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Diketiminate Silicon(II) and Related NHSi Ligands Generated in the Coordination Sphere of Nickel(0)

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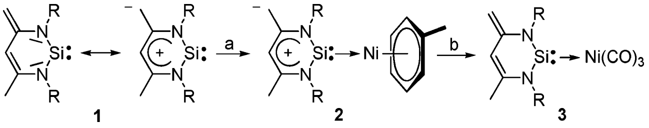
The properties of transition metal complexes are governed by the interaction of the central atom and the ligands. Triorgano phosphines and *N*-heterocyclic carbenes (NHCs) are important representatives of the class of strong two electron σ-donor ligands. Their successful utilization in many catalytic transformations originates not only from their convenient electronic properties but also from the variable steric protection they can provide for low coordinate metal sites. A distinct drawback of these ligands, however, is the restricted variability of their donor/acceptor capabilities toward metal centers in different oxidation states. Moreover, direct participation of ligands in bond activations—pursuant to the recently introduced concept of cooperating ligands[1]—is unlikely due to their low-lying HOMO orbitals and relatively large HOMO−LUMO gap. Alternatively, *N*-heterocyclic silylenes (NHSis) are promising strong σ-donor ligands that possess a HOMO−LUMO gap more suitable for, as an example, C−H activation[2] and have been known to be able to form isolable transition-metal complexes for more than a decade.[3] A common feature of silylene complexes in general—an inherent Lewis acidity of the silicon center[4]—has limited the number of donor-free examples and prevented their utilization as versatile alternatives to phosphines and NHCs in homogeneous catalysis. Up to now, suitable metal binding NHSi ligands with *tunable* donor/acceptor properties are currently unknown.

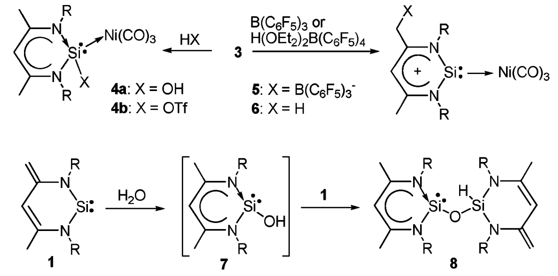
Here we report the first example of NHSi and related donor-stabilized silylene ligands generated in the coordination sphere of a metal where their donor/acceptor properties can be tuned to cover an astonishingly wide range from NHC- and organophosphine-like strong σ-donors and weak π-acceptors to PF_3-like weak σ-donors but strong π-acceptors. This has been achieved by taking advantage of the unusual reactivity of the zwitterionic silylene ligand **1**[5] (Scheme 1), bearing a nucleophilic, exocyclic methylene group and a Lewis acidic silicon(II) center.[6] Recently, we have shown that the ylide-character of **1** remains even in the $[Ni^0(\eta^6\text{-toluene})]$ complex **2**.[7] Facile replacement of the toluene ligand in **2** by three CO ligands leads to the $[Ni(CO)_3]$ complex **3** in high yield (Scheme 1). The NHSi ligand in **3** can be transformed, in the coordination sphere of nickel, to unprecedented NHSi ligands with remarkably variable donor/acceptor strengths. The CO stretching frequencies of the $Ni(CO)_3$ moiety in the novel complexes were used as an ideal probe of the donor/acceptor strength of the novel NHSi ligands. A previous attempt to synthesize a compound similar to **3**, starting from a stable NHSi and $[Ni(CO)_4]$, failed and instead resulted in the formation of $(NHSi)_2Ni(CO)_2$.[3a] Complex **3**, akin to the "free" ligand **1** and its precursor **2**, still exhibits an electron-rich butadiene moiety in the NHSi backbone, which can serve as a nucleophile toward Lewis acids. Accordingly, tris(pentafluorophenyl)borane and $[H(OEt_2)_2][B(C_6F_5)_4]$,[8] react smoothly at the nucleophilic terminus of **3** to yield complexes **5** and $\mathbf{6}\cdot[B(C_6F_5)_4]$, respectively (Scheme 2). Additionally, **5** can be produced on preparative scale by direct ligand exchange with CO on the recently described complex $[\mathbf{2}\cdot B(C_6F_5)_3]$.[7] The constitution of the latter was proven by X-ray structure analysis (see Figure 2). The ion pair $\mathbf{6}\cdot[B(C_6F_5)_4]$ was characterized by its distinctive IR(CO) stretching frequencies (vide infra) and a comparison of multinuclear NMR spectroscopic data with those of the closely related complex **5**.

