A two-coordinate Ni(I) silyl complex: CO2 insertion and oxidatively-induced silyl migrations

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Ryan J. Witzke[a] and T. Don Tilley[a*]

The synthesis and reactivity of the first open-shell two-coordinate silyl complex, (IPr)Ni–Si(SiMe$_3$)$_3$, (IPr = 1,3-di(2,6-di-*iso*-propylphenyl)imidazolin-2-ylidene) is reported. Reaction with CO_2 results in a novel κ^2-silylcarboxylate insertion product that possesses a distorted geometry. Oxidations of the Ni center, with $[Cp_2Fe][B(C_6F_5)_4]$ and Ph_3CCl, result in migratory rearrangements of the silyl ligand, apparently via related silylene intermediates. The distinct oxidation products are interconverted by reactions that introduce or remove chloride ($[Bu_4N]Cl$ and $LiB(C_6F_5)_4$, respectively).

There is considerable interest in the expansion of transition-metal silicon chemistry to new structural types, chemical conversions, and catalytic reactions.[1–6] Notably, much of the progress in this field is associated with a relatively narrow range of structure types for metal-silicon complexes involving saturated metal centers and commonly employed ancillary ligands such as cyclopentadienyl and phosphines. However, recent years have seen advances in catalytic applications of metal-silicon chemistry with exploration of unsaturation at both the transition-metal center[7,8] and silicon.[1] For example, the development of new compounds with electrophilic silylene[6,9–11] and σ-silane[1,12–15] ligands have enabled new mechanisms for hydrosilation catalysis. In addition, the enforcement of unsaturation at the metal center may be a factor in the performance of new hydrosilation catalysts based on the first-row transition-metals.[5,16,17] Thus, transition-metal silyl complexes with exceedingly low coordination numbers are expected to exhibit high reactivities and possibly new types of chemical conversions.[18]

This laboratory reported the two-coordinate Ni(II) amido complex $Ni[N(SiMe_3)DIPP]_2$ (DIPP = 2,6-$^iPr_2C_6H_3$) as an active alkene hydrosilation catalyst,[7] which operates by a yet unknown mechanism. This result further raises interest in developing an understanding of the chemical behavior of silyl ligands in exceedingly low-coordinate complexes. In this context, two-coordinate silyl complexes of open-shell transition-metals are unknown. However, previous attempts to obtain two-coordinate complexes of the bulky $–Si(SiMe_3)_3$ silyl ligand produced the three-coordinate species $\{M[Si(SiMe_3)_3]_2Cl\}^{\cdot-}$ (M = Cr, Mn, Fe) and $Fe[Si(SiMe_3)_3]_2(OEt_2)$.[19,20]

With the goal of isolating an open-shell, two-coordinate silyl complex, the investigation described here targeted the synthesis of an unsymmetrical monosilyl complex of Ni(I) with an N-heterocyclic carbene (NHC) co-ligand. Analogous d^{10} complexes of copper have been synthesized; however, reactivity studies have not been described.[21] The current study resulted in synthesis of the two-coordinate silyl complex (IPr)Ni–Si(SiMe$_3$)$_3$ (**1**), which has been subjected to the reactivity studies described below.

The yellow complex **1** (yellow-green in pentane) was synthesized by a salt metathesis reaction between $[(IPr)Ni(\mu\text{-}Cl)]_2$[22] and two equivalents of $(THF)_2KSi(SiMe_3)_3$[23] at ambient temperature in toluene, followed by crystallization from pentane in 56 % yield (eq. 1). The X-ray structure of **1** reveals a C–Ni–Si bond angle of 175.8(1)°, and Ni—Si and Ni—C bond lengths of 2.283(1) and 1.935(1) Å, respectively (Fig. 1). For comparison, the four-coordinate complexes $(I^iPr)_2Ni(SiR_2H)_2$ (R = Me, Et; I^iPr = 1,3-di-isopropyl-imidazolin-2-ylidene) possess average Ni—Si and Ni—C bond lengths of 2.253 Å and 1.924 Å, respectively.[24] The solution magnetic moment of **1**, determined by the Evans method, is 2.90 μ_B, which is higher than expected for a d^9 complex, presumably due to spin-orbit coupling. To the best of our knowledge, this is the first example of an open-shell two-coordinate transition-metal silyl complex.

