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# Silyliumylidene Ion Stabilized by Two $\sigma$ -Donating Ni(0)- and Pd(0)-Fragments

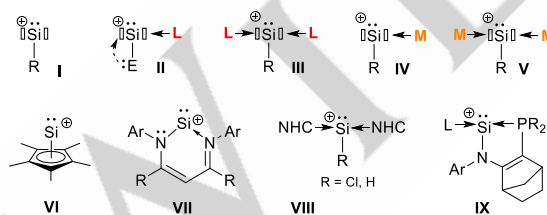
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**Abstract:** A silyliumylidene ion **2** stabilized by two  $\sigma$ -donating Ni(0)- and Pd(0)-fragments was successfully synthesized. Due to the  $\sigma$ -donation of M $\rightarrow$ Si interactions, **2** presents a pyramidalized cationic silicon center with a localized lone pair. The additional coordination of basic Pd(0) fragment to the mono-Ni(0)-stabilized silyliumylidene **1** results in a higher HOMO level and an unchanged HOMO-LUMO gap and thus, **2** remains highly reactive. Interestingly, the coordination mode at the Si center is closely related to the nature of M-ligands. Indeed, the donor/donor-stabilized silyliumylidene ion **2** has been transformed into a donor/acceptor-stabilized ion **13**, featuring a trigonal planar Si center with a vacant orbital, just via a ligand exchange reaction from PCy<sub>3</sub>/NHC toward PMe<sub>3</sub>.

Indeed, base-stabilized (amino)silyliumylidene ions **VII** (type **II**) have been isolated as stable complexes independently by Driess<sup>[6]</sup> and Aldridge<sup>[7]</sup> groups. A significant improvement has been provided by the introduction of a second  $\sigma$ -donating ligand (type **III**), allowing the isolation of small silyliumylidene ions **III** (R = H, Cl).<sup>[8]</sup> Thanks to an excellent stability, the parent silyliumylidene complex **VIII** (R = H) was successfully applied as an efficient catalyst for the hydroboration of carbonyl derivatives and *N*-formylation of amines.<sup>[9]</sup> We have also shown that the reactivity of silyliumylidene complexes **IX** can be controlled using different L-type ligands.<sup>[10]</sup> Even though numerous ligand-stabilized silyliumylidene ions **II** and **III** are available,<sup>[11]</sup> most of the L-ligands employed are limited to organic fragments and the use of transition metals (TMs) as  $\sigma$ -donating ligands remains scarce<sup>[12,13]</sup> despite the recent growing interest in Z-type ligands.<sup>[14]</sup> Indeed, the only example described to date is the mono-coordinated silyliumylidene **1** with a Ni(0)-based  $\sigma$ -donating ligand (type **IV**)<sup>[15]</sup> and, to the best of our knowledge, a silyliumylidene with two  $\sigma$ -donating TM-ligands **V** (metallic analogue of **III**) remains elusive, while several  $\mu$ -type bimetallic complexes of base-stabilized silyliumylidene ions have been described.<sup>[16]</sup> Here, we report the synthesis of silyliumylidene ion **2** stabilized by two Ni(0)- and Pd(0)-based  $\sigma$ -donating ligands (type **V**), which shows a high and unique reactivity allowing the synthesis of unprecedented hetero-binuclear complexes.

## Introduction



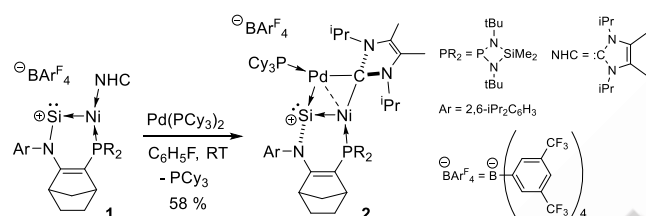
**Figure 1.** Silyliumylidene ion **I** and silyliumylidene complexes (**II** - **IX**).

Silyliumylidene ion **I**,<sup>[1]</sup> a Si(II) cation featuring a mono-substituted Si atom with a lone pair and two vacant orbitals, is generally a reactive transient species due to the highly electron-deficient cationic silicon center.<sup>[2,3]</sup> Although the chemistry of silyliumylidene ions has barely been developed due to their excessive instability/reactivity, since the first isolation of stable Cp<sup>\*</sup>-substituted silyliumylidene ion **VI**,<sup>[4]</sup> the situation has dramatically changed. Today, it is well established that such species can be thermodynamically stabilized by an electron-compensation through the coordination of  $\sigma$ -donating ligands (L) or the  $\pi$ -electron donation of Si-substituent (E) (Figure 1).<sup>[5]</sup>

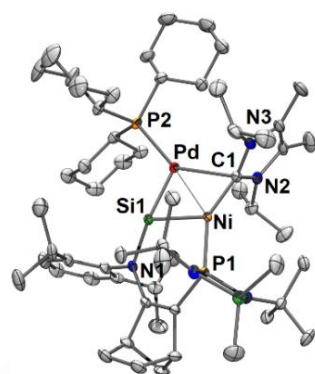
## Results and Discussion

Recently, we have synthesized a Ni(0)-stabilized silyliumylidene ion **1**<sup>[15]</sup>, from the corresponding neutral Si-chloro-substituted complex,<sup>[13]</sup> showing a particular coordination mode, probably promoted by the planar amidophosphine ligand forcing the coplanarity of Si/Ni moieties and favoring a T-shape geometry at the Ni center.<sup>[15]</sup> Silyliumylidene ion **1** is inherently electrophilic and readily reacts with a Lewis base (DMAP) affording a silyliumylidene complex with a mixed ligand system.<sup>[15]</sup> Thus, we

have considered the reaction of **1** with Pd(PCy<sub>3</sub>)<sub>2</sub> in order to introduce an additional electron-rich Pd(0) fragment. The reaction in C<sub>6</sub>H<sub>5</sub>F at room temperature cleanly affords cyclic silyliumylidene ion **2** supported by two  $\sigma$ -donating Ni(0)- and Pd(0)-centered ligands (Scheme 1). Complex **2** has been isolated as black crystals from a saturated C<sub>6</sub>H<sub>5</sub>F/pentane solution at -30 °C (yield: 58 %), and is stable at room temperature and quite persistent at 60 °C (*t*<sub>1/2</sub> = 2 days). **2** is thus more stable than the mono-ligated precursor **1** (*t*<sub>1/2</sub> = 2 days at room temperature). The <sup>31</sup>P-NMR spectrum exhibits an AX-system at 93.8 and 37.0 ppm (*J*<sub>PP</sub> = 57 Hz), in agreement with the presence of two phosphorus centers PR<sub>2</sub> and PCy<sub>3</sub> respectively. In the <sup>29</sup>Si-NMR spectrum, a doublet of doublets signal corresponding to the cationic Si atom was observed at 333.5 ppm (*J*<sub>SiP</sub> = 62.0 and 18.2 Hz), which is upfield shifted relative to that of precursor **1** (441 ppm)<sup>[15]</sup> but more strongly downfield shifted compared to Lewis base-stabilized silyliumylidene ions **III** (-82.3 – 1.5 ppm).<sup>[8,10]</sup> In the <sup>13</sup>C-NMR spectrum, the signal corresponding to the bridging carbon atom of NHC-ligand appears at 167.8 ppm (dd, *J*<sub>CP</sub> = 26.3 and 6.0 Hz).



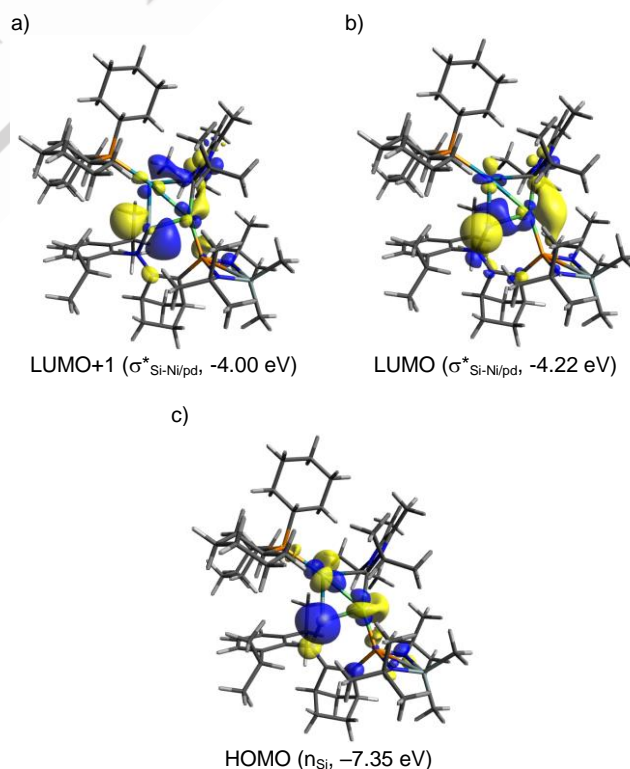
**Scheme 1.** Synthesis of Pd(0), Ni(0)-stabilized silyliumylidene ion **2**.



**Figure 2.** Molecular structure of **2**. Thermal ellipsoids represent 30 % probability. H and counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.761(2), Si1–Pd 2.256(1), Si1–Ni 2.135(1), Pd–Ni 2.559(1), Pd–C1 2.331(2), Ni–C1 1.946(2), Pd–P2 2.335(1), Ni–P1 2.143(1), Ni–Si1–N1 115.12(6), N1–Si1–Pd 133.79(6), Ni–Si1–Pd 71.25(2), Si1–Pd–P2 119.38(2), P2–Pd–C1 141.31(5), Si1–Pd–C1 98.64(5), Pd–C1–Ni 72.88(6), C1–Ni–P1 150.37(6), P1–Ni–Si1 91.84(2), C1–Ni–Si1 116.86(6).  $\Sigma^{\circ}$ <sub>Si1</sub> = 320.16°,  $\Sigma^{\circ}$ <sub>Ni</sub> = 359.07°,  $\Sigma^{\circ}$ <sub>Pd</sub> = 359.33°.

