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Nickel as a Lewis Base in a T-Shaped Nickel(0) Germylene Complex Incorporating a Flexible Bis(NHC) Ligand

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Abstract: Flexible, chelating bis(NHC) ligand **2**, able to accommodate both *cis*- and *trans*-coordination modes, was used to synthesize (**2**)Ni(η^2-cod), **3**. In reaction with $GeCl_2$, this produced (**2**)NiGeCl$_2$, **4**, featuring a T-shaped Ni(0) and a pyramidal Ge center. Complex **4** could also be prepared from [(**2**)GeCl]Cl, **5**, and Ni(cod)$_2$, in a reaction that formally involved Ni-Ge transmetalation, followed by coordination of the extruded $GeCl_2$ moiety to Ni. A computational analysis showed that **4** possesses considerable multiconfigurational character and the Ni→Ge bond is formed through σ-donation from the Ni 4s, 4p, and 3d orbitals to Ge. (NHC)$_2$Ni(cod) complexes **9** and **10**, as well as (NHC)$_2$GeCl$_2$ derivative **11**, incorporating ligands that cannot accommodate a wide bite angle, failed to produce isolable Ni-Ge complexes. The isolation of (**2**)Ni(η^2-Py), **12**, provides further evidence for the reluctance of the (**2**)Ni(0) fragment to act as a σ-Lewis acid.

The Lewis basicity of transition metals plays a key role in the formation of their complexes.[1] This includes the concepts of back bonding, as well as Z-type ligands[2] and metal-only Lewis pairs[3] for the most basic metals, with the latter leading to metal-only frustrated Lewis pairs.[4] In agreement with the increase in basicity for the heavier transition elements,[1,5] little has been reported so far on the chemistry of nickel Lewis bases,[3,6] in stark contrast to platinum.[3] Among the most basic compounds of nickel are the dicoordinate Ni(0) complexes, which are linear and highly reactive.[7] As opposite to Pd(0) and Pt(0), where dicoordinate complexes with phosphine and N-heterocyclic carbene (NHC) ligands are common, L$_2$Ni(0) complexes were isolated exclusively with bulky NHC substituents, even though the phosphine analogs are commonly postulated active species in Ni(0)-Ni(II) catalytic cycles.[8,9] (NHC)$_2$Ni(0) derivatives proved to be proficient precatalysts in a number of bond-forming transformations,[10] and their stoichiometric chemistry targeted

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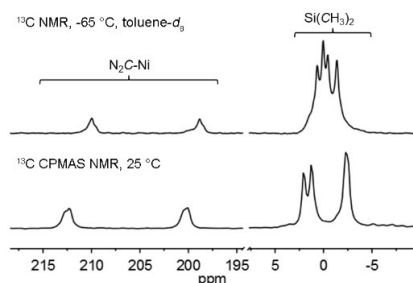11227 Saskatchewan Drive NW, Edmonton, AB, T6G 2G2 Canada

mostly the related oxidative addition reactions leading to Ni(I) and Ni(II) complexes.[11] While L$_2$Pt(0) moieties have been shown to act as lone pair donors in a variety of complexes,[12] there is no record of the lighter Ni congeners being able to emulate this binding mode.
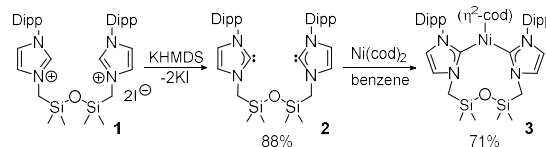
Scheme 1. Synthesis of ligand **2** and its complex **3**.

Aiming to investigate the Lewis acid-base chemistry of (NHC)$_2$Ni(0) species, we designed the flexible, chelating dicarbene ligand **2** that could stabilize both the linear Ni(0) starting material and its tri- and tetracoordinated reaction products expected to feature narrower C$_{NHC}$-Ni-C$_{NHC}$ angles. It was prepared from **1** (Scheme 1), and its reaction with Ni(cod)$_2$ afforded the pentane-soluble, thermally sensitive η^2-cyclooctadiene complex **3**. (NHC)$_2$Ni(η^2-cod) and (NHC)$_2$Ni(η^4-cod) complexes have been used extensively as precursors in lieu of (NHC)$_2$Ni.[13] The NMR analysis of diamagnetic derivative **3** was hindered by broad, poorly resolved resonances between 25 and -65 ºC. It was postulated that this was a consequence of conformational fluxionality involving flipping of the siloxane backbone and the reciprocal arrangement of the Dipp (2,6-di*iso*propylphenyl) substituents. A solid-state ^{13}C NMR spectrum featured four resonances corresponding to Me$_2$Si, and two resonances corresponding to the coordinated carbene carbons (200.2 and 212.5 ppm), as expected when they are not related through site symmetry. It mirrored the solution spectrum acquired at -65 ºC (Figure 1), indicating that a similar local chemical environment was preserved on NMR time scale due to reduced conformational fluxionality.