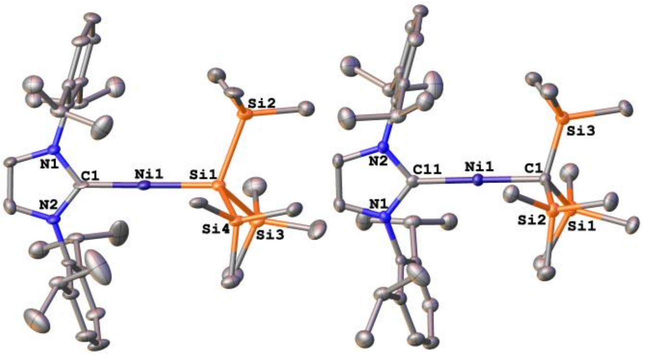

Fig. 1 Solid state structures of **1** (left) and **2** (right) shown with thermal ellipsoids at 50% probability. All hydrogens have been omitted for clarity.

The complex (IPr)Ni–C(SiMe$_3$)$_3$ (**2**) was obtained in a similar manner, by reaction of $[(IPr)Ni(\mu\text{-}Cl)]_2$ with 2 equivalents of

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[a] Department of Chemistry, University of California, Berkeley, California, USA. tdtilley@berkeley.edu

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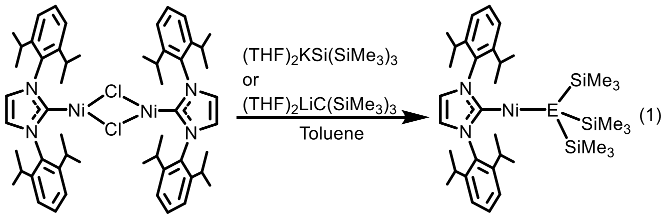
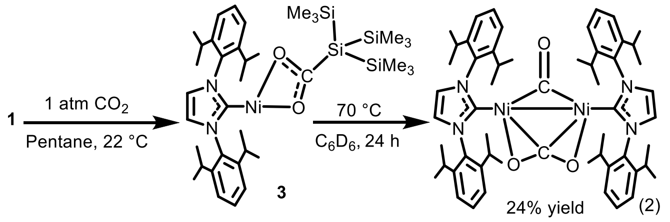
$(THF)_2LiC(SiMe_3)_3$[25] at -30 °C in toluene to give yellow crystals of **2** in 30 % yield (eq. 1). Complex **2** is also linear with a C–Ni–C bond angle of 175.9(12)° (Fig. 1), and Ni—C(alkyl) and Ni—C(NHC) bond lengths of 1.989(3) and 1.918(3) Å, respectively (Fig. 1). Hillhouse recently reported a similar two-coordinate complex, $(IPr)Ni–CH(SiMe_3)_2$, which has a slightly shorter Ni—C(alkyl) bond length of 1.968(3) Å, presumably due to the lower steric profile of the $–CH(SiMe_3)_2$ ligand. The solution magnetic moment of **2**, determined by the Evans method, is 3.01 μ_B and is also higher than the expected spin-only value.



E = Si (**1**), C (**2**)

The synthesis of **1** provided a compelling opportunity to explore the chemical properties of a silyl ligand in the unique coordination environment involving a paramagnetic, two-coordinate metal center. Furthermore, the availability of a carbon analogue, **2**, seemed to offer an interesting comparison. Treatment of **1** with one atmosphere of CO_2 (excess) resulted in formation of the κ^2-silylcarboxylate **3** *via* CO_2 insertion into the Ni—Si bond (eq. 2). Complex **3** has a distorted, T-shaped geometry (Fig. 2), with Ni—O bond distances of 1.978(1) and 2.078(1) Å. The two C—O bond lengths (1.252(2) and 1.263(1) Å) are approximately identical and indicate significant π-delocalization in the CO_2 fragment.



