A Bis(silylene)-Substituted *ortho*-Carborane as a Superior Ligand in the Nickel-Catalyzed Amination of Arenes

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Dedicated to Professor Herbert W. Roesky

Abstract: *The synthesis and structure of the first 1,2-bis-(NHSi)-substituted ortho-carborane [(LSi:)C]$_2$B$_{10}$H$_{10}$ (termed SiCCSi) is reported (NHSi = N-heterocyclic silylene; L = PhC(NtBu)$_2$). Its suitability to serve as a reliable bis(silylene) chelating ligand for transition metals is demostrated by the formation of [SiCCSi]NiBr$_2$ and [SiCCSi]Ni(CO)$_2$ complexes. The CO stretching vibration modes of the latter indicate that the Si^{II} atoms in the SiCCSi ligand are even stronger σ donors than the P^{III} atoms in phosphines and C^{II} atoms in N-heterocyclic carbene (NHC) ligands. Moreover, the strong donor character of the [SiCCSi] ligand enables [SiCCSi]NiBr$_2$ to act as an outstanding precatalyst (0.5 mol % loading) in the catalytic aminations of arenes, surpassing the activity of previously known molecular Ni-based precatalysts (1– 10 mol %).*

N-Heterocyclic silylenes (NHSis),[1] the silicon analogues of *N*-heterocyclic carbenes (NHCs), are no longer laboratory curiosities but valuable building blocks for the synthesis of new functional silicon compounds[2] that are accessible in multigram quantities; they can even serve as very effective σ donor ligands for transition metals (TMs).[3] In fact, the electronic nature of NHSi ligands, with a singlet electronic ground state akin to NHCs, leads to a strong σ-donor and π-acceptor character of the divalent Si center toward TM sites. Experimental data indicate that the σ-donor strengths of NHSi ligands can be greatly varied by modifying the nature of the heterocyclic backbone around the divalent Si atom,[3a] and DFT calculations indicate that they can compete with or even exceed the electronic features of commonly used NHCs or phosphine ligands with respect to σ-donor and π-acceptor strengths, ligand-to-metal charge transfer, and steric parameters.[4] Therefore, NHSis are attractive steering ligands in homogeneous catalysis.[5] Currently, the chelating bis-(silylene) ligands **A** and **D**, and the SiXSi pincer-type NHSi

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Scheme 1. Multidentate NHSi ligands.

ligands **B** (X = CH) and **C** (X = N) have been synthesized in our laboratory (Scheme 1).[6] TM complexes of the latter type of ligands can act as very active precatalysts in the borylation of benzenes,[7a] Sonogashira coupling,[7b] Kumada–Corriu coupling,[7c] the cyclotrimerization of alkynes, the co-cyclotrimerization of alkynes and organocyanides to form pyridines,[7d] the hydrosilylation of ketones,[7e–g] and the reduction of amides to amines.[7h] However, compared to the rich structural diversity of phosphine and NHC ligands, multidentate NHSi ligands are still scarce. Herein we report the synthesis of the first bis(NHSi) ligand (termed SiCCSi; Scheme 1) with an *ortho*-carborane backbone,[8] and its superior function in the Ni-catalyzed amination of arenes (Buchwald–Hartwig coupling reactions).
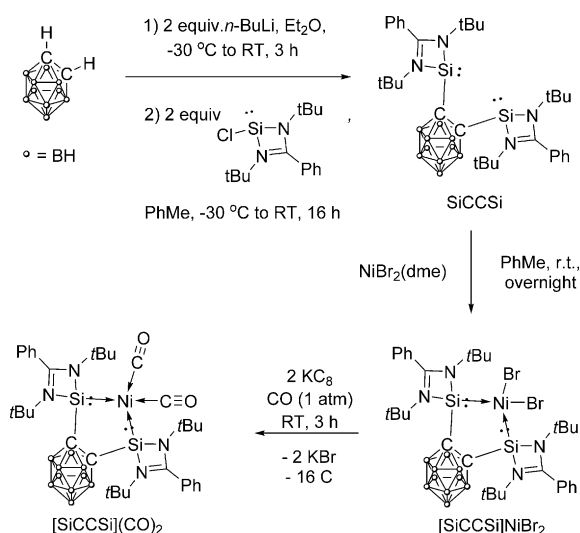
SiCCSi was synthesized and isolated in 84 % yield through a salt metathesis reaction of (LiC)$_2$B$_{10}$H$_{10}$ with *N,N'*-di-*tert*-butyl(phenylamidinato)chlorosilylene (Scheme 2). Single-crystal X-ray diffraction analysis of SiCCSi revealed that the Si^{II} atoms of the NHSi motifs pointed towards each other with an Si–Si distance of 3.267 Å to form a pre-organized chelating "pocket" for metal coordination (Figure 1, top). This allows SiCCSi to serve as a reliably strong chelating Si^{II} ligand for Ni^{II}, affording [SiCCSi]NiBr$_2$ after reacting with L$_2$NiBr$_2$ (L$_2$ = 1,2-dimethoxyethane). The ^{29}Si NMR signal at δ = 58.7 ppm is drastically downfield shifted compared to the "free" ligands (δ = 18.9 ppm) and other known NHSi-Ni^{II} complexes.[6,7a,b] Single-crystal X-ray analysis of [SiCCSi]-NiBr$_2$ revealed that the Ni^{II} center is, as expected, in a square-