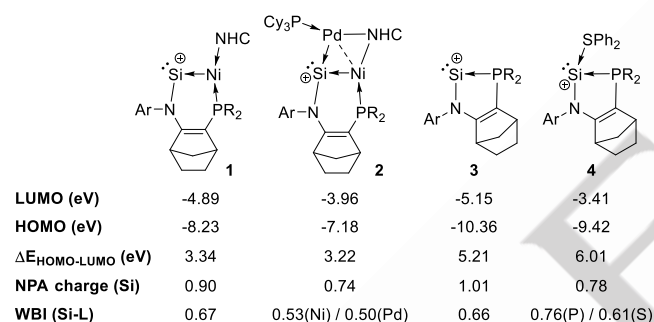
The structure of **2** was determined by X-ray crystallography which reveals a planar rhombic metallacycle (sum of interior angles: 359.60°) with Si-atom coordinated by both Pd(0)- and Ni(0)-fragments and the NHC ligand bridging the two metal centers (Figure 2).<sup>[17]</sup> The three-coordinate silicon center is strongly pyramidalized ( $\Sigma^{\circ}$ <sub>Si</sub> = 320.16°) similarly to the base-

stabilized silyliumylidene ions **III** ( $\Sigma^{\circ}$ <sub>Si</sub> = 273.9° – 328.7°).<sup>[8,10]</sup> This structural feature is in agreement with the presence of a localized lone pair at the Si-center and the two different TM-fragments attached to the vacant sites of Si center. Both TM centers in **2** adopt nearly planar ( $\Sigma^{\circ}$ <sub>Ni</sub> = 359.07°,  $\Sigma^{\circ}$ <sub>Pd</sub> = 359.33°) and distorted T-shape geometries with large P–M–C angles (P2–Pd–C1 141.3° and P1–Ni–C1 150.4°) similarly to **1** (P–Ni–C<sub>NHC</sub> 151.5°)<sup>[15]</sup> and other L<sub>2</sub>M(0)→E complexes (M = Ni, Pd, Pt, E = Lewis acid) [146.89(3) – 167.2(3)°].<sup>[14,18]</sup> The acuter P2–Pd–C1 angle than expected (ca. 150°) is certainly due to the steric congestion between bulky PCy<sub>3</sub> and aryl moieties. Indeed, with a simplified model **2'** (Me groups instead of *i*Pr, Cy, *t*Bu) the optimized structure shows the expected larger angle (P2–Pd–C1 154.6°). The Si1–Ni bond length [2.135(1) Å] is longer than that found for the mono-Ni(0)-coordinated complex **1** [2.108(1) Å], suggesting a reduced multiple bonding character due to the second TM-coordination. This value is at the upper limit of those observed for silylene→Ni(0) complexes featuring a certain Si=Ni double bond character (2.075 – 2.133 Å).<sup>[19]</sup> In contrast, the Si1–Pd bond length [2.256(1) Å] corresponds to a single bond [2.252 – 2.559 Å].<sup>[20]</sup> The distance between the bridging C1 (NHC) and Pd atoms [2.331(2) Å] is significantly longer than those of NHC→Pd(0) complexes [2.001(2) – 2.101(7) Å],<sup>[21]</sup> while the Ni–C1 bond length [1.946(1) Å] is similar to classical ones [1.92 – 1.94 Å]. It is worth noting that examples of complexes with a NHC ligand bridging two TMs are quite rare and most of them are coinage metal complexes<sup>[22–24]</sup> forming d<sup>10</sup>-d<sup>10</sup> interaction.<sup>[25]</sup> The Ni–Pd distance [2.559(1) Å] is shorter than the sum of covalent radii (2.73 Å),<sup>[26]</sup> while the Wiberg Bond Index (WBI) for this bond is negligible (0.08).



**Figure 3.** Molecular orbitals with their energy levels of **2** (a-c) calculated at M06/Def2TZVP//M06/6-31G(d) level of theory (isosurface level =  $\pm 0.045$  e/(a.u.)<sup>3</sup>).

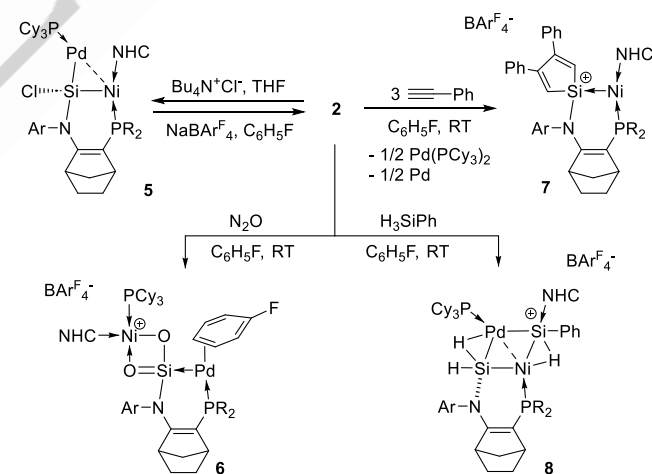
To gain further insight into the electronic properties of **2**, DFT calculation were performed at the M06/Def2TZVP//M06/6-31G(d) level of theory. As suggested by the strongly pyramidalized silicon center in **2**, the highest molecular orbital (HOMO,  $-7.35$  eV) is mainly localized at the silicon center and corresponds to the lone pair orbital (Figure 3c). The lowest unoccupied molecular orbitals, LUMO ( $-4.22$  eV) and LUMO+1 ( $-4.00$  eV), correspond to the anti-bonding orbitals for the combination of Si-Ni and Si-Pd bonds ( $\sigma^*_{\text{Si-Ni/Pd}}$ ) (Figure 3a,b). Due to the coordination of Pd(0)-fragment, the energy level of HOMO increases  $0.88$  eV relative to that of **1**, and the positive charge of Si atom is reduced ( $+0.92 \rightarrow +0.78$ ) (Figure 4). However, an unchanged HOMO-LUMO gap ( $3.13$  eV and  $3.37$  eV for **2** and **1** respectively), suggests that **2** should remain highly reactive. Upon coordination of non-metallic Ph<sub>2</sub>S-ligand to the related phosphine-stabilized silyliumylidene ion **3** to form complex **4**, that was described in our previous report,<sup>[10]</sup> (type IX in Figure 1), a similar trend in the elevation of HOMO level was observed ( $-9.50$  eV  $\rightarrow$   $-8.61$  eV), while, in this case, the HOMO-LUMO gap becomes larger ( $3.64$  eV  $\rightarrow$   $4.33$  eV), and thus decreases the reactivity. The reduced bond order (WBI) of Si-Ni bond in **2** ( $0.56$ ) compared to that in **1** ( $0.70$ ) indicates a decrease of Ni $\rightarrow$ Si  $\pi$ -donation<sup>[10]</sup> certainly due to the increased LUMO level induced by the Pd-coordination.



**Figure 4.** Comparison of frontier orbital energy levels and HOMO-LUMO energy gaps of metallic and non-metallic base-stabilized silyliumylidenes (**1-4**).

Natural Localized Molecular Orbital (NLMO) analysis of **2** indicates that the  $\sigma_{\text{Si-Pd}}$  and  $\sigma_{\text{Si-Ni}}$  bonding orbitals are mainly composed of d-orbitals of Ni (Si:  $9.0\%$ , Ni  $87.5\%$ ) and Pd (Si:  $8.1\%$ , Pd  $89.6\%$ ), which is consistent with their M $\rightarrow$ Si  $\sigma$ -donating character (M = Ni and Pd) (Figure S38). Furthermore, the same analysis also confirms that the lone pair orbital is localized at the Si atom ( $\text{LP}_{\text{Si}}$ ) with a considerably large contribution of silicon (Si:  $91.3\%$ , Pd:  $2.6\%$ , Ni:  $1.1\%$ ). The second-order perturbation theory of **2** detects donor-acceptor interactions from Ni/Pd-atoms toward Si center (Ni $\rightarrow$ Si:  $33.9$  kcal $\cdot$ mol $^{-1}$ , Pd $\rightarrow$ Si:  $22.7$  kcal $\cdot$ mol $^{-1}$  respectively), while they are smaller than that calculated for mono-coordinate complex **1** (Ni $\rightarrow$ Si:  $35.1$  kcal $\cdot$ mol $^{-1}$ ). Noteworthy, Nuclear Independent Chemical Shift (NICS) at the center and  $1$  Å above the center of four-membered ring of **2** indicates large negative values [ $\text{NICS}(0) = -41.1$ ,  $\text{NICS}(1) = -16.0$ ], suggesting an aromatic character. The considerably larger negative value of  $\text{NICS}(0)$  than that of  $\text{NICS}(1)$  is characteristic for the  $\sigma$ -aromaticity.<sup>[27]</sup> This  $\sigma$ -aromatic character of **2** is probably an important factor for stabilizing such particular electronic situation as well as the cyclic structure with the bridging NHC-ligand.

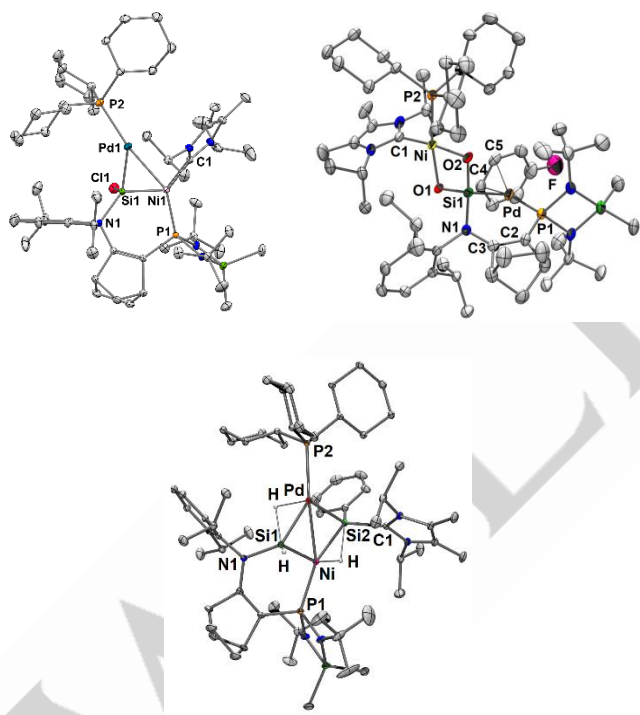
The strong electrophilic nature of silicon center was confirmed by the reaction of **2** with tetrabutylammonium chloride ( $\text{Bu}_4\text{N}^+\text{Cl}^-$ ) affording the neutral chloro- $\mu$ -silylene complex **5** (Scheme 2). Conversely, the addition of  $\text{NaBARF}_4$  to **5** cleanly regenerates **2** at room temperature. In the  $^{29}\text{Si}$ -NMR spectrum, a doublet of doublets signal was observed at  $135.4$  ppm ( $J_{\text{SiP}} = 72.2$  and  $19.8$  Hz) significantly upfield shifted from those observed for **2** ( $333.5$  ppm), suggesting a considerable change in the coordination environment of Si center in **5**. The X-ray structure of **5** exhibits a three membered-ring with the two Ni- and Pd-centers bridged by a silylene ligand (Figure 5 upper-left).<sup>[17]</sup> The structure also shows short Si-Ni [ $2.132(1)$  Å] and Si-Pd [ $\text{Si1-Pd1 } 2.268(1)$  Å] bond lengths, and a Pd-Ni bond [ $2.599(1)$  Å] only slightly longer than that observed for **2** [ $2.559(1)$  Å]. The related mono-silylene-bridged binuclear Pd(0)<sub>2</sub>-complexes, synthesized by Osakada [ $\text{Ph}_2\text{SiPd}_2(\text{PCy}_3)_3$ ]<sup>[28]</sup> and by Kira [ $\text{R}_2\text{SiPd}_2(\text{PMe}_3)_2$ ],<sup>[29]</sup> presents similar geometries with Si-Pd bond lengths [ $2.289 - 2.307$  Å], significantly shorter than those observed for bis-silylene-bridged Pd(0)<sub>2</sub>-complexes ( $2.382 - 2.400$  Å).<sup>[30]</sup> As Ni(0)-based binuclear-complexes, only one example of bis-silylene-bridged Ni(0)<sub>2</sub>-complex [ $\text{Si-Ni: } 2.280\text{-}2.309$  Å] is known<sup>[31]</sup> and, to the best of our knowledge, neither mono-silylene-bridged Ni(0)<sub>2</sub>- nor heterobinuclear Pd(0)-Ni(0)-complexes have not been described so far. A classical silylene-bridged binuclear complex character ( $\mu$ -type complex) of **5** was indicated by theoretical analysis. Indeed, Natural Localized Molecular Orbital (NLMO) and second-order perturbation theory analysis show a delocalized electron pair from silicon atom ( $e = 1.64$ ) to Ni- and Pd-centers [Si:  $78.2\%$ , Ni:  $6.9\%$ , Pd  $8.7\%$ , Figure S42] with almost the same donor-acceptor interaction energies [ $\text{LP}_{\text{Si}}\rightarrow\text{Ni: } 111.8$  kcal $\cdot$ mol $^{-1}$ ,  $\text{LP}_{\text{Si}}\rightarrow\text{Pd: } 113.6$  kcal $\cdot$ mol $^{-1}$ ].



