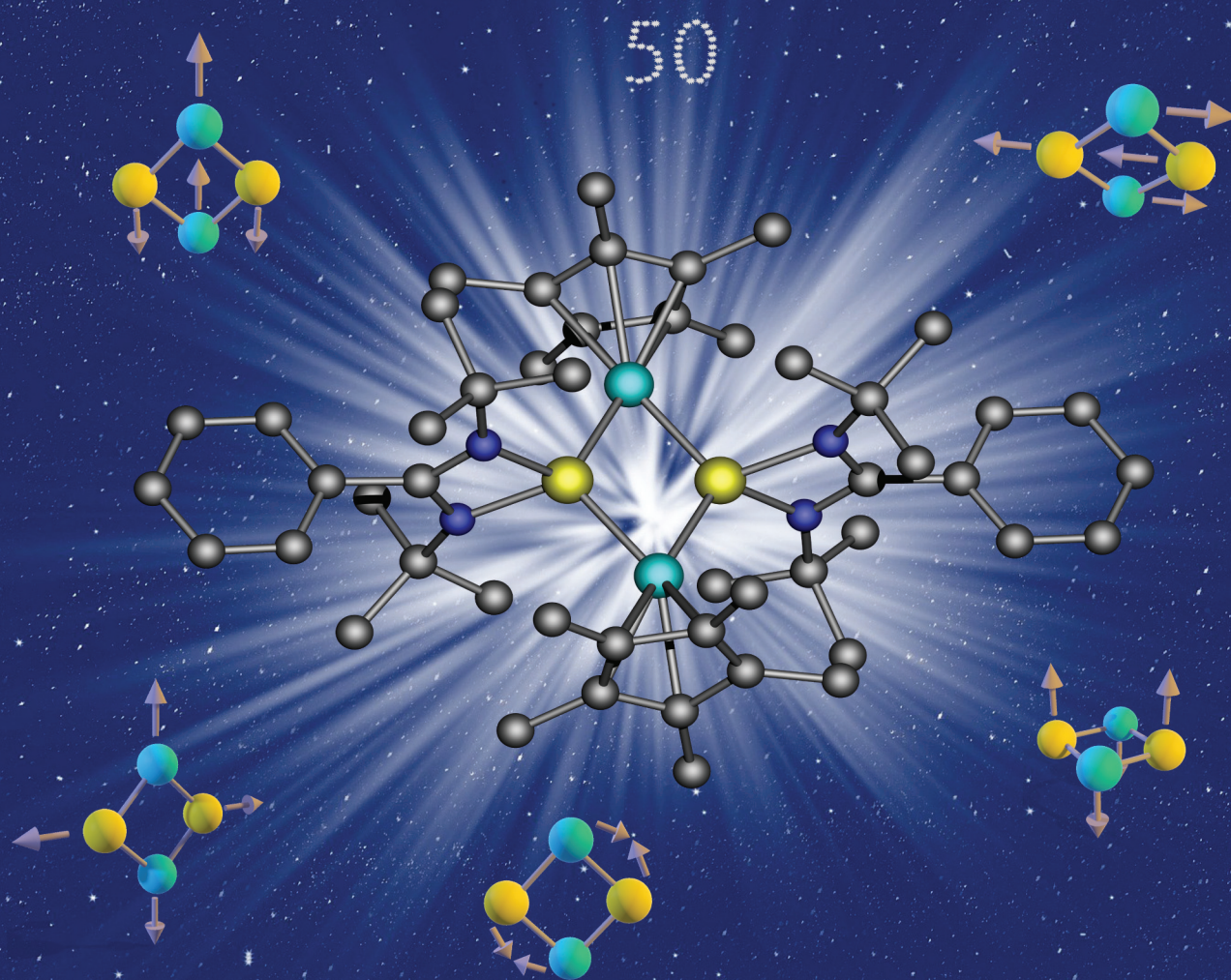


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A square planar silylene nickel four-membered ring†‡

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Herein the new nickel silylene $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)]_2$, which features a square planar central ring motif consisting of two silicon and two nickel atoms is presented. The title compound was obtained by an insertion of the Ni(0) precursor $[\text{Ni}(\text{cod})_2]$ (cod = 1,5-cyclooctadiene) in the Si–C bond of the silylene $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$. Analytic characterisation including mass spectrometry as well as IR and Raman spectroscopies was combined with quantum chemical calculations to get an insight on the bonding situation within the four-membered Si–Ni–ring.

