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The Striking Stabilization of Ni^0(η^6-Arene) Complexes by an Ylide-Like Silylene Ligand**

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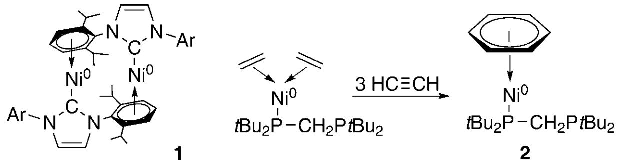
Dedicated to Professor Robert West

Strong σ donors that offer considerable steric protection are often the ligands of choice for stabilizing complexes of low-valent Group 10–12 transition metals. Investigations in this area have led to the development of superior catalysts and new catalytic transformations.[1] Phosphines and N-heterocyclic carbenes (NHCs) are very important classes of such ligands; recently, the latter have even been employed to stabilize some unprecedented main-group compounds.[2] Although silylenes are isolobal with phosphines and NHCs and are strong σ-donor ligands, the chemistry of their metal complexes is usually quite different from the latter. The distinct electrophilicity of the divalent silicon center requires specific methods for the synthesis of isolable silylene metal complexes.

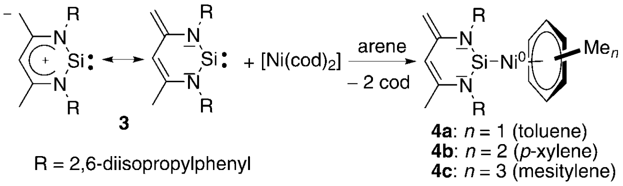
The substitution of precious metals in catalytic systems with cheaper and more abundant metals (e.g., Ni versus Pd) is a very attractive goal. However, this requires a redesign of the ligand sphere in many cases. For decades, neutral 6π-electron systems have been known to form useful, relatively stable (half)sandwich complexes with metal atoms (e.g., bis(arene) Group 6 metal systems).[3] Surprisingly little is known about d^{10}-metal (η^6-arene) complexes, such as Ni^0(η^6-arene) complexes. The low thermal stability of the {Ni^0(η^6-arene)} moiety and respective bis(η^6-arene) sandwich complexes may arise from the unbalanced electron-rich situation of the Ni center.

Only two examples of such Ni complexes that are stable enough to be characterized by single-crystal X-ray analysis have been reported to date. These are the dimeric NHC–Ni^0 complex **1**[4] and the phosphine Ni^0(η^6-benzene) complex **2**, which was obtained from the corresponding phosphine bis(η^2-ethene)Ni complex by cyclotrimerization of ethyne at the nickel center (Scheme 1).[5] No analogous silylene nickel complexes have been reported to date. Recently, we described the electronically versatile ylide-like silylene **3**,[6] which could be a suitable ligand for the synthesis of more electronically balanced Ni^0(η^6-arene) complexes. In fact, silylene **3** serves as a convenient ligand for the synthesis of the first isolable silylene Ni^0(η^6-arene) complexes **4a–c**.



Scheme 1. η^6-arene complexes **1** and **2**, which were characterized by single-crystal X-ray analysis.

The ylide-like silylene **3** was reacted with [Ni(cod)$_2$] (cod = cyclooctadiene) in toluene at −40 °C to furnish the silylene Ni^0(toluene) complex **4a**, which could be isolated in the form of red crystals in 66 % yield relative to [Ni(cod)$_2$] (Scheme 2).[7] In contrast to the phosphine derivative **2** reported by Pörschke et al.,[5] solutions of compounds **4a–d** in C$_6$D$_6$ are remarkably stable for weeks at ambient temperature and even survive heating at 80 °C for at least 12 h. Crystals of **4a** are stable up to 95 °C, but decompose to a large extent upon melting (m.p. 145 °C), as shown by ^{1}H NMR spectroscopy. The complexation of isolable N-heterocyclic silylenes (NHSi's) to metal centers usually causes characteristic downfield shifts $\Delta\delta$ of 20–60 ppm in the ^{29}Si NMR spectrum.[8] For **4a**, however, the difference is only 10.8 ppm (**3**: δ = 88.4 ppm, **4a**: δ = 99.2 ppm), which can be explained by the particular donor–acceptor properties of both silylene **3** and the {Ni^0(arene)} moiety: the latter is relatively electron-rich and therefore the Ni center is a weak σ acceptor (σ Lewis acid) but a strong π donor that facilitates metal–ligand π backbonding. On the other hand, silylene **3** can also serve as a strong σ donor (σ Lewis base) with a stronger π-acceptor ability than other NHSis because of its ylide-like resonance



Scheme 2. Synthesis of complexes **4a–c** by ligand exchange.