**Scheme 2.** Reactions of silyliumylidene ion **2**.

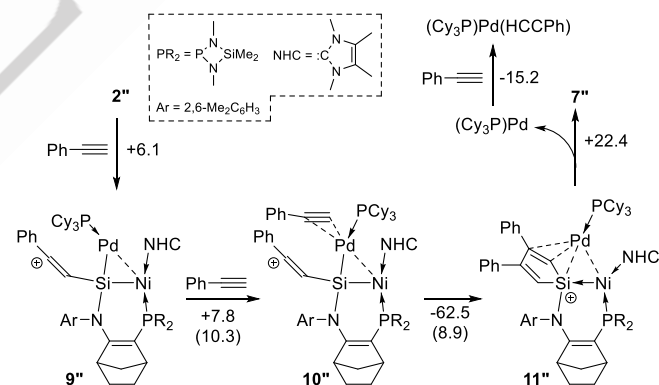
Despite the presence of a lone pair at the silicon center, probably due to a considerable steric hindrance, all attempts to react electrophiles failed. However, **2** reacts readily with  $\text{N}_2\text{O}$  in  $\text{C}_6\text{H}_5\text{F}$  giving a cationic Ni(II)-silacarboxylate complex **6** stabilized by a Pd(0)-donor ligand. The structure of complex **6** was confirmed by X-ray diffraction analysis (Figure 5, upper-right).<sup>[18]</sup> The  $^{31}\text{P}$ -NMR spectrum shows two singlet signals at  $63.2$  (PR<sub>2</sub>) and at  $23.2$  ppm (PCy<sub>3</sub>). Nevertheless, the complete NMR characterization of **6** in solution failed due to its poor

solubility in all organic solvents. The CP/MAS  $^{29}\text{Si}$ -NMR spectrum shows a signal at  $-24.8$  ppm. Monitoring the reaction by  $^{31}\text{P}$ -NMR spectroscopy at low temperature indicates that the oxidation starts above  $-10$  °C to give **6**, without any intermediate detected, probably due to a faster second oxidation step. Although the reaction mechanism is still unknown, and since the oxidation of base-stabilized silyliumylidene ions<sup>[10,32]</sup> and Ni(0) complexes<sup>[33]</sup> using mild oxidants such as  $\text{CO}_2$  and  $\text{N}_2\text{O}$  have already been described,  $\text{N}_2\text{O}$  probably oxidizes Si and Ni centers of **2** to generate an intermediate which subsequently rearranges to give **6**. It should be noted that only a few donor/acceptor-stabilized silacarboxylic acid derivatives are known,<sup>[34]</sup> and **6** is the first one with a metal-based donor/acceptor ligand system. The structure of **6** exhibits a significantly elongated Si-Pd bond length [2.328(1) Å] compared to those observed for the related silyliumylidene complexes **2** [2.268(1) Å] and **13** [2.232(1) Å], probably due to a reduced  $\pi$ -interaction geometry (Figure 5, upper-right).<sup>[17]</sup> The  $\sigma$ -donating character of Pd(0)-fragment in **6** is indicated by the characteristic T-shaped geometry with a large angle between the phosphine and  $\eta^2\text{-C}_6\text{H}_5\text{F}$  ligands [C4-Pd-P1 164.6(2)° and C5-Pd-P1 153.3(2)°] and the cationic Ni(II) center exhibits the expected square planar.



**Figure 5.** Molecular structures of **5** (upper left), **6** (upper right) and **8** (bottom). Thermal ellipsoids represent 30 % probability. H and disordered atoms (**6**) and counter anion (**6**, **8**) are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5**: Si1-N1 1.794(2), Si1-Ni1 2.132(1), Ni1-P1 2.123(1), Ni1-C1 1.955(2), Si1-Pd1 2.268(1), Pd1-Ni1 2.599(1), Si1-C11 2.143(1), Pd1-P2 2.238(1), N1-Si1-Ni1 117.12(6), N1-Si1-Pd1 130.94(6), Pd1-Si1-Ni1 72.33(2), C1-Ni1-P1 132.15(6), Ni1-Pd1-P2 171.07(2), C1-Ni1-Si1 134.50(6), P1-Ni1-Si1 93.29(2), Ni1-Pd1-Si1 51.43(2), P2-Pd1-Si1 134.27(2). **6**: Si1-O1 1.587(4), Si1-Pd 2.328(1), Pd-C4 2.443(5), Pd-C5 2.358(5), C4-C5 1.371(8), Si1-O1-Ni1 90.6(2), O1-Ni-O2 80.3(2), Ni-O2-Si1 88.0(2), O2-Si1-O1 101.2(2), N1-Si1-Pd 111.2(1), Si1-Pd-C4 99.2(1), Si1-Pd-C5 105.0(1), C4-Pd-P1 164.6(2), C5-Pd-P1 153.3(2), Si1-Pd-P1 90.9(1). **8**: N1-Si1 1.7665(12), Si1-Pd 2.3571(4), Pd-Si2 2.2928(4), Si2-Ni 2.2484(4), Ni-Si1 2.1882(4), Pd-Ni 2.6162(2), Ni-P1 2.1566(4), Pd-P2 2.3537(3), Ni-Si1-Pd 70.17(1), Si1-Pd-Si2 105.84(1), Pd-Si2-Ni 70.35(1), Si2-Ni-Si1 113.47(2).

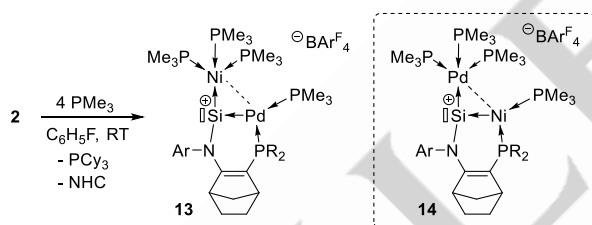
As expected from the small HOMO-LUMO energy gap and low LUMO energy level, silyliumylidene complex **2** exhibits a highly reactive character. Indeed, **2** readily reacts with phenylacetylene (HCCPh) to give the corresponding [2+2+1]-cycloadduct **7**, releasing a  $\text{Pd}(\text{PCy}_3)$  fragment (Scheme 2). Three equivalents of phenylacetylene are required to complete the reaction, and although NMR analysis of the reaction mixture provided no evidence for the fate of the excess of acetylene,<sup>[35]</sup> it probably promotes the elimination of Pd-moiety. DFT calculations using a simplified model **2''** (Me groups instead of *i*Pr, and *t*Bu, Figure 6) suggest that the reaction starts with the addition of HCCPh on the cationic Si atom to form a  $\mu$ -type complex **9''** presenting a similar geometry to that of chlorinated complex **5**. The subsequent coordination of 2<sup>nd</sup> HCCPh on Pd center (**10''**) followed by a formal [3+2]-cycloaddition affords a sila-cyclopentadienyl cation complex **11''**. Despite the endergonic first two steps, the cycloaddition step is strongly exergonic and proceeds with a reasonably small energy barrier ( $\Delta G$ :  $-62.5$  kcal·mol<sup>-1</sup>,  $\Delta G^\ddagger$ : 8.9 kcal·mol<sup>-1</sup>). The release of  $\text{Pd}(\text{PCy}_3)$  from **11''** is highly endergonic ( $\Delta G$ = 22.4 kcal·mol<sup>-1</sup>) and this is not compensated by the coordination of the third phenylacetylene molecule ( $\Delta G$ =  $-15.2$  kcal·mol<sup>-1</sup>). However, this process is strongly influenced by the steric congestion. Indeed, for the real system with bulkier substituents, the process for the release of  $\text{PdPCy}_3$  [**11**  $\rightarrow$  **7** +  $\text{Pd}(\text{PCy}_3)$ ] is exergonic ( $\Delta G$ =  $-3.2$  kcal·mol<sup>-1</sup>). Another possibility is to start the process by generating the mono-ligated complex **1''** via the dissociation of  $\text{PdPCy}_3$  from **2''**. However, this process is much more endergonic not only for the model compound **2''** ( $\Delta G_{2'' \rightarrow 1'' + \text{PdPCy}_3}$  = 45.1 kcal mol<sup>-1</sup>) but also for the more congested real molecule **2** ( $\Delta G_{2 \rightarrow 1 + \text{PdPCy}_3}$  = 45.7 kcal/mol). These results clearly indicate that this route is strongly disfavored.



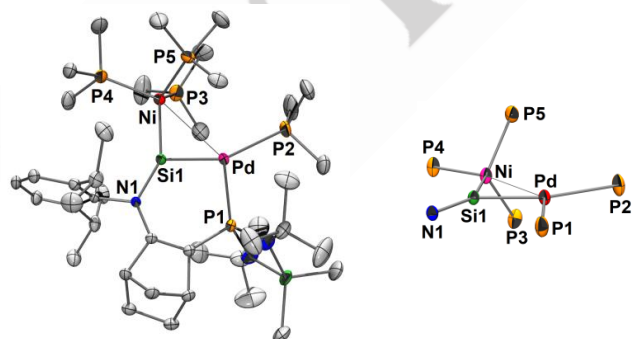
**Figure 6.** Calculated pathway for the reaction of **2'** with HCCPh (3 eq.). Gibbs energies of intermediates (and transition states) are in kcal·mol<sup>-1</sup>.