X-ray diffractometry revealed that **3** had a Y-geometry at nickel with chelating ligand **2** and η^2-1,5-cyclooctadiene completing the coordination sphere of the metal (Figure 2). The C1-Ni1-C19 angle measures 110.40(1)º, and there is substantial steric crowding around the metal (Figure S10), as well as an anagostic interaction involving the backbone. The postulated siloxane backbone ring flipping was modeled using DFT, and a barrier of 90 kJ·mol^{-1} was found for swapping the orientations of the NHC rings, accounting for the observed lack of time-averaged C_s-symmetry at low temperature in solution.

Figure 1. Selected regions from the solution and solid-state ^{13}C NMR spectra of **3**.

been documented for Ni(I),[17] Ni(II),[11d,18] and Ni(III),[18b,c] but so far not for Ni(0), although it is ubiquitous for the isoelectronic Cu(I).[19]

Scheme 2. Synthesis of T-shaped Ni(0) complex **4**.

Temperature-sensitive **4** was prepared via the reaction of **3** with GeCl$_2$ (Scheme 2). Its solution NMR characterization was also hindered by conformational equilibria leading to complex spectra and broad resonances. The solid-state ^{13}C NMR spectrum featured resonances in the expected ranges, including a prominent one corresponding to the carbene carbons at 182.2 ppm. An X-ray diffraction experiment revealed a (**2**)Ni-GeCl$_2$ structure featuring a T-shaped, tricoordinated nickel with a weak (<10 kJ·mol^{-1} by DFT) anagostic interaction *trans* to germanium (Figure 3). On undergoing the transformation from **3** to **4**, the bite angle of the chelating bis(NHC) ligand widens substantially, from 110.42(13)º to 167.2(3)º. Both *cis*- and *trans*-binding bis(NHC) complexes are known,[14] and interconversions of the two binding modes are known for non-chelating NHCs.[15] The ring-flipping barrier in **4** was calculated to be only 50 kJ·mol^{-1}.
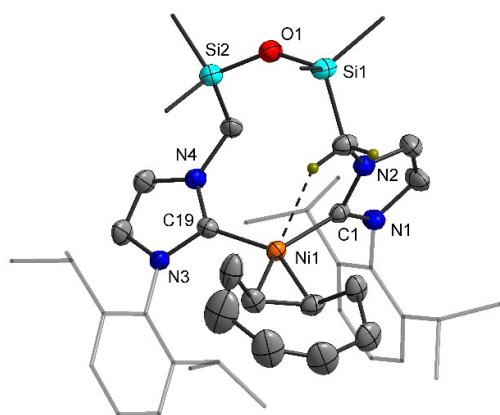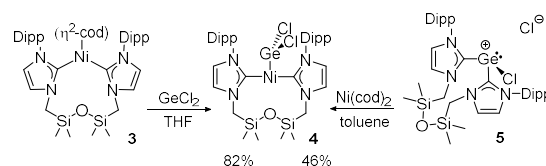

Figure 2. Solid-state structure of **3** with 50% probability ellipsoids. Most hydrogen atoms have been removed for clarity. Selected bond distances [Å] and angles [º]: Ni1-C 1.884(3), 1.911(3), Ni1···H 2.51(3), C1-Ni1-C19 110.42(13).