To our knowledge, there are only two other examples of CO_2 insertions into transition-metal—silicon bonds, involving the silyl complexes $Cp_2ScSiR_3(THF)$ (R_3 = $(SiMe_3)_3$, $^tBuPh_2$) and $(IPr)CuSiMe_2Ph$.[26,27] The resulting scandium product is dimeric, with bridging $–O_2CSiR_3$ ligands, whereas the Cu(I) ion is linearly coordinated by the NHC and carboxylate with no dative interaction from the carbonyl oxygen.

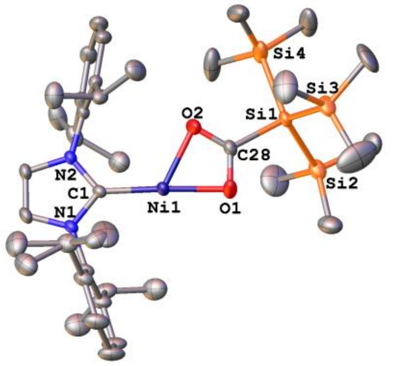
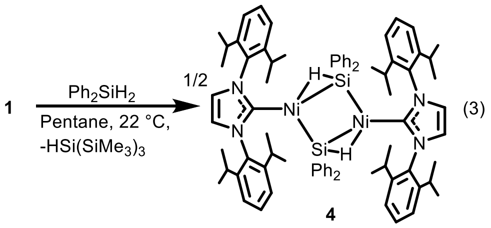


Fig. 2 Solid state structure of **3** with thermal ellipsoids at 50% probability. A rotationally disordered $–Si(SiMe_3)_3$ group and all hydrogens have been omitted for clarity.

Note that in general, a $MOC(O)SiR_3$ linkage is unstable toward formation of siloxide species, as found for silyl esters $(Me_3Si)_3SiCO_2SiR_3$ (R = Me, Ph, $SiMe_3$), which eliminate CO upon heating to give the corresponding disiloxanes.[28] Also, Marder found that $(IPr)CuO_2CSiMe_2Ph$ slowly extrudes CO to form the siloxide.[27] For comparison, complex **3** was observed to thermally decompose upon heating (70 °C, 24 h) to produce a mixture of products including $[(IPr)Ni]_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}CO_2)$ in 24% yield (eq. 2; by ^1H NMR spectroscopy). This complex was previously synthesized and characterized by Sadighi *et al*. by treatment of $[(IPr)Ni]_2$ with CO_2.[29] The fate of the silyl ligand remains unknown, and a ^1H NMR spectrum of the reaction mixture suggests formation of a complex mixture. The identified product indicates that **3** undergoes competitive CO- and CO_2-deinsertion.

Treatment of **1** in C_6D_6 with one atmosphere of CO resulted in reduction to Ni(0) with formation of $(IPr)Ni(CO)_3$[30] (65% after 24 h at 22 °C, by ^1H NMR spectroscopy). Similarly, treatment of **1** with an atmosphere of ethylene resulted in formation of $(IPr)Ni(C_2H_4)_2$[30] in 93% yield after 24 h at 22 °C. In each of these cases a complex mixture of silicon-containing products formed.

Reaction of **1** with diphenylsilane in toluene gave a precipitate of $[(IPr)Ni(\mu\text{-}SiHPh_2)]_2$ (**4**) in 64% isolated yield. This reaction involves silyl exchange to form $HSi(SiMe_3)_3$ (observed by ^1H NMR) and presumably $(IPr)NiSiHPh_2$, which then dimerizes to give **4** (eq 3). X-ray quality crystals of **4**, grown by layering a solution of Ph_2SiH_2 onto a solution of **1** in pentane, allowed for a structural determination. This complex possesses two different Ni–Si bond distances (2.257(1) and 2.200(1) Å), and this asymmetry is associated with two Ni-H-Si interactions on opposite sides of the molecule (these hydrogens were located in the electron difference map). Additionally, the Ni---Ni distance is 2.553(1) Å. Analogous $[(L)Ni(\mu\text{-}SiHPh_2)]_2$ complexes have been reported (L = PCy_3, P^iPr_3, and I^iPr), and a structural comparison shows that the identity of the L-type ligand has little effect on the Ni_2Si_2 core structure.[24,31,32] A comparable Co complex, $[(IPr)Co(\mu\text{-}SiHPh_2)]_2$ was recently reported by Deng and coworkers.[33] Similar to the Co analogue, **4** is only slightly soluble, impeding further characterization by NMR spectroscopy.