Silyliumylidene complex **2** also reacts with phenylsilane at room temperature to give a silane-bridged four-membered cyclic binuclear complex **8** (Scheme 2). Although the mechanism of the reaction is still unclear, the reaction probably starts with the double-activation of Si-H bonds of phenylsilane by Pd(0)- and Ni(0)-centers followed by an isomerization of intermediate through an hydride migration from M center to silyliumylidene fragment (or silyliumylidene insertion into M-H bond) to form **8**. The structure of **8** was confirmed by X-ray diffraction analysis (Figure 5-bottom).<sup>[17]</sup> A number of related binuclear complexes are known,<sup>[36-38]</sup> while heterobimetallic ones are still rare.<sup>[39]</sup>

Of particular interest, addition of an excess of  $\text{PMe}_3$  to **2** at room temperature leads to the replacement of NHC and  $\text{PCy}_3$  ligands and a position exchange between Ni and Pd atoms to afford the  $\mu$ -type silyliumylidene complex ion **13** featuring two metal fragments with different donor/acceptor roles (Scheme 3). This reaction probably starts with a simple ligand exchange to generate complex **14**, which then isomerizes to the experimentally observed complex **13**, although any intermediate signal cannot be detected by  $^{31}\text{P}$ -NMR spectroscopy. **13** was calculated to be thermally more stable than **14** ( $\Delta G_{14 \rightarrow 13} = -9.9 \text{ kcal mol}^{-1}$ ). The  $^{31}\text{P}$ -NMR spectrum shows a set of three signals: quartet at 80.0 ppm ( $J_{\text{PP}} = 47.3 \text{ Hz}$ ), doublet at  $-15.9 \text{ ppm}$  ( $J_{\text{PP}} = 47.3 \text{ Hz}$ ), and a broad signal at  $-49.2 \text{ ppm}$  in 1:3:1 ratio, corresponding to  $\text{PR}_2$ ,  $\text{PMe}_3$  ligands on Ni-atom and  $\text{PMe}_3$  ligand on Pd-center, respectively. The  $^{29}\text{Si}$ -NMR spectrum exhibits a down-field shifted signal at 290.3 ppm, similarly to the precursor **2** (333 ppm). Of particular interest, the structure of **13** exhibits a planar tricoordinate silicon center ( $\Sigma^\circ_{\text{Si}} = 359.88^\circ$ ), in agreement with a vacant orbital at the Si atom, in contrast to **2** presenting a pyramidalized silicon center with a lone pair (Figure 7).<sup>[17]</sup> This result demonstrates that the nature of ligands on metal centers crucially influences the structure of the corresponding bi-metallic silyliumylidene ion complexes. The Si–Ni [2.101(1) Å] and Si–N [1.733(2) Å] bond lengths are shorter than those of **2** [2.135(1) and 1.762(2) Å, respectively], suggesting an increased multiple bonding character certainly due to the  $\pi$ -donations from Ni and N atoms to the Si center (**13-B** and **13-C** in Figure 8). The Si–Pd bond length [2.232(1) Å] is similar to that observed for **2** [2.256(1) Å]. An unusually large N–Si–Ni angle [147.78(8)°] suggests the presence of a Ni–Pd interaction, despite the small WBI of Ni–Pd bond (0.06).

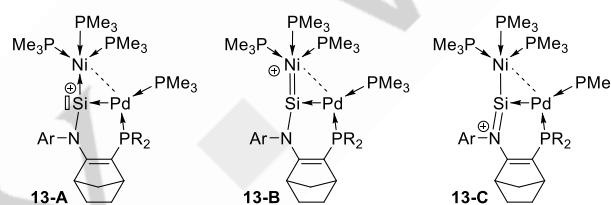


**Scheme 3.** Reaction of **2** with  $\text{PMe}_3$  and a possible intermediate **14**.



**Figure 7.** Molecular structure of **13**. Thermal ellipsoids represent 30 % probability. H and counter anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.733(2), Si1–Ni 2.101(1), Si1–Pd 2.232(1), Pd–Ni 3.068(1), Ni–P3 2.209(1), Ni–P4 2.221(1), Ni–P5 2.223(1), Pd–P1 2.283(1), Pd–P2 2.482(1), N1–Si1–Ni 147.78(8), N1–Si1–Pd 122.00(8), Pd–Si1–Ni 90.10(3), P1–Pd–P2 110.56(3), P1–Pd–Si1 93.90(3), P2–Pd–Si1 155.53(3).  $\Sigma^\circ_{\text{Si1}} = 359.88^\circ$ .

The MO analysis of **13** clearly confirms the presence of a vacant orbital at the Si atom (LUMO,  $-4.16 \text{ eV}$ ). The HOMO ( $-7.52 \text{ eV}$ ) corresponds to the combination of d-orbitals of Pd and Ni fragments (Figure S48). The Natural Localized Molecular Orbital (NLMO) analysis indicates that the lone pair at the Si atom is in the in-plane  $\sigma$ -type orbital, extending over the silicon, Ni- and Pd-centers (Si: 82.0%, Pd: 4.0%, Ni: 8.0%, Figure S49). However, according to the second-order perturbation theory on **13**, unlike the case of neutral Si-chlorinated complex **5**, the donor-acceptor interaction from Si to Ni/Pd-centers is considerably disproportionate and the Si–Ni interaction is considerably stronger ( $\text{LP}_{\text{Si}} \rightarrow \text{Ni}$ :  $85.6 \text{ kcal mol}^{-1}$ ,  $\text{LP}_{\text{Si}} \rightarrow \text{Pd}$ :  $31.0 \text{ kcal mol}^{-1}$ ) (**13-A** in Figure 8). In addition, two relatively weak Ni  $\rightarrow$  Si  $\pi$ -back-donation (in-plane and out-of-plane) were observed in **13** ( $4.7$  and  $9.2 \text{ kcal mol}^{-1}$ ), which is in good agreement with the experimentally observed Si–Ni short bond length (**13-B** in Figure 8). The Pd  $\rightarrow$  Si  $\sigma$ -donation was also suggested by NLMO analysis (Pd: 87.8%, Si: 8.1%, Figure S48), although it is weaker than that calculated for **2** ( $18.7 \text{ kcal mol}^{-1}$  for **13** versus  $22.7 \text{ kcal mol}^{-1}$  for **2**).



**Figure 8.** Some possible resonance structures of **13**.

## Conclusion

In conclusion, we have successfully synthesized a silyliumylidene ion **2** stabilized by two  $\sigma$ -donating Ni(0)- and Pd(0)-fragments. In **2**, the two metal centers are bridged by a NHC ligand to form a rhombic and  $\sigma$ -aromatic metallacycle. The original coordination mode in **2** induces a strongly pyramidalized cationic silicon center with a localized lone pair, clearly demonstrating the  $\sigma$ -donating character of Pd(0)- and Ni(0)-ligands. Despite the stabilization by the two metal ligands, **2** exhibits a small HOMO-LUMO energy gap and thus a high reactivity. The original reactivity of **2** allowed to synthesize unique compounds such as the mono-silylene-bridged heterobinuclear complex **5** as well as the sila-carboxylate **6** stabilized by a metal-based-donor/acceptor system. In addition, it was demonstrated that the coordination mode at the silyliumylidene center is closely related to the nature of ligands on the two metal-fragments. Indeed, a ligand exchange from  $\text{PCy}_3/\text{NHC}$  to  $\text{PMe}_3$ , induces the transformation of a donor/donor-stabilized silyliumylidene ion **2** into a metal-based donor/acceptor-stabilized one **13**, featuring a trigonal planar Si center with a vacant orbital. Further investigation on the reactivity of **2** and its applications are in progress.

## Experimental Section

### General

All manipulations were performed under inert atmosphere of argon by using Schlenk or high-pressure NMR tube techniques. Dry, oxygen-free solvents were employed.  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  NMR spectra were recorded on Bruker Avance II 300MHz, Avance III HD 400 MHz and Avance I and II 500 MHz spectrometers.  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  as internal standard.  $^{31}\text{P}$  NMR chemical shifts are expressed in ppm relative to 85 %  $\text{H}_3\text{PO}_4$ .  $^{11}\text{B}$  chemical shifts are relative to  $\text{BF}_3\cdot\text{OEt}_2$  and  $^{19}\text{F}$  chemical shifts are relative to  $\text{CFCl}_3$  as external reference. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet.  $^1\text{H}$  and  $^{13}\text{C}$  resonance signals were attributed by means of 2D COSY, HSQC and HMBC experiments. Field desorption (FD) mass spectra were acquired on a JEOL JMS-T100GCV time of flight mass spectrometer equipped with an EI/FI(FD) combination ion source. The Ni(0)-stabilized silyliumylidene **1**<sup>[15]</sup> was synthesized as previously reported.

## Syntheses

**Compound 2:** In an NMR tube, to a mixture of **1** (122 mg, 0.075 mmol) and  $\text{Pd}(\text{PCy}_3)_2$  (50 mg, 0.075 mmol, 1.0 equiv.),  $\text{C}_6\text{H}_5\text{F}$  (0.5 mL) was added at room temperature. After overnight, all volatiles were removed under reduced pressure. Compound **2** was crystallized by a two-layer technique [ $\text{Et}_2\text{O}$ /pentane solution (0.1 : 0.4 mL)] at room temperature and was obtained as black crystals (88 mg, 58%). Crystals suitable for X-ray diffraction analysis were obtained from saturated  $\text{Et}_2\text{O}$ /pentane solution at  $-30^\circ\text{C}$ . Mp. 165-167  $^\circ\text{C}$  (decomp.).

**Compound 2 from 5:** In an NMR tube, to a mixture of **5** (74 mg, 0.062 mmol) and  $\text{NaBARF}_4$  (55 mg, 0.062 mmol, 1.0 equiv.),  $\text{C}_6\text{H}_5\text{F}$  (0.5 mL) was added at room temperature. After 5 min, full conversion of **5** to **2** was confirmed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The reaction mixture was filtered and the filtrate was concentrated (ca. 0.1 mL) under reduced pressure. Compound **2** was crystallized from a  $\text{C}_6\text{H}_5\text{F}$ /pentane solution (0.1 : 0.5 mL) at  $-30^\circ\text{C}$  and was obtained as black crystals (121 mg, 96%).  $^1\text{H}$  NMR (400 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 0.30$  (s, 3H,  $\text{SiMe}_2$ ), 0.37 (s, 3H,  $\text{SiMe}_2$ ), 0.67 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 0.89 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 0.94 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.04 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.04 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.09 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.10 (s, 9H,  $\text{CH}_{3\text{IBu}}$ ), 1.14 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.14 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.20 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.20 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.21 (s, 9H,  $\text{CH}_{3\text{IBu}}$ ), 1.27 (d,  $J_{\text{HH}} = 7.0$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.28 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.31 (d,  $J_{\text{HH}} = 7.0$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.34 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.36 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.45 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.47 (d,  $J_{\text{HH}} = 7.0$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.47 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.50 (d,  $J_{\text{HH}} = 7.0$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.53 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.54 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.64 (m, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.81 (s, 3H,  $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 1.83 (s, 3H,  $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 2.34 (s, 1H,  $\text{CH}_{\text{bridgehead}}$ ), 3.11 (sept,  $J_{\text{HH}} = 6.9$  Hz, 1H,  $\text{CH}_{\text{IPr-Dip}}$ ), 3.18 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}_{\text{IPr-Dip}}$ ), 3.34 (s, 1H,  $\text{CH}_{\text{bridgehead}}$ ), 4.19 (sept,  $J_{\text{HH}} = 7.0$  Hz, 1H,  $\text{CH}_{\text{IPr-NHC}}$ ), 5.56 (sept,  $J_{\text{HH}} = 7.0$  Hz, 1H,  $\text{CH}_{\text{IPr-NHC}}$ ), 7.05-7.15 (m, 3H,  $\text{CH}_{\text{Ar}}$ ), 7.62 (s, 4H,  $\text{CH}_{\text{B-Ar}}$ ), 8.29 (s, 8H,  $\text{CH}_{\text{B-Ar}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 4.4$  ( $\text{SiMe}_2$ ), 5.8 (d,  $J_{\text{CP}} = 2.7$  Hz,  $\text{SiMe}_2$ ), 9.9 ( $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 10.2 ( $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 21.9 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 22.9 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 23.6 ( $\text{CH}_{3\text{IPr-Dip}}$ ),