Very similar (Cy$_3$P)$_2$Pt^0-ECl$_2$ and (Cy$_3$P)(IMes)Pt^0-ECl$_2$ complexes (E = Ge, Sn, Pb; P-Pt-P = 156.90(3) - 163.62(2)º; C-M-P = 165.11(7) - 166.37(7)º) have been reported.[12] In these analogues the metal-metalloid bond was described as featuring mainly σ-electron donation from Pt.[12b,d,16] The T-geometry has
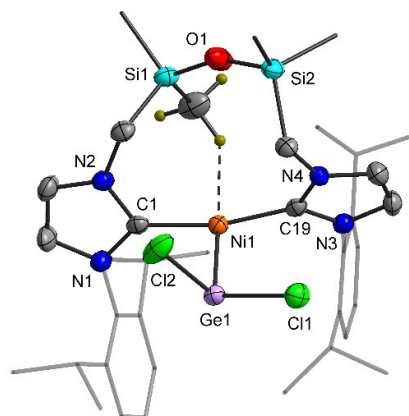

Figure 3. Solid-state structure of **4** with 50% probability ellipsoids. Most hydrogen atoms have been removed for clarity. Selected bond distances [Å] and angles [º]: Ni1-Ge1 2.2854(11), Ni1-C 1.902(7), 1.884(7), Ge1-Cl 2.340(2), 2.3363(18), Ni1···H 2.47(4), C1-Ni1-C19 167.2(3), C-Ni1-Ge1 92.96(19), 97.26(19), Cl1-Ge1-Cl2 94.69(4), Ge1-Ni1···H 172.8(9).

The singlet DFT solution of **4** showed symmetry breaking, indicative of multiconfigurational character. Multireference QD-NEVPT2//CASSCF calculations performed on a simplified model system **4'** (see ESI) confirmed that the wave function consists of three major configurations: a closed-shell Ni 3d^{10} configuration (21 %) and two open-shell Ni 3d^9 configurations (26 and 21 %) with a Ni-Ge bonding interaction. The nature of the metal-metalloid bond can be understood by analyzing the fractionally occupied natural orbitals of **4'** in terms of the fragments (**2'**)Ni(0) and GeCl$_2$ (Figure 4; see Figure S15 for a more complete diagram). Altogether nine electrons occupy the five Ni$_{3d}$ orbitals in **4'** (146-150), with the tenth electron distributed over three orbitals (151-153) composed of the Ge$_{4p}$ orbital of GeCl$_2$ (orbital 34) along with the bonding and antibonding combinations of C$_{2p}$ and Ni$_{4s-4p}$ orbitals of (**2'**)Ni(0) (orbitals 118 and 119). Of these, orbital 151 is clearly metal-metalloid bonding and, for the most part, responsible of the stability of the complex **4'**. Furthermore, the 3d$_{z^2}$ orbital of Ni (orbital 115) shows some delocalization onto Ge$_{4p}$ (orbital 34), giving rise to a minor bonding component (orbital 148). Thus, two separate dative Ni→Ge interactions play a role in stabilizing **4'**. In contrast, the GeCl$_2$ lone pair (orbital 33)

has only a minor influence on the metal-metalloid bond as back-bonding interactions are virtually absent in **4'** (orbital 145).
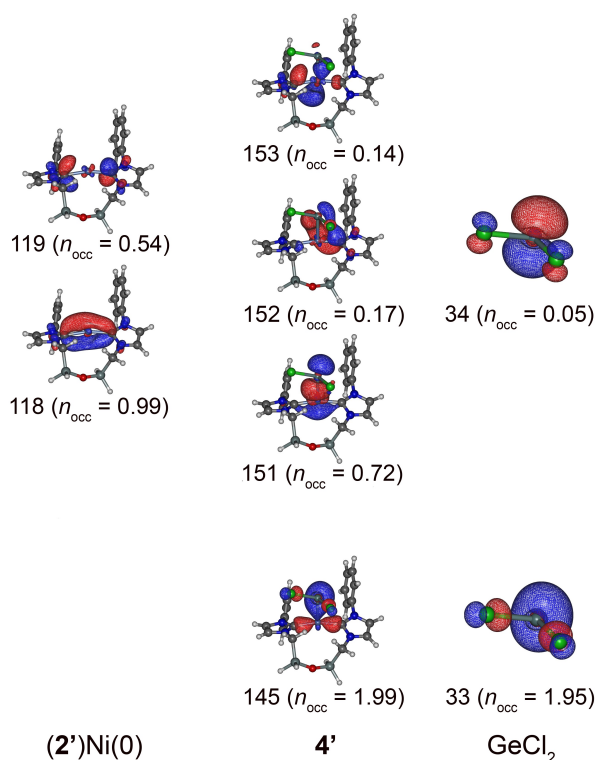

153 (n_{occ} = 0.14)

119 (n_{occ} = 0.54)

152 (n_{occ} = 0.17)   34 (n_{occ} = 0.05)

118 (n_{occ} = 0.99)

151 (n_{occ} = 0.72)

145 (n_{occ} = 1.99)   33 (n_{occ} = 1.95)

(2')Ni(0)   **4'**   GeCl$_2$

Figure 4. Selected natural orbitals of (2')Ni(0), **4'** = (2')Ni→GeCl$_2$, and GeCl$_2$ with their occupancies.