Scheme 2. Synthesis of the [SiCCSi]NiBr$_2$ and [SiCCSi]Ni(CO)$_2$ complexes.
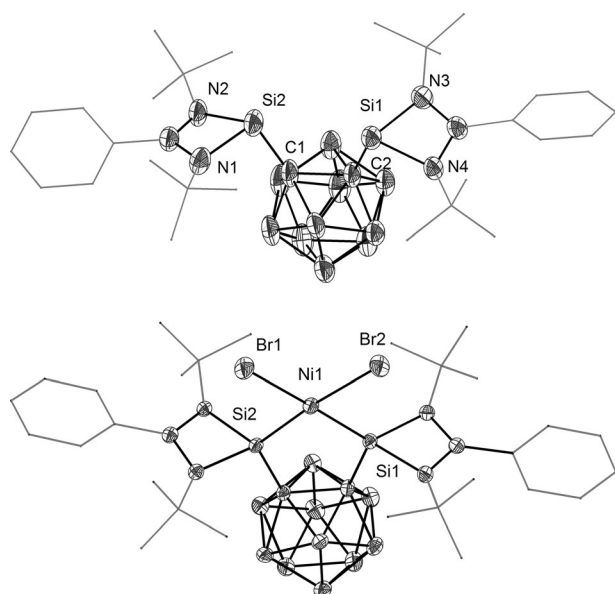

Figure 1. Molecular structure of SiCCSi (top) and [SiCCSi]NiBr$_2$ (bottom). Thermal ellipsoids are set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.
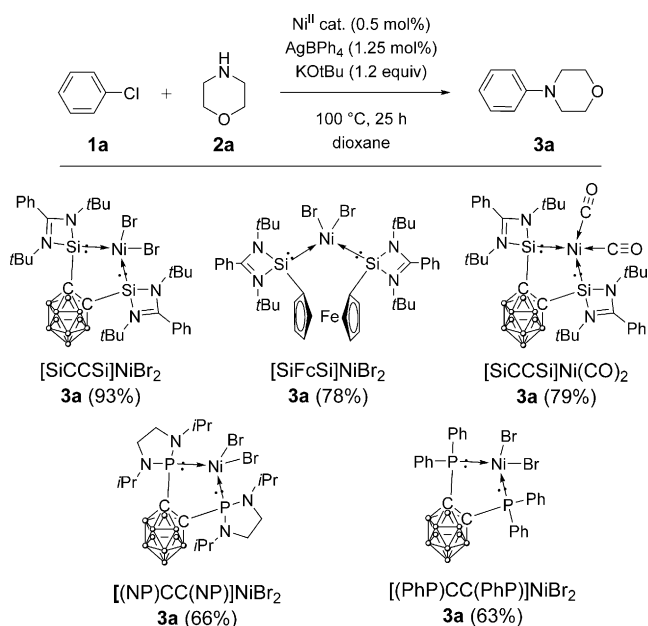
planar environment (Figure 1, bottom). The Ni(1)−Si(1) (2.1378(5) Å) and Ni(1)−Si(2) (2.1447(5) Å) distances are shorter than those in NHSi-Ni^{II} complexes supported by pincer-type **B** (2.1737(7) Å)[7b] and related NHC-NHSi ligands.[7c]