23.8 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 24.4 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 25.4 ( $\text{CH}_{2\text{Norb}}$ ), 25.6 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 26.1 ( $\text{CH}_{2\text{cyclohexyl}}$ ), 26.7 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 26.9 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 27.6 (d,  $J_{\text{CP}} = 9.2$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 27.6 (d,  $J_{\text{CP}} = 12.9$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 27.8 ( $\text{CH}_{2\text{Norb}}$ ), 28.7 ( $\text{CH}_{\text{IPr-Dip}}$ ), 28.7 ( $\text{CH}_{\text{IPr-Dip}}$ ), 30.3 ( $\text{CH}_{2\text{cyclohexyl}}$ ), 32.0 (d,  $J_{\text{CP}} = 3.9$  Hz,  $\text{CH}_{3\text{IBu}}$ ), 32.4 (d,  $J_{\text{CP}} = 7.4$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 32.4 (d,  $J_{\text{CP}} = 5.7$  Hz,  $\text{CH}_{3\text{IBu}}$ ), 34.0 ( $J_{\text{CP}} = 13.2$  Hz,  $\text{CH}_{\text{cyclohexyl}}$ ), 44.4 ( $\text{CH}_{\text{bridgehead}}$ ), 45.4 (d,  $J_{\text{CP}} = 10.9$  Hz,  $\text{CH}_{\text{bridgehead}}$ ), 47.6 (d,  $J_{\text{CP}} = 3.9$  Hz,  $\text{CH}_{2\text{Norb}}$ ), 51.0 (d,  $J_{\text{CP}} = 3.2$  Hz,  $\text{C}_{\text{IBu}}$ ), 51.9 (d,  $J_{\text{CP}} = 4.2$  Hz,  $\text{C}_{\text{IBu}}$ ), 55.1 ( $\text{CH}_{\text{IPr-NHC}}$ ), 55.5 ( $\text{CH}_{\text{IPr-NHC}}$ ), 119.7 (d,  $J_{\text{CP}} = 40.4$  Hz,  $\text{P}=\text{CN}$ ), 118.0 (br sept,  $J_{\text{CF}} = 3.7$  Hz,  $p\text{-CH}_{\text{B-Ar}}$ ), 124.5 ( $\text{CH}_{\text{Ar}}$ ), 124.8 ( $\text{CH}_{\text{Ar}}$ ), 124.9 (q,  $J_{\text{CF}} = 272.4$  Hz,  $\text{CF}_3$ ), 128.7 ( $\text{CH}_{\text{Ar}}$ ), 129.9 (qq,  $J_{\text{CF}} = 31.6$  Hz,  $J_{\text{CB}} = 2.7$  Hz,  $m\text{-C}_{\text{B-Ar}}$ ), 130.0 ( $\text{C}=\text{C}_{\text{NHC}}$ ), 135.4 ( $o\text{-CH}_{\text{B-Ar}}$ ), 135.8 ( $\text{N}-\text{C}_{\text{Ar}}$ ), 146.1 ( $i\text{Pr}-\text{C}_{\text{Ar}}$ ), 146.5 ( $i\text{Pr}-\text{C}_{\text{Ar}}$ ), 160.8 (d,  $J_{\text{CP}} = 22.9$  Hz,  $\text{PC}=\text{CN}$ ), 162.8 (q,  $J_{\text{CB}} = 49.6$  Hz,  $ipso\text{-C}_{\text{B-Ar}}$ ), 167.8 (dd,  $J_{\text{CP}} = 26.3$  and  $6.0$  Hz,  $\text{C}_{\text{carbene}}$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -6.0$  ( $\text{BARF}_4$ ).  $^{19}\text{F}$  NMR (470 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -62.4$  (s,  $\text{BARF}_4$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 93.8$  (d,  $J_{\text{PP}} = 57.3$  Hz,  $\text{PN}_2$ ), 37.0 (d,  $J_{\text{PP}} = 57.3$  Hz, Si-satellite:  $J_{\text{PSi}} = 62.3$  Hz,  $\text{PCy}_3$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79 MHz,  $25^\circ\text{C}$ ,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 333.5$  (dd,  $J_{\text{SiP}} = 62.0$  and  $18.2$  Hz, N-Si-Ni), 10.5 (d,  $J_{\text{SiP}} = 1.7$  Hz,  $\text{SiMe}_2$ ).

**Compound 5:** In an NMR tube, to a solution of **2** (80 mg, 0.40 mmol) in THF (0.4 mL),  $\text{Bu}_4\text{NCl}$  (11 mg, 0.04 mmol, 1.0 equiv.) was added at room temperature. After overnight, all volatiles were removed under reduced pressure. Compound **5** was crystallized from a saturated  $\text{C}_6\text{H}_5\text{F}$  solution (ca. 0.1 mL) at  $-30^\circ\text{C}$  and was obtained as black crystals (32 mg, 67%). Crystals suitable for X-ray diffraction analysis were obtained from saturated  $\text{C}_6\text{H}_5\text{F}$  solution at room temperature. Mp. 173-176  $^\circ\text{C}$  (decomp.).  $^1\text{H}$  NMR (300 MHz,  $25^\circ\text{C}$ ,  $\text{THF}-d_6$ ):  $\delta = 0.40$  (s, 3H,  $\text{SiMe}_2$ ), 0.43 (s, 3H,  $\text{SiMe}_2$ ), 0.96 (m, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.02 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.08 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.12 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.12 (m, 9H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.30 (s, 9H,  $\text{CH}_{3\text{IBu}}$ ), 1.32 (overlapped, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.39 (m, 3H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.42 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.43 (s, 9H,  $\text{CH}_{3\text{IBu}}$ ), 1.47 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.50 (m, 3H,  $\text{CH}_{\text{cyclohexyl}}$ ), 1.56 (m, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.57 (d,  $J_{\text{HH}} = 6.8$  Hz, 6H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.61 (m, 12H,  $\text{CH}_{2\text{cyclohexyl}}$ ), 1.68 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-NHC}}$ ), 1.71 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H,  $\text{CH}_{3\text{IPr-Dip}}$ ), 1.71 (overlapped, 1H,  $\text{CH}_{2\text{Norb}}$ ), 1.80 (m, 4H,  $\text{CH}_{2\text{Norb}}$  and  $\text{CH}_{2\text{cyclohexyl}}$ ), 2.18 (s, 6H,  $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 2.34 (m, 1H,  $\text{CH}_{\text{bridgehead}}$ ), 3.41 (m, 1H,  $\text{CH}_{\text{bridgehead}}$ ), 3.85 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}_{\text{IPr-Dip}}$ ), 4.02 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}_{\text{IPr-Dip}}$ ), 4.96 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}_{\text{IPr-NHC}}$ ), 5.93 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H,  $\text{CH}_{\text{IPr-NHC}}$ ), 7.08-7.13 (m, 3H,  $\text{CH}_{\text{Ar}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $25^\circ\text{C}$ ,  $\text{THF}-d_6$ ):  $\delta = 6.5$  ( $\text{SiMe}_2$ ), 7.1 (d,  $J_{\text{CP}} = 4.9$  Hz,  $\text{SiMe}_2$ ), 10.5 ( $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 10.7 ( $\text{C}=\text{C}-\text{CH}_{3\text{NHC}}$ ), 22.3 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 22.8 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 22.3 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 23.2 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 25.5 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 25.7 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 26.2 ( $\text{CH}_{3\text{IPr-Dip}}$ ), 27.1 (d,  $J_{\text{CP}} = 11.4$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 27.1 ( $\text{CH}_{2\text{Norb}}$ ), 28.4 (d,  $J_{\text{CP}} = 10.4$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 28.5 ( $\text{CH}_{\text{IPr-Dip}}$ ), 28.6 ( $\text{CH}_{2\text{cyclohexyl}}$ ), 28.6 ( $\text{CH}_{\text{IPr-Dip}}$ ), 29.2 ( $\text{CH}_{3\text{IPr-NHC}}$ ), 29.5 ( $\text{CH}_{2\text{Norb}}$ ), 30.8 (d,  $J_{\text{CP}} = 5.2$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 31.5 (d,  $J_{\text{CP}} = 6.6$  Hz,  $\text{CH}_{2\text{cyclohexyl}}$ ), 32.4 (d,  $J_{\text{CP}} = 5.2$  Hz,  $\text{CH}_{3\text{IBu}}$ ), 33.7 (d,  $J_{\text{CP}} = 4.2$  Hz,  $\text{CH}_{3\text{IBu}}$ ), 35.2 (d,  $J_{\text{CP}} = 8.0$  Hz,  $\text{CH}_{\text{cyclohexyl}}$ ), 44.5 (d,  $J_{\text{CP}} = 2.4$  Hz,  $\text{CH}_{\text{bridgehead}}$ ), 46.3 (d,  $J_{\text{CP}} = 4.2$  Hz,  $\text{CH}_{2\text{Norb}}$ ), 46.6 (d,  $J_{\text{CP}} = 11.4$  Hz,  $\text{CH}_{\text{bridgehead}}$ ), 51.3 (d,  $J_{\text{CP}} = 4.5$  Hz,  $\text{C}_{\text{IBu}}$ ), 51.5 (d,  $J_{\text{CP}} = 5.9$  Hz,  $\text{C}_{\text{IBu}}$ ), 54.2 ( $\text{CH}_{\text{IPr-NHC}}$ ), 54.4 ( $\text{CH}_{\text{IPr-NHC}}$ ), 117.4 (d,  $J_{\text{CP}} = 29.3$  and  $1.9$  Hz,  $\text{P}=\text{CN}$ ), 124.1 ( $\text{CH}_{\text{Ar}}$ ), 124.5 ( $\text{CH}_{\text{Ar}}$ ), 124.5 ( $\text{C}=\text{C}_{\text{NHC}}$ ), 125.7 ( $\text{C}=\text{C}_{\text{NHC}}$ ), 126.6 ( $\text{CH}_{\text{Ar}}$ ), 139.6 ( $\text{N}-\text{C}_{\text{Ar}}$ ), 149.1 ( $i\text{Pr}-\text{C}_{\text{Ar}}$ ), 149.6 ( $i\text{Pr}-\text{C}_{\text{Ar}}$ ), 164.2 (d,  $J_{\text{CP}} = 22.5$  Hz,  $\text{PC}=\text{CN}$ ), 193.4 (d,  $J_{\text{CP}} = 8.0$  Hz,  $\text{C}_{\text{carbene}}$ ).  $^{31}\text{P}\{^1\text{H}\}$

NMR (121MHz, 25 °C, THF-*d*<sub>6</sub>):  $\delta$  = 24.0 (d,  $J_{PP}$  = 86.7 Hz, Si-satellite:  $J_{PSi}$  = 72.8 Hz, PCy<sub>3</sub>), 101.8 (d,  $J_{PP}$  = 86.7 Hz, PN<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59 MHz, 25 °C, THF-*d*<sub>6</sub>):  $\delta$  = 1.4 (SiMe<sub>2</sub>), 135.4 (dd,  $J_{SiP}$  = 72.2 and 19.5 Hz, N-Si-P).