The frontier orbitals of **4'** suggest a non-integer oxidation state of +½ for Ni, assuming that the electrons in orbitals 151-153 are distributed equally between Ni and Ge. However, considering the relative importance of the 3d^{10} configuration on the overall wave function and the lack of any significant contribution from configurations in which the Ge$_{4p}$ orbital is doubly occupied, the system is best approximated as a Ni(0) complex in which the electrons forming the dative metal-metalloid bond are exclusively from Ni. The preference of **4** for a T-shaped geometry over the Y-shape usually observed in three-coordinate Ni(0) complexes[19] can be rationalized with the bonding interaction in orbital 118 of (2')Ni(0): any bending of the C–Ni–C moiety would weaken the C-Ni bonds and, consequently, destabilize also the metal-metalloid bond in **4'** (orbital 151). The importance of d^{9}s^1 vs. d^{10}s^0 electron configurations in the chemistry of nickel and its heavier congeners has been discussed,[20] and the T-geometry for tricoordinate d^9-nickel complexes, albeit in oxidation state I, is well documented.[17]

The Ni-Ge bond in **4** (2.2854(11) Å) is slightly longer than that recorded in the related, Y-shaped Ni(0) complexes (Ph$_3$P)$_2$Ni-GeX$_2$ (X = [(N(SiMe$_3$)$_2$], 2,4,6-(CF$_3$)$_3$C$_6$H$_2$) (2.206(1) and 2.1814(7) Å). The Ni-Ge interaction in these derivatives was

described as a classic case of σ-bonding, π-backbonding with a planar, σ-donating germylene.[21] The acute P-Ni-P angles in the latter compounds (113.81(4) and 118.10(5)° vs. C-Ni-C 167.2(3)° in **4**) and the planar coordination environment at germanium (vs. pyramidal with a Ni-Ge/GeCl$_2$ angle of 66.2(3)° in **4**) strongly suggest a different Ni-Ge binding mode. N-heterocyclic germylenes (NHGes) have lower Lewis acidity than GeCl$_2$ owing to N→Ge-π-donation, and it was of interest to assess the impact of this factor on the Ni-Ge bonding. The reaction of **3** with a neopentyl substituted NHGe[22] resulted in ligand displacement (Scheme 3) with formation of a homoleptic Ni(NHGe)$_4$ complex (Figure S6).
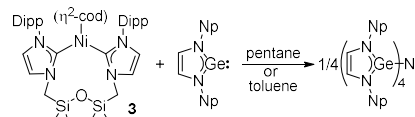

Scheme 3. Reaction of **3** with an N-heterocyclic germylene.

Germylene and stannylene complexes **5** and **6** were prepared as shown in Scheme 4. The broad resonances in the room temperature ^{1}H NMR spectrum of **5** sharpened upon cooling in a manner typical for conformational equilibrium in the slow exchange regime. A lineshape analysis yielded the activation parameters ΔH$^{\neq}$ = 32.7 kJ·mol^{-1} and ΔS$^{\neq}$ = -96 J·mol^{-1}·K^{-1}, suggesting an associative chloride exchange rather than ring flipping dynamics.[23] Complex **5** crystallizes as an ion pair, [(**2**)GeCl]Cl (Figure S4), while **6** has a disphenoidal (**2**)SnCl$_2$ structure (Figure S5). Reaction of Ni(cod)$_2$ with **5** led to transmetalation where Ni(0) replaced GeCl$_2$, followed by coordination of the extruded metalloid fragment to Ni(0) to form complex **4** (Scheme 2). This type of castling reaction relying on the Lewis-amphoteric properties of germanium is to our knowledge unprecedented.
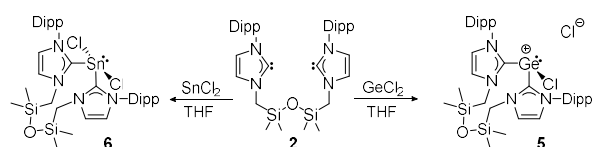
Scheme 4. Synthesis of complexes **5** and **6**.