Reduction of [SiCCSi]NiBr$_2$ with KC$_8$ in the presence of CO furnished the corresponding Ni^0 complex [SiCCSi]Ni-(CO)$_2$. Its ^{29}Si NMR signal appears at $\delta = 86.0$ ppm, which is, in turn, significantly downfield shifted compared to [SiCCSi]-NiBr$_2$, thus indicating strong π-acceptor character for the CO ligands. Single-crystal X-ray diffraction data for [SiCCSi]Ni-(CO)$_2$ and DFT calculations confirm tetrahedral geometry

around the Ni^0 center (see Figures S14 and S14A in the Supporting Information). The IR stretching vibration frequencies of the CO groups in [SiCCSi]Ni(CO)$_2$ were observed at $\nu = 1982$ and 1934 cm^{-1}. These observed frequencies are red-shifted compared to [LSi:(CH$_2$)NHCNi(CO)$_2$] ($\nu = 1952$, 1887 cm^{-1})[7c] and [(NHC^{Cy})$_2$Ni(CO)$_2$] ($\nu = 1949$, 1878 cm^{-1}; Cy = cyclohexyl)[8b] but blue-shifted compared to {[(R$_2$PC)$_2$B$_{10}$H$_{10}$]Ni(CO)$_2$} (R = Ph: $\nu = 2021$ and 1966 cm^{-1}; R = Et: $\nu = 2013$ and 1955 cm^{-1}),[8c] and [(NHC^{Mes})$_2$Ni(CO)$_2$] ($\nu = 2051$, 1887 cm^{-1}; Mes = 2,4,6-Me$_3$C$_6$H$_2$).[8b] This suggests that the σ-donor strength of SiCCSi can be larger than that of NHC or phosphine ligands and even exceeds that of the [SiFcSi] ligand **D** in [SiFcSi]NiBr$_2$, which was synthesized and structurally characterized as well (see Figure S15 and Table S6 in the Supporting Information). DFT calculations showed elongation of the Ni−Si distances in [SiFcSi]NiBr$_2$ vs. [SiCCSi]NiBr$_2$, which indicates weaker donor ability of the SiFcSi ligand towards Ni.[4] The calculated charge of the Ni center is + 0.72 in [SiCCSi]NiBr$_2$ and + 0.78 in [SiFcSi]NiBr$_2$ (see the Supporting Information). We also calculated the Si-Ni-Si angle. The somewhat smaller bite angle of [SiCCSi]-NiBr$_2$ (89.33°) vs. [SiFcSi]NiBr$_2$ (91.01°) might also predict increased catalytic activity in the oxidative addition step, which has been suggested for phosphines before.[9]

Both complexes were successfully applied in Ni-mediated Buchwald–Hartwig amination reactions of arenes. The original reports on this important C−N bond-formation reaction were based on molecular palladium precatalysts.[10] Since then, however, reports utilizing first-row TM complexes have appeared.[11] Among these, either structurally defined Ni complexes or the combination of Ni^{II} salts with different ligands such as phosphines, NHCs, and various nitrogen-donor-based ligands have been shown to act as suitable precatalysts in amination reactions.[12, 13] Herein, we show that applying the stronger SiCCSi donor ligand leads to the most active Ni precatalyst reported to date.