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structure (Scheme 2); that is, the complementary relaylike donor–acceptor ability encoded in **3** affords, among other effects, decreased π bonding from N to Si and thus allows for increased nickel→silicon π backbonding.

The ^{1}H NMR spectrum of **4a** in C_6D_6 shows signals for the aromatic protons of the complexed toluene ligand around $\delta = 5.3$ ppm, which is consistent with the upfield shift reported for other metal (η^6-arene) complexes.[5,9] Even fresh solutions of **4a** in C_6D_6 readily liberate small amounts of uncoordinated toluene. With time, the relative intensity of the corresponding signals increases, together with those of a new species. The remarkable similarities of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra allow the identification of the new species as the complex [(**3**)Ni(C_6D_6)] (**4d**), which forms an equilibrium with **4a** in solution. The exchange of η^6-coordinated arene ligands of transition metals is well-established, mostly for complexes of Group 6 and Group 8 transition metals.[10] This process usually requires elevated temperatures, coordinating solvents, Lewis acid catalysts, or free ligand coordination sites. The low stability of analogous d^{10}-metal (η^6-arene) complexes has previously limited the extension of such investigations to Ni, Pd, and Pt systems.

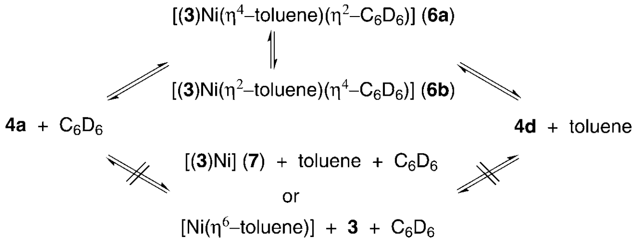
The dimeric NHC Ni^0 complex **1** undergoes slow dissociation in C_6D_6 solutions, but the proposed product, the corresponding NHC Ni^0(benzene) species, could not as yet be characterized.[4] Complexes [(**3**)Ni(*p*-xylene)] (**4b**) and [(**3**)Ni(mesitylene)] (**4c)** were prepared in a similar fashion to **4a** in order to study this process in more detail. The relative stability of complexes **4a**–**d** was calculated by using the Gibbs free energy equation from the molar ratios of the components at equilibrium in C_6D_6 solutions, which were kept under nitrogen at ambient temperature for up to 30 days. The stability of the complexes appears to increase as the number of methyl substituents increases from C_6D_6 to mesitylene (Table 1), that is, complexes with more electron-rich arene ligands are thermodynamically favored. Samples of **4a** equilibrate faster than those of **4b** or **4c** ($t_{1/2}$(**4a**) = 18 min, $t_{1/2}$(**4b**) = 166 min, $t_{1/2}$(**4c**) = 22 d). These findings agree very well with results obtained from studies of metal (η^6-arene) complexes of other metals.[10]

Table 1: Kinetic and thermodynamic data for arene exchange between **4a** and **4d**.

Complex[a]	Silylene[b]	ΔG [kJ mol^{-1}][c]	Half-life[d]
4a	–	−1.7	18 min
4a	1 equiv	−1.9	22 min
4a	2 equiv	−1.7	23 min
4b	–	−3.5	166 min
4c	–	–	22 d

[a] $c = 0.14$ M. [b] Excess silylene **3**. [c] Relative to **4d**. [d] In C_6D_6.

It seems likely that the equilibration process takes place through the formation of either a free 12-electron silylene Ni^0 complex **7** or 18-electron [(**3**)Ni^0(η^4-arene)(η^2-arene′)] complexes (**6a**,**b**; Scheme 3). Similar intermediates, which comprise the latter arene complexes, but with other metals, have been proposed on the basis of computational and experimental results.[10] Another pathway could involve the dissociation of the silylene ligand **3** from the metal center (Scheme 3, bottom). The observation that the arene exchange is relatively slow for sterically encumbered mesitylene and that the presence of additional free silylene **3** has only a small effect on the kinetics (Table 1) strongly supports the existence of the intermediates **6a**,**b**. No indication of the formation of homoleptic Ni^0(silylene)$_x$ complexes, which were observed in cases of other isolable NHSi's ($x = 3$, 4) or in the case of related NHCs ($x = 2$), was observed.



Scheme 3. Reaction pathways for arene ligand exchange between **4a** and **4d**.