**Compound 6:** In a pressure NMR tube, **2** (80 mg, 0.040 mmol) in C<sub>6</sub>H<sub>5</sub>F (0.4 mL), was exposed to a 3 bar of N<sub>2</sub>O at room temperature. The reaction progress was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and completed after 15 min. All the volatiles were removed under reduced pressure and the residues were washed with pentane (0.5 mL x 3) to obtain **6** as a dark orange solid (55 mg, 68 %). Crystals suitable for X-ray diffraction analysis were obtained from a C<sub>6</sub>H<sub>5</sub>F solution at room temperature. Due to the low solubility of **6** even in THF, *o*-dichlorobenzene or heated C<sub>6</sub>H<sub>5</sub>F solution, full characterization of **6** by NMR in solution was unsuccessful. <sup>31</sup>P{<sup>1</sup>H} CP MAS NMR (Vr = 12.8 kHz):  $\delta$  = 14.0 (PCy<sub>3</sub>), 29.8 (PCy<sub>3</sub>), 58.0 (PN<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} CP MAS NMR (Vr = 12.5 kHz):  $\delta$  = 24.8 (N-Si-Pd), 11.7 (SiMe<sub>2</sub>).

**Compound 7:** In an NMR tube, to a solution of **2** (80 mg, 0.040 mmol) in C<sub>6</sub>H<sub>5</sub>F (0.4 mL), phenylacetylene (13  $\mu$ L, 0.12 mmol, 3 equiv.) was added at room temperature. Resulting precipitates were filtered and the filtrate was dried under reduced pressure. The residue was washed with pentane (1.0 mL x 3) to obtain **7** as a black solid (40 mg, 54%).

**Compound 7 from 1:** In an NMR tube, to a C<sub>6</sub>H<sub>5</sub>F (0.7 mL) solution of **1** (150 mg, 0.095 mmol), phenylacetylene (23  $\mu$ L, 0.210 mmol, 2.0 equiv.) was added at room temperature. All the volatiles were removed under reduced pressure and the residue was washed with pentane (1.0 mL x 3) to obtain **7** as a black solid (104 mg, 60%). <sup>1</sup>H NMR (500 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 0.58 (s, 3H, SiMe<sub>2</sub>), 0.63 (s, 3H, SiMe<sub>2</sub>), 1.05 (d,  $J_{HH}$  = 6.7 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.16 (d,  $J_{HH}$  = 6.7 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.17 (d,  $J_{HH}$  = 6.7 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.28 (m, 1H, CH<sub>2</sub>Norb), 1.54 (d,  $J_{HH}$  = 6.7 Hz, 12H, CH<sub>3</sub>IPr-NHC), 1.54 (overlapped, 3H, CH<sub>3</sub>IPr-Dip), 1.60 (m, 1H, CH<sub>2</sub>Norb), 1.61 (s, 9H, CH<sub>3</sub>IBu), 1.64 (s, 9H, CH<sub>3</sub>IBu), 1.73 (m, 2H, CH<sub>2</sub>Norb), 1.78 (m, 2H, CH<sub>2</sub>Norb), 1.98 (br s, 6H, C=C-CH<sub>3</sub>NHC), 2.49 (s, 1H, CH<sub>bridgehead</sub>), 3.12 (sept,  $J_{HH}$  = 6.7 Hz, 1H, CH<sub>IPr-Dip</sub>), 3.28 (s, 1H, CH<sub>bridgehead</sub>), 3.47 (sept,  $J_{HH}$  = 6.7 Hz, 1H, CH<sub>IPr-Dip</sub>), 5.48 (br s, 1H, CH<sub>IPr-NHC</sub>), 5.94 (d,  $J_{HP}$  = 4.5 Hz, 1H, Si-CH=CPh), 6.18 (br s, 1H, CH<sub>IPr-NHC</sub>), 6.46 (d,  $J_{HP}$  = 1.6 Hz, 1H, Si-CH=CPh), 6.48 (d,  $J_{CP}$  = 7.0 Hz, 2H, CH<sub>Ar</sub>), 6.83 (dd,  $J_{HH}$  = 8.3 and 1.4 Hz, 2H, CH<sub>Ar</sub>), 7.03-7.09 (m, 2H, CH<sub>Ar</sub>), 7.12-7.23 (m, 4H, CH<sub>Ar</sub>), 7.25-7.34 (m, 2H, CH<sub>Ar</sub>), 7.37-7.42 (m, 1H, CH<sub>Ar</sub>), 7.59 (s, 4H, CH<sub>B-Ar</sub>), 7.76 (s, 8H, CH<sub>B-Ar</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 5.3 (d,  $J_{CP}$  = 3.1 Hz, SiMe<sub>2</sub>), 5.4 (d,  $J_{CP}$  = 0.8 Hz, SiMe<sub>2</sub>), 10.1 (C=C-CH<sub>3</sub>NHC), 22.3 (CH<sub>3</sub>IPr-NHC), 23.1 (CH<sub>3</sub>IPr-NHC), 24.7 (CH<sub>3</sub>IPr-Dip), 24.8 (CH<sub>3</sub>IPr-Dip), 24.9 (CH<sub>3</sub>IPr-Dip), 25.1 (CH<sub>3</sub>IPr-Dip), 25.9 (CH<sub>2</sub>Norb), 27.7 (CH<sub>2</sub>Norb), 27.8 (CH<sub>IPr-Dip</sub>), 28.3 (CH<sub>IPr-Dip</sub>), 34.8 (d,  $J_{CP}$  = 5.2 Hz, CH<sub>3</sub>IBu), 35.2 (d,  $J_{CP}$  = 5.2 Hz, CH<sub>3</sub>IBu), 42.6 (CH<sub>bridgehead</sub>), 46.4 (d,  $J_{CP}$  = 5.2 Hz, CH<sub>2</sub>Norb), 46.5 (d,  $J_{CP}$  = 8.7 Hz, CH<sub>bridgehead</sub>), 50.8 (CH<sub>IPr-NHC</sub>), 51.7 (d,  $J_{CP}$  = 1.4 Hz, C<sub>IBu</sub>), 51.8 (d,  $J_{CP}$  = 1.5 Hz, C<sub>IBu</sub>), 105.3 (d,  $J_{CP}$  = 55.5 Hz, PC=CN), 117.1 (br sept,  $J_{CF}$  = 4.6 Hz, *p*-CH<sub>B-Ar</sub>), 124.2 (CH<sub>Ar-Dip</sub>), 124.5 (CH<sub>Ar-Dip</sub>), 126.6 (q,  $J_{CF}$  = 272.4 Hz, CF<sub>3</sub>), 127.0 (CH<sub>Ar-Ph</sub>), 127.2 (CH<sub>Ar-Ph</sub>), 127.3 (C=C<sub>NHC</sub>), 127.4 (CH<sub>Ar-Ph</sub>), 127.6 (CH<sub>Ar-Ph</sub>), 127.6 (CH<sub>Ar-Dip</sub>), 127.8 (CH<sub>Ar-Ph</sub>), 127.9 (CH<sub>Ar-Ph</sub>), 128.3 (Si-CH=CPh), 129.1 (qq,  $J_{CF}$  = 27.5 Hz,  $J_{CB}$  = 2.9 Hz, *m*-C<sub>B-Ar</sub>), 131.4 (d,  $J_{CP}$  = 4.5 Hz, Si-CH=CPh), 134.6 (*o*-CH<sub>B-Ar</sub>), 138.7 (C<sub>Ar-Ph</sub>), 138.9 (N-

C<sub>Ar</sub>), 139.6 (C<sub>Ar-Ph</sub>), 145.5 (*i*Pr-C<sub>Ar</sub>), 147.1 (*i*Pr-C<sub>Ar</sub>), 153.9 (CH=C<sub>Ph</sub>), 154.9 (CH=C<sub>Ph</sub>), 162.1 (q,  $J_{CB}$  = 49.8 Hz, *ipso*-C<sub>B-Ar</sub>), 173.6 (d,  $J_{CP}$  = 63.8 Hz, C<sub>carbene</sub>), 176.6 (d,  $J_{CP}$  = 20.1 Hz, PC=CN). <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -6.3 (BAr<sub>4</sub><sup>F</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -62.7 (s, BAr<sub>4</sub><sup>F</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 81.7 (PN<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (59 MHz, 25 °C, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 15.4 (d,  $J_{SiP}$  = 67.0 Hz, N-Si-Ni), 14.8 (d,  $J_{SiP}$  = 101 Hz, SiMe<sub>2</sub>). FD-MS (positive): m/z: Calcd for [C<sub>56</sub>H<sub>81</sub>N<sub>5</sub>NiPSi<sub>2</sub>]<sup>+</sup> 968.5; Found 968.6.