Our initial screening experiments revealed that just 0.5 mol% loading of [SiCCSi]NiBr$_2$ can effectively catalyze the reaction of phenyl chloride **1** with morpholine **2** in high yield (93%) after 25 h at 100 °C in the presence of catalytic amounts of AgBPh$_4$ and 1.2 molar equivalents of KOtBu as a base (Scheme 3). In contrast, using Ni(dme)Br$_2$ as a precatalyst leads to moderate yields of **3a** (24%; Table S9, Entry 1 in the Supporting Information). Moreover, poisoning studies and control experiments showed that the reaction is mediated by a molecular nickel catalyst (Table S9, Entries 18–19). Since the [SiFcSi]NiBr$_2$ precatalyst resulted in lower yields of **3a** (78%; Scheme 3), we reason that the higher activity of [SiCCSi]NiBr$_2$ is due to the stronger donor character of SiCCSi towards Ni^{II}, which facilitates the oxidative addition step at the Ni site. For comparison of the catalytic performance of [SiCCSi]NiBr$_2$ with that of related Ni^{II} complexes containing the bis(diphenylphosphine)-[14] and bis-(cyclodiaminophosphine)-substituted *o*-carborane ligands, the [(NP)CC(NP)]NiBr$_2$ and [(PhP)CC(PPh)]NiBr$_2$ complexes were synthesized, fully characterized, and tested in the catalytic amination of **1** with **2** under identical reaction conditions (Scheme 3). This revealed that both phosphine complexes catalyze the formation of **3a** in considerably lower

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Scheme 3. Catalytic performance of different chelating bis(NHSi) and bis(phosphine) nickel precatalysts in the Buchwald–Hartwig coupling of phenyl chloride **1** with morpholine **2** to give **3a**.

yields (66 and 63%, respectively; for details see Tables S9, S10) than [SiCCSi]NiBr$_2$ (93%).

Next, we studied the effect of different leaving groups. It was shown that changing from iodide to trifluoromethylsulfonate (TfO) lowers the overall rate of the reaction from 87% to 11% (conversion after 25 hours; Table 1, Entries 2–5). Moreover, the reaction of aryl halides bearing electron-donating group at the *para* position yielded lower conversions, while electron-withdrawing groups at the *para* position increase the overall reaction rate (CF$_3$ > H > Me > OMe;

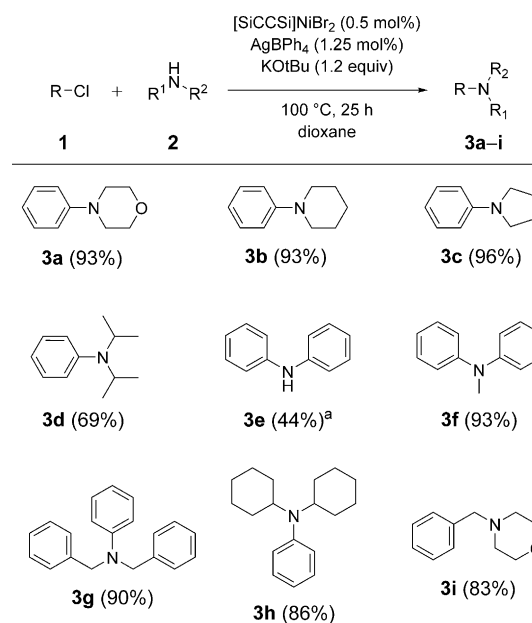**Table 1:** [SiCCSi]NiBr$_2$-catalyzed amination of various aryl halides.[a]

ArX (1)		Conversion[b]	Selectivity [%][b]
R	X	%	3′
1	H	Cl	76	99
2	4-Me	Cl	62	99
3	4-Me	Br	86	97
4	4-Me	I	87	45[c]
5	4-Me	OTf	11	15
6	4-OMe	Cl	61	98
7	4-CF$_3$	Cl	81	98
8	2-Me	Cl	33	99
9	3-Me	Cl	50	96

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), [SiCCSi]NiBr$_2$ (0.5 mol%), AgBPh$_4$ (1.25 mol%), KOtBu (1.2 equiv), T = 100 °C, solvent = dioxane (1.5 mL), internal standard = decane, t = 16 h. [b] Conversions and selectivities were determined by GC and GC/MS using decane as internal standard and based on the substrate **1**. [c] Homocoupling product formed.