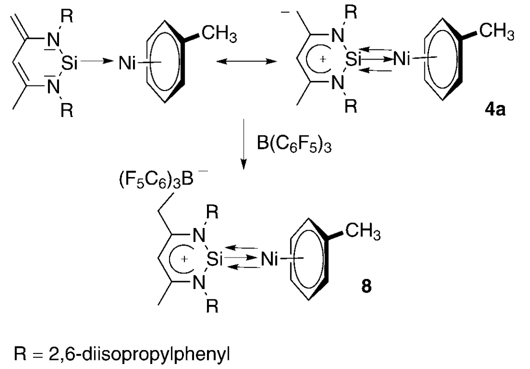
The ^{1}H NMR spectra of mixtures of complex **4a** and excess silylene **3** in C_6D_6 show resonances for only **4a**, **3**, and **4d**.

An explanation for the unusual stability of the silylene nickel (η^6-arene) systems **4** can be formulated on the basis of calculations on **4a**.[7] The highest occupied molecular orbital (HOMO) of **4a** was calculated to consist mainly of the electron-rich butadiene moiety of the silylene backbone, together with a significant contribution of the lone pairs of electrons on the nitrogen atom (Figure 1). HOMO−1 and HOMO−2 show the presence of a noteworthy double Ni→Si π back-bonding (Figure 1), which originates from the overlap of the Ni 3d$_{xz}$ and 3d$_{yz}$ orbitals with the 3p$_x$ and 3p$_y$ orbitals of silicon, respectively. Accordingly, the unexpected stability of the silylene Ni^0(η^6-arene) complexes **4** results from the balanced σ,π-acid–base synergism between the ylide-like silylene **3** and the {Ni^0(arene)} moiety, which involves a strong Si→Ni σ bonding by the strong σ donor **3** and double Ni→Si π back-bonding. The large π-electron-acceptor character of the silylene ligand is manifested in the HOMO of **4a**, which was calculated to consist mainly of the electron-rich butadiene moiety of the silylene backbone along with significant

Figure 1. Calculated HOMO (left), HOMO−1 (center), and HOMO−2 (right) orbitals of **4a**.

contribution of the lone pairs of electrons on the nitrogen atom.

In agreement with the calculations and analogous to the particular reactivity of the silylene **3**,[11] complex **4** should exhibit an ylide-like mesomeric structure (Schemes 2 and 4). While the Si center, as in other silylene metal complexes, is still electrophilic, the electron-rich methylene moiety should retain its nucleophilic character. In fact, the reaction of **4a** with tris(pentafluorophenyl)borane yields the Ni complex **8** in quantitative yield (Scheme 4). It is astonishing that the electronic properties of silylene **3** can be manipulated while it is coordinated to a labile {Ni(arene)} moiety, without breaking the Si–Ni bond. The C–B bond formation and the generation of a formal positive charge within the Si heterocycle are evident from ^{1}H NMR spectroscopic data. The features of the NMR spectra resemble those observed for the related zwitterionic borane adduct of **3** with $B(C_6F_5)_3$.[11a] Thus, the exocyclic methylene protons in **8** exhibit a singlet signal ($\delta = 2.98$ ppm, **4a**: $\delta = 3.26$, 3.88 ppm) and the signal of the C–H ring proton of the NHSi ligand is shifted by about 1–2 ppm into the aromatic region ($\delta = 6.5$–7.4 ppm) and concealed by other resonances.



Scheme 4. Mesomeric structures of **4a** and synthesis of complex **8**.

As expected, a singlet signal is observed at $\delta = 79.4$ ppm in the ^{29}Si NMR spectrum of **8**, which corresponds to an upfield shift relative to **3** ($\delta = 88.4$ ppm) and **4a** ($\delta = 99.2$ ppm) by 9.0 and 19.8 ppm, respectively. Presumably, this shift arises from increased Ni→Si π back-donation.

Single crystals of **4a** and **8** suitable for X-ray crystallography[12] were grown in *n*-hexane and toluene, respectively (Figures 2 and 3). In both structures, the Ni atom is η^6-coordinated almost symmetrically by one molecule of toluene. The Ni–toluene centroid distances (**4a**: 159.2 pm, **8**: 162.1 pm) are similar to that of phosphine complex **2** (160.6 pm). The presence of a Lewis acid in compound **8** generates a formal positive charge within the six-membered Si heterocycle and has some influence on its electronic structure. The Si–N bonds in **8** are longer than those in **4a** (average: 178.3 pm, **4a**: 173.8 pm) because of the weaker Si–N π interaction, which increases the π-acceptor capabilities of the Si center in **8** compared to that of **4a**. Stronger π back-bonding from the {Ni^0(arene)} moiety to the Si p_x and p_y orbitals results in the decrease of the Si–Ni distance (**8**: 203.7 pm, **4a**: 206.0 pm, the shortest Si–Ni distances reported to date). The facile access to **4a–c** and **8** could pave the way to novel nickel-mediated catalytic transformations.