Scheme 1. Mesomeric Structures of Ylide-like Silylene **1** and Synthesis of Complexes $[\mathbf{1}\cdot Ni(\eta^6\text{-Toluene})]$, **2**, and $[\mathbf{1}\cdot Ni(CO)_3]$, **3**[a]



[a] R = 2,6-$^iPR_2C_6H_3$; (a) +$[Ni(cod)_2]$, - 2COD toluene; (b) CO, toluene.

Scheme 2. Synthesis of the Unique Silylene−$Ni(CO)_3$ Complexes **4a**, **4b**, **5**, $\mathbf{6}\cdot[B(C_6F_5)_4]$, and Siloxy-Terminated NHSi **8**. OTf = OSO_2CF_3



The electron-withdrawing CO ligands of complex **3** ultimately cause an increased Lewis acidity of the silicon center due to decreased Ni→Si π-backbonding as compared to complex **2**. The synergism of σ,π acid/base facilitates the addition of different strength Brønsted acids exclusively to the silylene ligand at the 1,4 positions. While the reaction of the "free" silylene **1** with water furnishes exclusively the donor-stabilized siloxo-silylene **8**, instead of the expected donor stabilized hydroxo-silylene **7** (Scheme 2),[6c] the $Ni(CO)_3$ moiety in **3** is able to tame the silicon lone pair and prevents an insertion into the O−H bond. Thus, the unique silicon(II) hydroxide complex **4a** was prepared by slow diffusion of water into a hexane solution of complex **3** (Scheme 2). Remarkably, the addition of water and other electrophiles to **3** enables the donor/acceptor abilities of the silicon ligand to be tuned considerably while still coordinated to the Ni(0) center and without changing its ligand sphere any further (see later).

This reactivity is in distinct contrast to the well-studied reactions of other transition metal silylene complexes with water and alcohols where the silicon−metal bond is either broken by 1,1 addition to the silicon(II) center or remains intact by 1,2 addition across the silicon−metal bond.[9] Because of the high electrophilicity of the Si(II) atom, complex **4a** is also found as a minor byproduct during the synthesis of **3** in the presence of traces of water.

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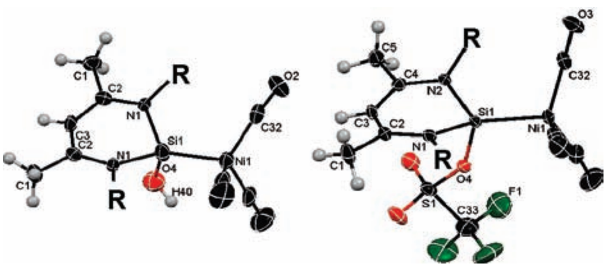


Figure 1. Molecular structures of **4a** (left), and **4b** (right) with thermal ellipsoids drawn at 50% probability level; hydrogen atoms are omitted for clarity, except for those of C1−C5 and O4 (**4a**). Selected bond length [pm] and angles [deg]: (**4a**) Si−Ni, 224.03(12); Si−O, 176.8(3); Ni−C, 179.3 (average); Si−N, 180.7(2); N−Si−N, 96.30(15). (**4b**) Si−Ni, 219.42(6); Si−O, 182.86(15); Ni−C, 182.4 (average); Si−N1, 181.08(17); Si−N2, 180.51(17); N−Si−N, 97.73(8). R = 2,6-^{i}PrC$_6$H$_3$.