Table 1, Entries 1–2, 6–7). These results show that the reaction rate depends on the electronic nature of the substrates applied in the reaction. Since aryl substrates with substituents at the *para* position gave higher yields compared to those with substituents in the *meta* and *ortho* positions (in the order 4-Me > 3-Me > 2-Me; Table 1, Entries 2, 8–9), steric effects play a role as well.

The remarkable catalytic performance of [SiCCSi]NiBr$_2$ was further demonstrated using various amines with different steric and electronic properties (Scheme 4). It was found that the amination of phenyl chloride results in moderate to

Scheme 4. Catalytic performance of the [SiCCSi]NiBr$_2$ precatalyst in the Buchwald–Hartwig coupling of phenyl chloride with different amines. [a] triphenylamine formed as a byproduct.

excellent yields (44 to 96%) depending on the steric and electronic nature of the amine substrates, as was the case with varying the aryl substituent. In general, bulky substituents on the amine substrates hamper the catalytic performance of the catalyst, thus resulting in lower yields (e.g., diisopropylamine **3d**, 69%, Scheme 4). The relatively low yield of **3e** (44%) is likely due to the fact that **3e** undergoes further transformation with phenyl chloride to form triphenyl amine as a byproduct. It was also shown that the reaction of benzyl chloride with morpholine proceeds very efficiently, giving **3i** in 83% yield.

As previously proposed for this type of coupling reaction,[15] and according to a control experiment in the presence of 2,2,6,6-tetramethyl-l-piperidinoxyl (TEMPO; Table S9, Entry 20), we reason that the catalytic cycle starts with the formation of [SiCCSi]Ni^0 as the catalytically active species through the known base-assisted reduction of [SiCCSi]NiBr$_2$ by amines. The former complex undergoes oxidative addition of an aryl halide and subsequent replacement of the halide anion by an amide substrate to give the corresponding [SiCCSi]Ni(Ar)NR$_2$ intermediate. The desired C–N coupling

product is then liberated through a reductive elimination step to regenerate the Ni⁰ catalyst. Accordingly, the Ni⁰-based [SiCCSi]Ni(CO)$_2$ complex can also be used as a precatalyst but results in significantly lower yields of the desired C−N coupling products (e.g., 22% lower yield for **3a** compared to [SiCCSi]NiBr$_2$), thus indicating that CO decreases the activity of the catalyst due to favorable OC→Ni coordination. The higher catalytic activity of [SiCCSi]Ni compared to [SiFcSi]Ni and related bis(phosphine)Ni systems is in accord with a stronger donor character of [SiCCSi], which facilitates the oxidative addition step at Ni⁰, whilst its steric bulk favors the reductive elimination step, thus enabling a superior steering role of that ligand throughout the reaction.

In summary, the first chelating bis(NHSi)-substituted *o*-carborane ligand, SiCCSi, was synthesized and fully characterized. Due to its extraordinarily strong σ-donor character, the corresponding [SiCCSi]NiBr$_2$ complex surpasses the catalytic activity of the Ni-based precatalysts reported to date for Buchwald–Hartwig amination reactions of aryl halides with secondary amines.

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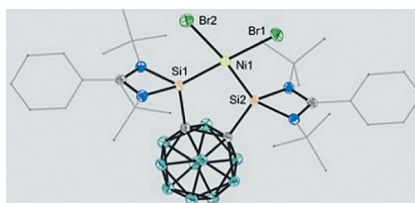**These are not the final page numbers!** ↗↗

Communications

Homogeneous Catalysis

Y.-P. Zhou, S. Raoufmoghaddam,
T. Szilvási, M. Driess* ———— ▮▮▮▮–▮▮▮▮

A Bis(silylene)-Substituted *ortho*-Carborane as a Superior Ligand in the Nickel-Catalyzed Amination of Arenes

The right bite: A chelating bis-N-heterocyclic silylene ligand bridged by an *o*-carborane (SiCCSi) and its corresponding Ni complexes (see example) were synthesized, fully characterized, and successfully applied in Ni-catalyzed Buchwald–Hartwig coupling reactions. [SiCCSi]NiBr$_2$ is the most active precatalyst for this transformation that has been reported to date.