dry nitrogen. The resulting light yellow powder was analyzed by solution ^{1}H NMR as well as solid-state MAS ^{29}Si NMR spectroscopy. ^{29}Si NMR (79.4 MHz, solid state, 25 °C): δ −17.9, 97.6. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): ratio of **5**:**16** 4:6.

Synthesis of L′Si(SH)−Ni(CO)$_3$ (17). A 3 mL portion of gaseous H_2S was added via syringe to a solution of complex **13** (74 mg, 0.126 mmol) in toluene (3 mL) at −60 °C. The reaction mixture was slowly warmed to room temperature overnight. The yellow solution was removed, and the green precipitate was recrystallized from toluene to give yellow crystals (21 mg, 27%). ^{1}H NMR (400 MHz, toluene-d$_8$, 25 °C): δ 0.93, 1.17, 1.34, 1.42 (each d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.30 (s, 1H, S*H*), 1.52 (s, 6H, CH_3), 3.13, 4.11 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 5.17 (s, 1H, γ-*H*), 6.9 − 7.2 (m, 6H, H_{aryl}) ppm. ^{13}C{^{1}H} NMR (101 MHz, toluene-d$_8$, 25 °C): δ 24.0 ($CH(CH_3)_2$), 24.1 (CH_3), 24.1, 25.9, 26.8 ($CH(CH_3)_2$), 28.9, 29.6 ($CH(CH_3)_2$), 103.8 (γ-*C*), 124.7, 125.9, 129.2, 139.9, 143.5, 147.0 (C_{aryl}), 169.5 ($NCCH_3$), 198.8 (*C*O) ppm. ^{29}Si NMR (79.5 MHz, toluene-*d*$_8$, 25 °C): δ 52.3 ppm. IR (toluene, cm^{-1}): ν(CO) 1985, 2054. EI MS (70 eV): *m/z* (%) 536 (1) $[M - 3CO]^+$, 478 (15) $[M - Ni(CO)_3]^+$, 463 (100) $[M - Ni(CO)_3 - CH_3]^+$, 435 (15) $[M - Ni(CO)_3 - {}^iPr]^+$. Anal. Calcd for $C_{32}H_{42}N_2O_3SSiNi$: C, 61.8; H, 6.8; N, 4.5. Found: C, 62.4; H, 6.7; N, 4.4.

Synthesis of L′Si(NH$_2$)−Ni(CO)$_3$ (23a). NH_3 was passed through a Schlenk flask with a cooled solution (−60 °C) of complex **13** (176 mg, 0.30 mmol) in toluene (10 mL) for about 1 min. Then the yellow reaction mixture was slowly warmed to room temperature. All volatiles were removed in vacuo, and the residue was recrystallized in toluene (114 mg, 63%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.98, 1.19, 1.37, 1.40 (each d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.48 (s, 6H, CH_3), 1.52 (s, 2H, NH_2), 3.17, 3.56 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 4.89 (s, 1H, γ-H), 7.0 −7.4 (m, 6H, H_{aryl}) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ 23.8 (CH_3), 23.8, 24.1, 24.7, 26.2 ($CH(CH_3)_2$), 28.5, 29.5 ($CH(CH_3)_2$), 100.0 (γ-*C*), 124.7, 125.3, 128.5, 140.6, 143.3, 145.9 (C_{aryl}), 166.2 ($NCCH_3$), 200.6 (*C*O) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6, 25 °C): δ 32.6 ppm. IR (toluene, cm^{-1}): ν(CO) 1965, 1978, 2046. EI MS (70 eV): *m/z* (%) 547 (0.3) $[M - 2CO]^+$, 519 (3) $[M - 3CO]^+$, 461 (9) $[M - Ni(CO)_3]^+$, 446 (100) $[M - Ni(CO)_3 - CH_3]^+$, 418 (24) $[M - Ni(CO)_3 - {}^iPr]$. Anal. Calcd for $C_{32}H_{43}N_3O_3SiNi$: C, 63.6; H, 7.2; N, 7.0. Found: C, 63.9; H, 7.4; N, 6.6.