**Compound 8:** In an NMR tube, to a mixture of **2** (80 mg, 0.040 mmol) in C<sub>6</sub>H<sub>5</sub>F (0.4 mL), PhSiH<sub>3</sub> (5  $\mu$ L, 0.040 mmol) was added at room temperature. After overnight, all volatiles were removed under reduced pressure and the residue was washed with pentane (0.5 mLx3) to obtain **8** as a dark orange solid (62 mg, 74%). Crystals suitable for X-ray diffraction analysis were obtained from a saturated C<sub>6</sub>H<sub>5</sub>F solution at room temperature. NOTE: The signals of both protons of the SiH<sub>2</sub> moiety of the main product in <sup>1</sup>H NMR (4.20 and 4.23 ppm) were observed in similar regions. This is probably due to the rapid exchange between non-bridged Si-H and Si-H bridged to the Pd atom in the NMR time scale. On the other hand, in the case of the minor product, the signals from each proton appear in regions typical for bridged/non-bridged Si-H groups [2.10 and 6.66 ppm respectively]. A similar exchange of bridged/non-bridged Si-H groups was also observed for the related [(Pd(PCy<sub>3</sub>)<sub>2</sub>( $\mu$ -HSiXR)<sub>2</sub>)] complexes, which exhibited two Si-H signals at 6.72 and 1.03 ppm below -60°C and a single broad signal around 4 ppm at 30°C in <sup>1</sup>H-NMR.<sup>[37b]</sup> (Major isomer, 54%) <sup>1</sup>H NMR (500 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -1.55 (dd,  $J_{HP}$  = 4.3 Hz and 7.4 Hz, Si-satellite:  $J_{Hsi}$  = 50.4 Hz, 1H, Si-H-Ni), 0.32 (s, 3H, SiMe<sub>2</sub>), 0.39 (s, 3H, SiMe<sub>2</sub>), 0.80 (m, 9H, CH<sub>2</sub>cyclohexyl), 0.89 (m, 1H, CH<sub>2</sub>Norb), 0.97 (d,  $J_{HH}$  = 6.5 Hz, 6H, CH<sub>3</sub>IPr-NHC), 0.97 (overlapped, 6H, CH<sub>2</sub>cyclohexyl), 0.98 (s, 9H, CH<sub>3</sub>IBu), 1.07 (m, 2H, CH<sub>2</sub>Norb), 1.12 (d,  $J_{HH}$  = 6.8 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.14 (d,  $J_{HH}$  = 7.3 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.15 (d,  $J_{HH}$  = 7.0 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.19 (d,  $J_{HH}$  = 6.9 Hz, 3H, CH<sub>3</sub>IPr-Dip), 1.23 (d,  $J_{HH}$  = 5.1 Hz, 6H, CH<sub>3</sub>IPr-NHC), 1.23 (s, 9H, CH<sub>3</sub>IBu), 1.30 (m, 1H, CH<sub>2</sub>Norb), 1.32 (m, 3H, CH<sub>2</sub>cyclohexyl), 1.44 (m, 3H, CH<sub>2</sub>cyclohexyl), 1.45 (m, 6H, CH<sub>2</sub>cyclohexyl), 1.50 (m, 6H, CH<sub>2</sub>cyclohexyl), 1.65 (m, 2H, CH<sub>2</sub>Norb), 1.78 (s, 6H, CH<sub>3</sub>NHC), 2.43 (m, 1H, CH<sub>bridgehead</sub>), 3.26 (sept,  $J_{HH}$  = 6.9 Hz, 1H, CH<sub>IPr-Dip</sub>), 3.33 (m, 1H, CH<sub>bridgehead</sub>), 3.35 (sept,  $J_{HH}$  = 6.7 Hz, 1H, CH<sub>IPr-Dip</sub>), 4.20 (dd,  $J_{HH}$  = 7.2 Hz,  $J_{HP}$  = 2.7 Hz, Si-satellite:  $J_{Hsi}$  = 150.0 Hz, 1H, SiH<sub>2</sub>), 4.23 (d,  $J_{HH}$  = 7.3 Hz, Si-satellite:  $J_{Hsi}$  = 150.0 Hz, 1H, SiH<sub>2</sub>), 5.50 (br, 2H, CH<sub>IPr-NHC</sub>), 7.03-7.10 (m, 3H, CH<sub>Ar-Dip</sub>), 7.13-7.19 (m, 3H, CH<sub>Ph</sub>), 7.24 (d,  $J_{HH}$  = 7.2 Hz, 2H, CH<sub>Ph</sub>), 7.54 (s, 4H, CH<sub>B-Ar</sub>), 8.18 (s, 8H, CH<sub>B-Ar</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 5.7 (SiMe<sub>2</sub>), 6.6 (d,  $J_{CP}$  = 3.0 Hz, SiMe<sub>2</sub>), 10.1 (CH<sub>3</sub>NHC), 20.9 (CH<sub>3</sub>IPr-NHC), 22.0 (CH<sub>3</sub>IPr-NHC), 23.5 (CH<sub>3</sub>IPr-Dip), 23.8 (CH<sub>3</sub>IPr-Dip), 26.3 (CH<sub>3</sub>IPr-Dip), 26.5 (CH<sub>3</sub>IPr-Dip), 26.9 (CH<sub>2</sub>Norb), 27.5 (d,  $J_{CP}$  = 13.5 Hz, CH<sub>2</sub>cyclohexyl), 28.3 (CH<sub>2</sub>Norb), 28.5 (CH<sub>IPr-Dip</sub>), 28.6 (CH<sub>IPr-Dip</sub>), 30.1 (CH<sub>2</sub>cyclohexyl), 31.7 (d,  $J_{CP}$  = 5.0 Hz, CH<sub>2</sub>cyclohexyl), 32.9 (d,  $J_{CP}$  = 5.7 Hz, CH<sub>3</sub>IBu), 33.0 (d,  $J_{CP}$  = 6.2 Hz, CH<sub>3</sub>IBu), 34.2 (d,  $J_{CP}$  = 13.6 Hz, CH<sub>2</sub>cyclohexyl), 43.6 (CH<sub>bridgehead</sub>), 44.9 (CH<sub>2</sub>Norb), 46.7 (d,  $J_{CP}$  = 8.2 Hz, CH<sub>bridgehead</sub>), 51.2 (d,  $J_{CP}$  = 3.9 Hz, C<sub>IBu</sub>), 51.4 (d,  $J_{CP}$  = 4.0 Hz, C<sub>IBu</sub>), 53.4 (CH<sub>IPr-NHC</sub>), 117.5 (d,  $J_{CP}$  = 42.3 Hz, NC=C<sub>P</sub>), 118.0 (sept,  $J_{CF}$  = 4.0 Hz, *p*CH<sub>B-Ar</sub>), 124.4 (CH<sub>Ar</sub>), 124.6 (CH<sub>Ar</sub>), 125.2 (q,  $J_{CF}$  = 272.4 Hz, CF<sub>3</sub>), 127.8 (CH<sub>Ph</sub>), 128.3 (CH<sub>Ar</sub>), 129.7 (CH<sub>Ph</sub>), 129.9 (qq,  $J_{CF}$  = 32.0 Hz,  $J_{CB}$  = 2.7 Hz, *m*C<sub>B-Ar</sub>), 129.9 (C=C<sub>NHC</sub>), 134.0 (CH<sub>Ph</sub>), 135.4 (*o*CH<sub>B-Ar</sub>), 140.2 (SiC<sub>Ph</sub>), 140.8 (N-C<sub>Ar</sub>), 147.2 (*i*Pr-C<sub>Ar</sub>), 147.3 (*i*Pr-C<sub>Ar</sub>), 149.7 (d,  $J_{CP}$  = 3.0 Hz, C<sub>carbene</sub>), 162.8 (q,  $J_{CB}$  = 49.8 Hz, *ipso*-C<sub>B-Ar</sub>), 172.3 (d,  $J_{CP}$  = 20.2 Hz, PC=CN). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -6.1 (s, BAr<sub>4</sub><sup>F</sup>). <sup>19</sup>F NMR (471 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -62.5 (s, BAr<sub>4</sub><sup>F</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 81.8 (d,  $J_{PP}$  = 48.1 Hz, PN<sub>2</sub>), 43.8 (d,  $J_{PP}$  = 48.2 Hz, PCy<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, 25 °C, C<sub>6</sub>H<sub>5</sub>F/C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 91.5 (d,  $J_{SiP}$  = 91.5 Hz, SiPh), 92.5 (dd,  $J_{SiP}$  = 41.4 Hz and 73.5 Hz, SiH<sub>2</sub>), 10.9 (d,  $J_{SiP}$  = 3.0 Hz, SiMe<sub>2</sub>). (Minor



isomer, 46%)  $^1\text{H}$  NMR (500 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -1.92$  (td,  $J_{\text{HP}} = 2.5$  Hz and 5.9 Hz, Si-satellite :  $J_{\text{Hsi}} = 53.0$  Hz, 1H, Si-H-Ni), 0.29 (s, 3H, SiMe<sub>2</sub>), 0.42 (s, 3H, SiMe<sub>2</sub>), 0.82 (m, 9H, CH<sub>2</sub>cyclohexyl), 0.97 (d,  $J_{\text{HH}} = 8.7$  Hz, 6H, CH<sub>3</sub>iPr-NHC), 1.00 (s, 9H, CH<sub>3</sub>iBu), 1.02 (m, 1H, CH<sub>2</sub>Norb), 1.07 (d,  $J_{\text{HH}} = 6.7$  Hz, 3H, CH<sub>3</sub>iPr-Dip), 1.09 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H, CH<sub>3</sub>iPr-Dip), 1.13 (d,  $J_{\text{HH}} = 7.4$  Hz, 3H, CH<sub>3</sub>iPr-Dip), 1.17 (m, 2H, CH<sub>2</sub>Norb), 1.19 (overlapped, 12H, CH<sub>2</sub>cyclohexyl), 1.19 (s, 9H, CH<sub>3</sub>iBu), 1.23 (d,  $J_{\text{HH}} = 7.4$  Hz, 6H, CH<sub>3</sub>iPr-NHC), 1.34 (overlapped, 3H, CH<sub>2</sub>cyclohexyl), 1.36 (d,  $J_{\text{HH}} = 6.8$  Hz, 3H, CH<sub>3</sub>iPr-Dip), 1.40 (m, 6H, CH<sub>2</sub>cyclohexyl), 1.44 (m, 3H, CH<sub>2</sub>cyclohexyl), 1.47 (m, 1H, CH<sub>2</sub>Norb), 1.50 (m, 2H, CH<sub>2</sub>Norb), 1.76 (s, 6H, CH<sub>3</sub>NHC), 2.10 (dd,  $J_{\text{HH}} = 6.6$  Hz,  $J_{\text{HP}} = 10.5$  Hz, Si-satellite :  $J_{\text{Hsi}} = 110.0$  Hz, 1H, SiH), 2.32 (m, 1H, CH<sub>bridgehead</sub>), 3.31 (overlapped, 1H, CH<sub>iPr-Dip</sub>), 3.33 (m, 1H, CH<sub>bridgehead</sub>), 3.57 (sept,  $J_{\text{HH}} = 6.8$  Hz, 1H, CH<sub>iPr-Dip</sub>), 5.41 (m, 2H, CH<sub>iPr-NHC</sub>), 6.66 (overlapped, Si-satellite :  $J_{\text{Hsi}} = 190.8$  Hz, 1H, Si-H-Pd), 7.03-7.10 (m, 3H, CH<sub>Ar-Dip</sub>), 7.13-7.19 (m, 3H, CH<sub>Ph</sub>), 7.29 (d,  $J_{\text{HH}} = 7.5$  Hz, 2H, CH<sub>Ph</sub>), 7.54 (s, 4H, CH<sub>B-Ar</sub>), 8.18 (s, 8H, CH<sub>B-Ar</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 5.6$  (SiMe<sub>2</sub>), 6.9 (d,  $J_{\text{CP}} = 2.9$  Hz, SiMe<sub>2</sub>), 10.0 (CH<sub>3</sub>NHC), 21.4 (CH<sub>3</sub>iPr-NHC), 22.1 (CH<sub>3</sub>iPr-NHC), 22.9 (CH<sub>3</sub>iPr-Dip), 24.8 (CH<sub>3</sub>iPr-Dip), 25.1 (CH<sub>3</sub>iPr-Dip), 26.2 (CH<sub>2</sub>Norb), 27.0 (CH<sub>3</sub>iPr-Dip), 26.1 (d,  $J_{\text{CP}} = 13.4$  Hz, CH<sub>2</sub>cyclohexyl), 28.0 (CH<sub>iPr-Dip</sub>), 28.6 (CH<sub>iPr-Dip</sub>), 28.7 (CH<sub>2</sub>Norb), 30.4 (CH<sub>2</sub>cyclohexyl), 31.3 (d,  $J_{\text{CP}} = 4.1$  Hz, CH<sub>2</sub>cyclohexyl), 32.8 (d,  $J_{\text{CP}} = 5.8$  Hz, CH<sub>3</sub>iBu), 32.9 (d,  $J_{\text{CP}} = 5.7$  Hz, CH<sub>3</sub>iBu), 33.8 (d,  $J_{\text{CP}} = 13.7$  Hz, CH<sub>2</sub>cyclohexyl), 43.6 (CH<sub>bridgehead</sub>), 46.5 (d,  $J_{\text{CP}} = 4.2$  Hz, CH<sub>2</sub>Norb), 47.0 (d,  $J_{\text{CP}} = 8.2$  Hz, CH<sub>bridgehead</sub>), 50.8 (d,  $J_{\text{CP}} = 3.0$  Hz, C<sub>t</sub>Bu), 51.2 (d,  $J_{\text{CP}} = 3.0$  Hz, C<sub>t</sub>Bu), 53.2 (CH<sub>iPr-NHC</sub>), 116.0 (d,  $J_{\text{CP}} = 43.5$  Hz, NC=CP), 118.0 (sept,  $J_{\text{CF}} = 4.0$  Hz, pCH<sub>B-Ar</sub>), 124.5 (CH<sub>Ar</sub>), 124.8 (CH<sub>Ar</sub>), 125.2 (q,  $J_{\text{CF}} = 272.4$  Hz, CF<sub>3</sub>), 127.4 (CH<sub>Ph</sub>), 128.4 (CH<sub>Ph</sub>), 129.9 (qq,  $J_{\text{CF}} = 32.0$  Hz,  $J_{\text{CB}} = 2.7$  Hz, mC<sub>B-Ar</sub>), 129.9 (C=C<sub>NHC</sub>), 133.9 (CH<sub>Ph</sub>), 135.4 (oCH<sub>B-Ar</sub>), 140.0 (SiC<sub>Ph</sub>), 141.4 (N-C<sub>Ar</sub>), 146.7 (iPr-C<sub>Ar</sub>), 147.4 (iPr-C<sub>Ar</sub>), 149.5 (d,  $J_{\text{CP}} = 3.3$  Hz, C<sub>carbene</sub>), 162.8 (q,  $J_{\text{CB}} = 49.8$  Hz, ipso-C<sub>B-Ar</sub>), 171.5 (d,  $J_{\text{CP}} = 20.3$  Hz, PC=CN).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -6.1$  (s, BA<sup>F</sup><sub>4</sub>),  $^{19}\text{F}$  NMR (471 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -62.5$  (s, BA<sup>F</sup><sub>4</sub>),  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 83.7$  (d,  $J_{\text{PP}} = 47.4$  Hz, PN<sub>2</sub>), 42.8 (d,  $J_{\text{PP}} = 47.4$  Hz, PCy<sub>3</sub>),  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 96.8$  (d,  $J_{\text{SiP}} = 93.0$  Hz, SiPh), 100.7 (dd,  $J_{\text{SiP}} = 36.9$  Hz and 73.5 Hz, SiH<sub>2</sub>), 11.5 (d,  $J_{\text{SiP}} = 3.4$  Hz, SiMe<sub>2</sub>). FD-MS (positive): m/z: Calcd for [C<sub>64</sub>H<sub>110</sub>N<sub>5</sub>NiP<sub>2</sub>PdSi<sub>3</sub>]<sup>+</sup> 1258.6; Found 1258.7.