Alkyl complex **2** proved to be very unreactive, presumably due to its steric congestion. Treatment of **2** with an atmosphere of CO_2 resulted in no reaction after 1 h at 22 °C and decomposition after 1 h at 60 °C (in benzene-d_6, by NMR spectroscopy). Similarly, treatment with C_2H_4 or Ph_2SiH_2 gave no reaction after 24 h at 22 °C. Thus, the much lower reactivity of **2** may be attributed to its sterically protected metal center (resulting from the shorter bonds associated with the alkyl ligand) and perhaps to the presence of a stronger Ni—C (vs. Ni—Si) bond.

Cyclic voltammetry (CV) studies were performed to learn more about the range of oxidation states available to complexes **1** and **2**. Each complex exhibits two irreversible oxidations in *ortho*-difluorobenzene (*o*-DFB). (Complex **1** at -0.32 and 0.60 V vs. Cp_2Fe/Cp_2Fe^+; complex **2** at -0.089 and 1.22 V vs. Cp_2Fe/Cp_2Fe^+). Additionally, both complexes were resistant to electrochemical

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reduction to 2.70 V. An attempt to chemically reduce **1** with 1.1 equivalents of KC_8 at -78 °C in toluene produced a red crystalline product that was not characterized due to its thermal instability. Similar attempts to reduce and oxidize **2**, with one equivalent of KC_8 or $[Cp_2Fe][B(C_6F_5)_4]$, have not yet provided well-defined products.

Consistent with the observed irreversibility of electrochemical oxidation, the chemical oxidation of **1** results in substantial rearrangement chemistry. A solution of **1** in *o*–DFB reacted with $[Cp_2Fe][B(C_6F_5)_4]$ to give red crystals after workup. Surprisingly, X-ray crystallography revealed that the product (**5**) results from fragmentation of the silyl ligand with formation of a Ni—$SiMe(SiMe_3)_2$ linkage, a $SiMe_2$ ligand that bridges to the carbene carbon atom (now dissociated from the metal), and the DIPP-bound Ni center (Fig. 3).

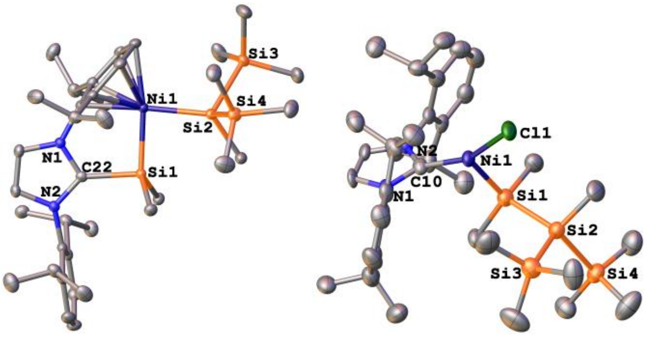


Fig. 3 Solid state structure of **5** (left) and **6** (right) with thermal ellipsoids at 50% probability. The $B(C_6F_5)_4$ anion of **5** and all hydrogen atoms were omitted for clarity.