To explore whether the ability of **2** to accommodate a wide range of bite angles was essential to the chemistry reported above, cis-chelators **7** and **8**[24] were used to prepare nickel complexes **9**[13d] and **10** (Figure S7), as well as germanium derivative **11** (Scheme 5, Figure S8). Reactions of **9** or **10** with GeCl$_2$, and reaction of **11** with Ni(cod)$_2$ produced intractable mixtures of products. While the influence of the N-substituent (Dipp vs tBu) on the stability of compound **4** cannot be neglected,[25] this result confirms that the ability of ligand **2** to stabilize (NHC)$_2$Ni-GeCl$_2$ species is exceptional.
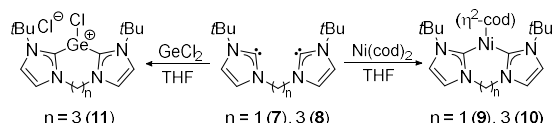
Scheme 5. Synthesis of derivatives **9-11**.

The reaction of **3** with pyridine produced an equilibrium mixture from which pyridine π-adduct **12** was isolated by crystallization (Figure 5). The η^2-coordination mode has been observed for L_2Ni(0) species (L = R_3P, NHC) with quinoline and N-coordinated pyridine.[9a, 26 a] The preference for π *vs.* σ-coordination in **12** highlights the reluctance of the (NHC)$_2$Ni(0) fragment to act as a σ-Lewis acid.[26b]
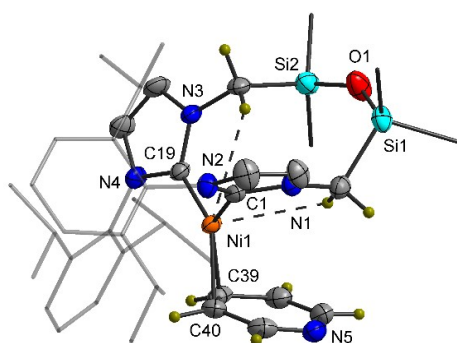

Figure 5. Solid-state structure of **12** with 50% probability ellipsoids. Most hydrogen atoms have been removed for clarity. Selected bond distances [Å] and angles [º]: Ni1-C1 1.922(3), Ni1-C19 1.915(3), Ni1···H 2.76(4), 2.82(3), C1-Ni1-C19 116.28(15).

In conclusion, chelating, flexible bis(NHC) ligand **2** can accommodate a wide range of bite angles, from 93.0(3)º in **6** to 167.2(3)º in **4**. It formed Ni(0) complexes **3**, **4**, and **12**, with good crystallization properties and complex NMR spectra, owing to slow equilibria between several conformers. Nickel-germanium complex **4**, which displays a T-geometry that is unprecedented for Ni(0), could be prepared either via substitution of COD by GeCl$_2$ in **3**, or via transmetallation of **5** with Ni(cod)$_2$, followed by coordination of the extruded metalloid fragment to Ni, in a unique castling-like reaction. The unusual Ni-Ge bonding in **4** is best described as a dative Ni(0)→Ge(II) interaction with two components: a weak σ-donation from Ni_{3d} to Ge_{4p}, representing a minor contribution, and a one-electron σ-donation from Ni_{4s-4p} to GeCl$_2$. The poor σ-Lewis acidity of the 14-valence-electron (NHC)$_2$Ni(0) fragment is further supported by the formation of η^2-pyridine adduct **12**. Chelating ligands **7** and **8**, which cannot accommodate wide bite angles, were unable to support Ni-Ge complexes analogous to **4**, and neither were N-heterocyclic germylenes due to their lower Lewis acidity. This work proves that, with the judicious choice of ligands, nickel-only Lewis bases can parallel the remarkable reactivity previously observed only for the more basic platinum analogues. It also shows that the

d^9s^1 electronic structure can play an important role in the chemistry of metal complexes usually typecast as $3d^{10}$.

Experimental Section

Experimental details, NMR spectra, computational details, as well as the relevant crystallography tables are provided in the Supporting Information. CCDC 1861471-1861479 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: N-heterocyclic carbene • nickel • metal-only Lewis pairs • germanium • T-geometry

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