**Compound 13:** In an NMR tube, to a solution of **2** (100 mg, 0.050 mmol) in  $\text{C}_6\text{H}_5\text{F}$  (0.4 mL),  $\text{PMe}_3$  in toluene (0.25 mL, 1.0 M, 0.25 mmol, 4 equiv.) was added at room temperature. After overnight, all volatiles were removed under reduced pressure and the residue was washed with pentane (0.5 mL x 3). Compound **13** was crystallized by a two-layer technique [Et<sub>2</sub>O/pentane solution (0.1 : 0.5 mL)] at room temperature and was obtained as black crystals (49 mg, 53%). Crystals suitable for X-ray diffraction analysis were obtained from a saturated Et<sub>2</sub>O/pentane solution at -30 °C. Mp. 153-156 °C (decomp.).  $^1\text{H}$  NMR (500 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 0.09$  (s, 3H, SiMe<sub>2</sub>), 0.15 (s, 3H, SiMe<sub>2</sub>), 0.65 (d,  $J_{\text{HP}} = 6.1$  Hz, 27H, Ni-PMe<sub>3</sub>), 0.72 (d,  $J_{\text{HH}} = 8.4$  Hz, 1H, CH<sub>2</sub>Norb), 0.79 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H, CH<sub>3</sub>iPr), 0.79 (s, 9H, CH<sub>3</sub>iBu), 0.81 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H, CH<sub>3</sub>iPr), 0.85 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H, CH<sub>3</sub>iPr), 0.86 (s, 9H, CH<sub>3</sub>iBu), 0.88 (overlapped, 1H, CH<sub>2</sub>Norb), 0.89 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H, CH<sub>3</sub>iPr), 0.90 (br s, 9H, Pd-PMe<sub>3</sub>), 1.07 (m, 1H, CH<sub>2</sub>Norb), 1.21 (m, 1H, CH<sub>2</sub>Norb), 1.31 (m, 1H, CH<sub>2</sub>Norb), 1.36 (m, 1H, CH<sub>2</sub>Norb), 1.97 (s, 1H, CH<sub>bridgehead</sub>), 2.73 (sept,  $J_{\text{HH}} = 6.9$  Hz, 1H, CH<sub>iPr</sub>), 2.76 (sept,  $J_{\text{HH}} = 6.9$  Hz, 1H, CH<sub>iPr</sub>), 3.09 (s, 1H, CH<sub>bridgehead</sub>), 6.86-6.90 (m, 3H, CH<sub>Ar</sub>), 7.28 (s, 4H, CH<sub>B-Ar</sub>), 7.96 (s, 8H, CH<sub>B-Ar</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 4.7$  (SiMe<sub>2</sub>), 5.8 (d,  $J_{\text{CP}} = 5.2$  Hz, SiMe<sub>2</sub>), 18.3 (br s, Pd-PMe<sub>3</sub>), 22.3 (CH<sub>3</sub>iPr), 22.4 (CH<sub>3</sub>iPr), 23.4 (dt,  $J_{\text{CP}} = 20.2$  and 5.8 Hz, Ni-PMe<sub>3</sub>), 24.9 (CH<sub>3</sub>iPr), 25.3 (CH<sub>2</sub>Norb), 25.5 (CH<sub>3</sub>iPr),

26.9 (CH<sub>2</sub>Norb), 27.9 (CH<sub>iPr</sub>), 28.0 (CH<sub>iPr</sub>), 31.1 (d,  $J_{\text{CP}} = 6.4$  Hz, CH<sub>3</sub>iBu), 31.6 (d,  $J_{\text{CP}} = 6.4$  Hz, CH<sub>3</sub>iBu), 44.5 (CH<sub>bridgehead</sub>), 45.5 (d,  $J_{\text{CP}} = 10.4$  Hz, CH<sub>bridgehead</sub>), 47.1 (d,  $J_{\text{CP}} = 3.5$  Hz, CH<sub>2</sub>Norb), 50.2 (d,  $J_{\text{CP}} = 5.2$  Hz, C<sub>t</sub>Bu), 50.5 (d,  $J_{\text{CP}} = 2.9$  Hz, C<sub>t</sub>Bu), 117.8 (d,  $J_{\text{CP}} = 13.9$  Hz, PC=CN), 117.1 (br sept,  $J_{\text{CF}} = 4.6$  Hz, p-CH<sub>B-Ar</sub>), 124.4 (CH<sub>Ar</sub>), 124.6 (CH<sub>Ar</sub>), 126.6 (q,  $J_{\text{CF}} = 272.4$  Hz, CF<sub>3</sub>), 127.8 (CH<sub>Ar</sub>), 129.1 (qq,  $J_{\text{CF}} = 27.5$  Hz,  $J_{\text{CB}} = 2.9$  Hz, m-C<sub>B-Ar</sub>), 134.6 (o-CH<sub>B-Ar</sub>), 136.8 (N-C<sub>Ar</sub>), 145.6 (iPr-C<sub>Ar</sub>), 146.3 (iPr-C<sub>Ar</sub>), 161.2 (d,  $J_{\text{CP}} = 26.6$  Hz, PC=CN), 162.1 (q,  $J_{\text{CB}} = 49.8$  Hz, ipso-C<sub>B-Ar</sub>).  $^{11}\text{B}\{^1\text{H}\}$  (160 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -6.3$  (BA<sup>F</sup><sub>4</sub>).  $^{19}\text{F}$  NMR (470 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = -62.8$  (s, BA<sup>F</sup><sub>4</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 80.6$  (q,  $J_{\text{PP}} = 47.3$  Hz, PN<sub>2</sub>), -15.8 (d,  $J_{\text{PP}} = 47.9$  Hz, Ni-PMe<sub>3</sub>), -49.2 (br s, Pd-PMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz, 25 °C,  $\text{C}_6\text{H}_5\text{F}/\text{C}_6\text{D}_6$ ):  $\delta = 290.3$  (br m, N-Si-Ni), 12.9 (d,  $J_{\text{SiP}} = 6.1$  Hz, SiMe<sub>2</sub>).

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[40–58]</sup>

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## Conflict of Interests

The authors declare no conflict of interest.

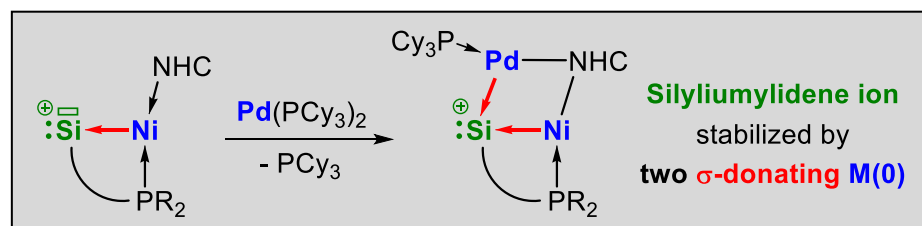
**Keywords:** silyliumylidene ion • base-stabilized species • Z-ligand • nickel(0) • palladium(0)

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## Entry for the Table of Contents



A silyliumylidene ion stabilized by two Ni(0)- and Pd(0)-based  $\sigma$ -donating ligands was synthesized. Its particular coordination mode was characterized by a pyramidalized silicon center with a lone pair. Interestingly, a ligand exchange reaction leads to a significant change in the coordination mode to form a metal-based donor/acceptor-stabilized silyliumylidene ion, characterized by a vacant orbital at the Si center. Despite the stabilization by the two metal ligands, the silyliumylidene complex remains highly reactive.