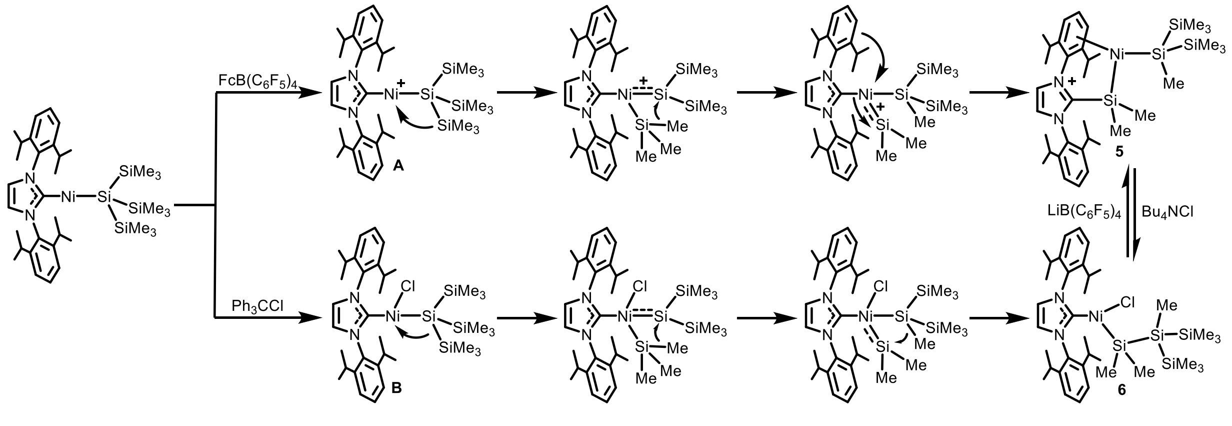
A likely mechanism for this process is illustrated in Scheme 1, which proposes that oxidation to $[(IPr)Ni–Si(SiMe_3)_3]^+$ initiates migration of a $–SiMe_3$ group to the cationic Ni(II) center. This oxidatively induced α-migration is followed by 1,3-transfer of a methyl group to generate a dimethylsilylene ligand. Finally, the IPr ligand shifts to provide donor-stabilization to the silylene, and η^6-coordination of the DIPP group to Ni. Note that previous work from this laboratory showed that attempts to generate the silyl complexes $(Me_3P)_3M–Si(SiMe_3)_3$ (M = Rh or Ir) produced unobserved, reactive intermediates that appear to result from similar sequences of 1,2-silyl and 1,3-methyl migrations.[34,35] In the case of Rh, an apparent $Rh(=SiMe_2)[SiMe(SiMe_3)_2]$ intermediate was trapped with 2-butyne. Oxidation of **1** at -77 °C resulted in formation of a purple solution indicative of a potential intermediate. However, attempts to trap intermediates with acetonitrile, diphenylacetylene, and bis(trimethylsilyl)acetylene were unsuccessful. In each case, **5** was the only observed product.

Treatment of **1** with a different oxidant, trityl chloride, allowed isolation of a second oxidation product related to **5**, $(IPr)NiCl[SiMe_2SiMe(SiMe_3)_2]$ (**6**; Fig. 3). The formation of **6** appears to involve a similar set of migration steps; however, the presence of the chloride ligand prevents a change in coordination mode for IPr. Trityl chloride likely acts as an inner sphere oxidant to form $(IPr)NiCl[Si(SiMe_3)_3]$ which then undergoes migrations to form **6** (Scheme 5). To provide more evidence for this process, $[(IPr)NiCl(\mu\text{-}Cl)]_2$[36] was treated with $(THF)_2KSi(SiMe_3)_3$ in toluene to independently generate the putative, transient intermediate $(IPr)NiCl[Si(SiMe_3)_3]$, and indeed this reaction produced **6** in 52.2% yield (by ^1H NMR spectroscopy).

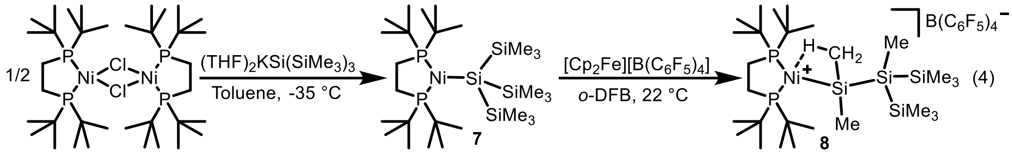
Given the structural similarities between **5** and **6**, it would seem that they form *via* analogous mechanisms. In support of this, the two complexes are readily interconverted (Scheme 1). Thus, addition of one equivalent of $[Bu_4N]Cl$ to **5** produced **6** as the sole product in 84% isolated yield, and a salt metathesis reaction between **6** and $LiB(C_6F_5)_4$ gave **5** in 54% isolated yield.