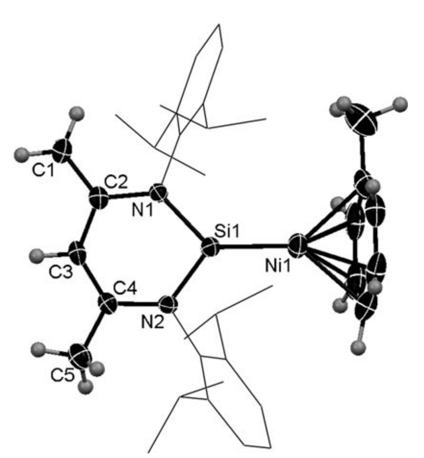


Figure 2. Molecular structure of **4a**. Hydrogen atoms (except those at C1, C3, C5, and η^6-toluene) are omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm] and angles [°]: Si1–Ni1 205.97(10), Si1–N (average) 173.8, Ni1–toluene(centroid) 159.2, Ni1–C 211.3(3)–213.4(3), Ni1–C (average) 212.0; N1-Si1-N2 99.32(14), N1-Si1-Ni1 129.74(10).

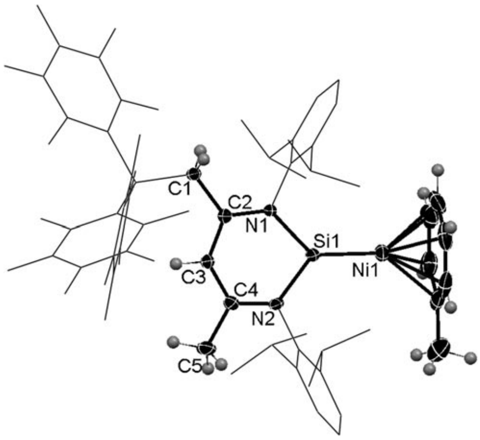


Figure 3. Molecular structure of **8**. Hydrogen atoms (except those at C1, C3, C5 and η^6-toluene) are omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm] and angles [°]: Si1–Ni1 203.69(6), Si1–N (average) 178.33, Ni1–toluene(centroid) 162.1, Ni1–C 210.1(2)–217.5(2), Ni1-C (average) 213.5; N1-Si1-N2 96.54(8), N1-Si1-Ni1 133.74(6).

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[12] Compound **4a**: monoclinic, red block, space group $P21/c$, $a = 13.7834(3)$, $b = 14.3800(3)$, $c = 16.8151(4)$ Å, $\beta = 95.091(2)$, $V = 3319.69(13)$ Å^3, $Z = 4$, $\rho_{\mathrm{calc}} = 1.192\ \mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.646\ \mathrm{mm^{-1}}$, 30 533 collected reflections, 5827 crystallographically independent reflections [$R_{\mathrm{int}} = 0.0732$], 3654 reflections with $I > 2\sigma(I)$, $\theta_{\max} = 25.00°$, $R(F_o) = 0.0377$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.0820$ (all data), 371 refined parameters. Compound **8**: triclinic, red rod, space group $P\bar{1}$, $a = 12.7437(3)$, $b = 12.9350(5)$, $c = 18.0635(4)$ Å, $\alpha = 84.0140(10)$, $\beta = 77.879(2)$, $\gamma = 61.5040(10)°$, $V = 2558.48(13)$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.438\mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.496\ \mathrm{mm^{-1}}$, 21 375 collected reflections, 8964 crystallographically independent reflections [$R_{\mathrm{int}} = 0.0152$], 7802 reflections with $I > 2\sigma(I)$, $\theta_{\max} = 25.00°$, $R(F_o) = 0.0375$ ($I > 2\sigma(I)$), $wR(F_o^2) = 0.0942$ (all data), 677 refined parameters. The data of **4a** and **8** were collected on a Oxord Diffraction Xcalibur S Sapphire at 150(2) K ($\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[13] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Absorption corrections were performed by using the SCALE3 ABSPACK program.[14] CCDC 716094 (**4a**) and 716095 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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