Synthesis of L′Si(NH^{i}Pr)−Ni(CO)$_3$ (23b). Isopropylamine (5.7 μL) was added to a solution of complex **13** (39 mg, 0.066 mmol) in toluene (3 mL) at −60 °C. The reaction mixture was slowly warmed to room temperature overnight. All volatiles were removed in vacuo, and the residue was crystallized in hexane (12 mg, 29%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 1.03, 1.05, 1.17, 1.34, 1.44 (each d, $^3J_{HH}$ = 6.8 Hz, 6H; $CH(CH_3)_2$), 1.48 (s, 6H, CH_3), 1.49 (s, 1H, N*H*), 2.84 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, $NH{-}CH(CH_3)_2$), 3.00, 3.98 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 5.05 (s, 1H, γ-*H*), 7.0−7.3 (m, 6H, H_{aryl}) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ 23.9 (CH_3), 24.6, 24.8, 25.1, 25.5, 26.4 ($CH(CH_3)_2$), 27.3, 29.1, 47.3 ($CH(CH_3)_2$), 102.6 (γ-*C*), 125.1, 125.5, 128.6, 141.2, 144.0, 146.3 (C_{aryl}), 167.8 ($NCCH_3$), 200.8 (*C*O) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6, 25 °C): δ 28.3 ppm. IR (hexane, cm^{-1}): ν(CO) 1968, 1981, 2048. EI MS (70 eV): *m/z* (%) 589 (1) $[M - 2CO]^+$, 561 (5) $[M - 3CO]^+$, 559 (5) $[M - 2CO - CH_3]^+$, 503 (17) $[M - Ni(CO)_3]^+$, 488 (100) $[M - Ni(CO)_3 - CH_3]^+$, 460 (28) $[M - Ni(CO)_3 - {}^iPr]^+$. Anal. Calcd for $C_{35}H_{49}N_3O_3SiNi$: C, 65.0; H, 7.6; N, 6.5. Found: C, 65.7; H, 7.0; N, 6.0.

Synthesis of L′Si(NHNHPh)−Ni(CO)$_3$ (23c). Phenylhydrazine (6.2 μL, 0.063 mmol) was added to a solution of complex **13** (37 mg, 0.063 mmol) in toluene (3 mL) at −60 °C. The reaction mixture was slowly warmed to room temperature overnight. All volatiles were removed in vacuo, and the residue was crystallized in hexane (17 mg, 39%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 0.94, 1.00, 1.38, 1.39 (each d, $^3J_{HH}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.51 (s, 6H, CH_3), 3.12, 3.40 (each sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$), 3.98 (s, 1H, N*H*), 4.95 (s, 1H, N*H*), 5.13 (s, 1H, γ-*H*), 6.7−7.3 (m, 11H, H_{aryl}) ppm. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ 23.8 (CH_3), 24.1, 24.2, 24.8, 26.1 ($CH(CH_3)_2$), 27.7, 28.4 ($CH(CH_3)_2$), 101.5 (γ-*C*), 112.5, 119.5, 124.9, 125.5, 128.8, 129.5, 140.3, 143.5, 146.6, 150.2 (C_{aryl}), 168.9 ($NCCH_3$), 200.1 (*C*O) ppm. ^{29}Si NMR (79.5 MHz, C_6D_6, 25 °C): δ 25.7 ppm. IR (hexane, cm^{-1}): ν(CO) 1973, 1985, 2051. EI MS (70 eV): *m/z* (%) 610 (1) $[M - 3CO]^+$, 522 (41) $[M - Ni(CO)_3]^+$, 537 (100) $[M - Ni(CO)_3 - CH_3]^+$, 522 (16) $[M - Ni(CO)_3 - 2CH_3]^+$, 509 (45) $[M - Ni(CO)_3 -$

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(35) Sheldrick, G. M. SHELX-97 Program for Crystal Structure Determination; Universität Göttingen, Göttingen, Germany1997.

^{i}Pr]$^+$. Anal. Calcd for $C_{38}H_{48}N_4O_3SiNi$: C, 65.6; H, 7.0; N, 8.0. Found: C, 65.5; H, 6.4; N, 7.8.

Theoretical Calculations. DFT calculations were performed employing the simplified model compounds **5′**, **15a′**, **15b′**, and **16′** at the B3LYP level using 6-31G(d) basis sets of the GAUSSIAN-03 program package. Optimized structures of model compounds were obtained without symmetry constraints.

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Supporting Information Available: Text, figures, tables, and CIF files giving details of the X-ray crystal structure analyses of **12c**,**d**, **16**, **17**, and **23a−c**, solid-state MAS ^{29}Si NMR spectrum of the product mixture from **5** and gaseous H_2S, and coordinates of the optimized model compounds **5′**, **15a′**, **15b′**, and **16′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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