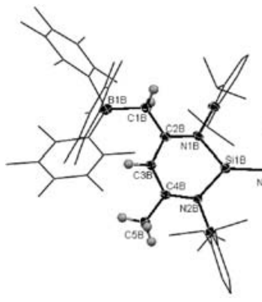
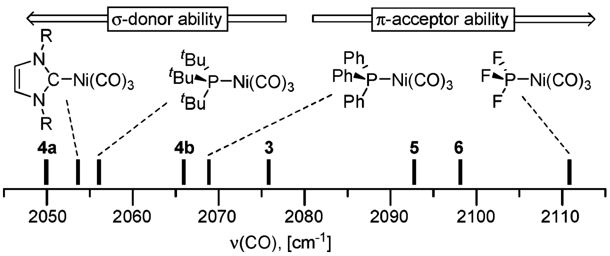


Figure 2. Molecular structure of **5** (one of two crystallographically independent molecules in the unit cell) with thermal ellipsoids drawn at 50% probability level, hydrogen atoms are omitted for clarity, except for those of C1−C5. Selected bond length [pm] and angles [deg]: Si−Ni, 217.85(12), 216.63(12); Ni−C, 179.2 (average); Si−N, 175.9 (average); N−Si−N, 97.93 (average).

Compound **4a** (Figure 1) is the first example of a transition metal complex featuring a terminal, donor-stabilized silicon(II) hydroxide ligand. Similarly, complex **3** reacts with trifluoromethanesulfonic acid to yield the contact ion pair **4b**. The weakly coordinating triflate anion is bound to the highly electrophilic Si center in the solid state (Figure 1) as well as in solution. The ^{29}Si NMR chemical shifts of **4a**,**b** are similar (**4a**: $\delta = 35.0$, **4b**: 38.8 ppm) and distinctively different from those of neutral and cationic silylene complexes with tricoordinate Si(II) atoms in **3**, **5**, **6** (**3**, $\delta = 142.1$; **5**, 134.3; **6**, 131.2 ppm). The silicon(II) centers of compounds **4a**,**b** deviate significantly from tetrahedral coordination with all N−Si−X (X = N, O) angles being smaller than 97 (**4a**) and 98° (**4b**) as expected for *N*-donor-stabilized silylene complexes. The distance between silicon and the weakly coordinating triflate anion is rather long (Si−O: 182.9 pm (**4b**) vs 176.8 pm (**4a**)), and, in regard to its electron deficiency, the silylene of complex **4b** can be positioned somewhere in-between the zwitterionic silylene moiety of complex **5** (Figure 2) and the tetracoordinate, electron-rich silicon center of complex **4a**.

Carbonyl stretching frequencies are used regularly to compare the donor capabilities of ligands in different Ni(CO)$_3$ complexes.[10] The novel ligands described here exert a rather diverse effect on the Ni(CO)$_3$ moiety. The zwitterionic ligand of complex **5** and the cationic ligand of complex **6** are, as expected, the weakest σ-donors and good π-acceptors[7] and thus comparable with PF$_3$, also a weak σ-donor and good π-acceptor (Chart 1).

Chart 1. Comparison of Ni(CO)$_3$ Carbonyl Stretching Frequencies (A$_1$-Mode) of Novel Complexes with Those of Analogues Phosphine and NHC Systems. R = 2,4,6-Me$_3$C$_6$H$_2$



In comparison to **5** and **6**, silylene **1** of complex **3** gains some donor strength because the nitrogen lone pairs do not need to compensate for a positive charge within the ligand backbone and can therefore interact with the silicon(II) center more strongly, which also decreases the π-acceptor capability of ligand **1**. Among the examples selected from the literature, [Ph$_3$P−Ni(CO)$_3$] is a reasonable counterpart for the complexes **3** and **4b**. By contrast, the silicon(II) hydroxide ligand of **4a** has the ligand properties of ^{t}Bu$_3$P and conventional NHCs (strong σ-donors, weak π-acceptors). Our results demonstrate an astonishing variability of silicon(II)-based ligand characteristics that can be achieved by modifying the substitution pattern of the Si(II) center and the NHSi ligand backbone while still in the coordination sphere of Ni(0). The ambivalent reactivity of the novel silylene complexes, discussed herein, could provide access to new types of catalysts with NHSi-based ligands.

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Supporting Information Available: Experimental procedures, characterization of products, and details on X-ray crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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