The two pathways outlined in Scheme 1 suggest that the 1,2-migration of a silyl group to Ni(II) is possible in both two- and three-coordinate geometries (in intermediates **A** and **B**). To further probe this question, a new three-coordinate silyl complex, $(dtbpe)Ni–Si(SiMe_3)_3$ (**7**, dtbpe = $1,2\text{-}{}^tBu_2PCH_2CH_2P^tBu_2$), was synthesized *via* a salt metathesis reaction between $[(dtbpe)Ni(\mu\text{-}Cl)]_2$ and 2 equivalents of $(THF)_2KSi(SiMe_3)_3$ at -35 °C in toluene (eq. 4). Crystallization of **7** in 61% yield gave maroon crystals. The solution magnetic moment of **7**, determined by the Evans method, is 1.42 μ_B, consistent with a d^9, S = ½ complex.

Complex **7** is structurally similar to a three-coordinate silyl complex synthesized by the Hillhouse group, $(dtbpe)Ni–SiHMes_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$),[37] which undergoes an oxidatively-induced 1,2-hydrogen migration from Si to Ni(II). Treatment of **7** with one equivalent of $[Cp_2Fe][B(C_6F_5)_4]$ in *o*-DFB gave orange crystals of **8**, that by X-ray crystallography contain a rearranged silyl ligand identical to that of complex **6** (eq. 4). This is consistent with the hypothesis that three-coordinate Ni(II) can participate in this type of rearrangement. The structure (Fig. SC7, ESI) also features an agostic C-H-Ni interaction involving a silicon-bound methyl group. Attempts to observe evidence of the agostic interaction by IR spectroscopy (KBr pellet) and variable temperature ^1H NMR spectroscopy (down to -73 °C, toluene-d_8) were unsuccessful.



Scheme 1. Proposed mechanisms for oxidative rearrangements of **1**. $B(C_6F_5)_4^-$ anion omitted for clarity.



In summary, the studies described above give an initial description of the behaviour of a silyl ligand in the coordination sphere of a two-coordinate, 3*d*-metal center. The open-shell nature of complex **1** is also a very rare property for silyl complexes that may well contribute to discovery of new reactivity modes. Indeed, the observed reactivity for **1** is quite pronounced relative to that typically associated with late metal silyl derivatives, and compared to the analogous alkyl derivative **2**. Note that late-metal silyl complexes are usually more stable, and less reactive, than corresponding alkyl derivatives - especially toward insertion chemistry.[38,39] The observed insertion of CO_2 into the Ni(I)–Si bond of **1**, resulting in a novel coordination mode for the κ^2-silylcarboxylate **3**, is notable with respect to the growing interest in Ni(I) species for catalytic CO_2 activation.[40,41] In this context, it may be relevant that the Ni(I)–Si bond is also reactive toward silyl exchange and an Si–H bond activation in Ph_2SiH_2.

Interestingly, the electron count at Ni plays a critical role in defining reactivity for the silyl ligand in this two-coordinate system. Removal of an electron greatly activates the $–Si(SiMe_3)_3$ toward migration chemistry in the presumed $[(IPr)Ni^{II}–Si(SiMe_3)_3]^+$ intermediate, and promotes a likely 1,2-migration of a $–SiMe_3$ group to nickel that initiates the observed rearrangement to **5**. The rearrangements to **6** and **8** presumably occur via the three-coordinate intermediates, $(IPr)Ni^{II}Cl[Si(SiMe_3)_3]$ and $[(dtbpe)Ni^{II}–Si(SiMe_3)_3]^+$, and the coordination number at the Ni center seems to have a strong influence on the eventual silyl migration product.

The likely involvement of silylene ligands in this rearrangement chemistry suggests possibilities for catalytic processes involving nickel silylene intermediates.[1,6,9,11,42,43] Very few α-migrations have been identified for open-shell 3*d* metals,[44] but a more thorough understanding of such fundamental steps are expected to enable new transformations for these more sustainable metals. Future investigations of low-coordinate species of this type will focus on this possibility.

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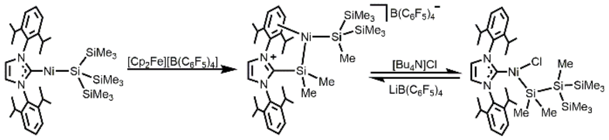

Synthesis of first open-shell two-coordinate silyl complex and its oxidatively-induced silyl rearrangements.