Introduction

Since the isolation of decamethylsilicocene, divalent molecular silicon species, called “silylenes”, have fascinated many chemists and led to the exploitation of an incredibly rich and vast field of research.^{1–6} This development was fuelled by stabilization of divalent silicon atoms as heavy carbon analogues using N-heterocycles, which lead to the synthesis of four-, five- and six-membered N-heterocyclic silylenes.^{7–12} Among these, the amidinate functionalized four-membered ring is one of the most intensely investigated systems.^{12–25} One reason for the great interest lies in the scaffold of these silylenes comprising not only the amidinate but also another monoanionic ligand attached to the silicon atom. This additional moiety can be varied over a wide range and thus allows for great flexibility in the steric demand as well as the electronic properties present on the silylene.¹⁹ One of those combinations is the pentamethylcyclopentadienyl ligand (Cp^*) as coligand in addition to the amidinate $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$, which

results in a silylene, that can be regarded as an intermediate between the aforementioned decamethylsilicocene and silylenes bearing multiple amidinate ligands.^{20–22,26–29} Recently, we showed that $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$ readily complexes the elements zinc, rhodium and iridium. In all these cases, $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$ acts as a Lewis base. For further reactivity studies, we aimed to treat $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$ with Ni(0) as it is more reactive than the previously used nickel precursors. Ni-compounds are known for their catalytic properties and their ability to activate relatively inert bonds (e.g. C–F).^{30–33} In general, C–X activation initiated by nickel compounds proceeds *via* oxidative addition of the C–X bond to the nickel complex. This can also be viewed as an insertion of the nickel atom into the respective bond.^{32,34,35} Recently, this kind of reactivity was also observed with silylenes.^{36–46}

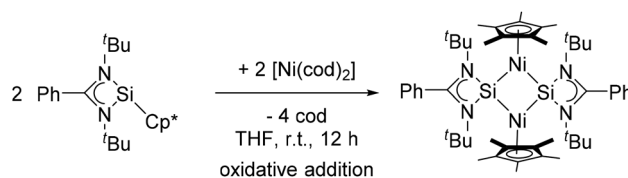
Results and discussion

As a suitable Ni(0) precursor, we chose bis(cyclooctadiene) nickel ($[\text{Ni}(\text{cod})_2]$) (cod = 1,5-cyclooctadiene). Condensation of THF to a solid mixture of $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$ and $[\text{Ni}(\text{cod})_2]$ at -88°C followed by a slow warm-up to room temperature resulted in a colour change of the solution from yellow over green to dark red (Scheme 1). From this solution red crystals suitable for X-ray diffraction of $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)]_2$ formed over the course of several hours. During the reaction, an insertion of the nickel atom into the Si–Cp* bond lead to formation of a four-membered ring consisting of two nickel

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† This work is dedicated to the memory of Anthony J. Downs, a distinguished inorganic chemist, and a dear friend.

‡ Electronic supplementary information (ESI) available: Experimental procedures, mass spectra, IR and RAMAN spectra, XRD data, ORTEP plots and details to quantum chemical calculations. CCDC 2105223. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt02846d

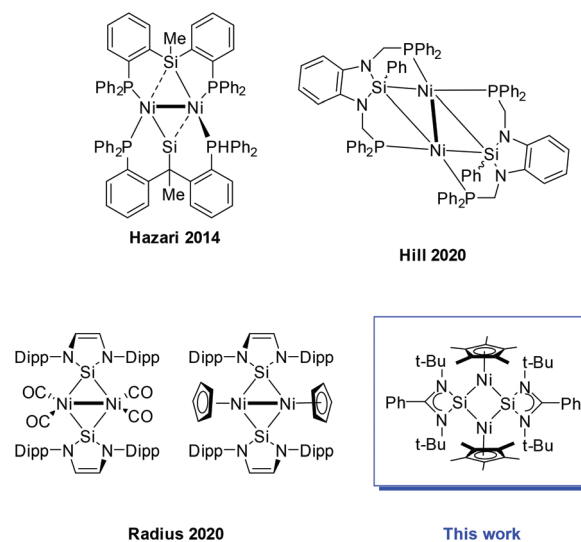


Scheme 1 Synthesis of $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)]_2$.

and two silicon atoms. The molecular structure in the solid state (Fig. 1) shows each nickel atom in a trigonal planar environment of two silylenes and one Cp* ligand. In addition to their coordination onto the nickel atoms, the silylenes are coordinated by the bis-*tert*-butyl-benzamidinate ligand. The Si–Ni bond is rather long (Ni–Si 2.2579(12), Ni'–Si or Ni–Si' 2.2632(13) Å) compared to other literature known silylene nickel compounds.^{36–46} The distance between the nickel atom and the Cp* centroid (Ni–Cp*_{ctr} 1.8992(8) Å) is also large compared to literature values.^{47–49} The structural parameters of the amidinate ligand do not deviate from the starting material. In general, four-membered [M–Si(II)]₂-rings (M = transition metal) are rare^{50–53} and only a few examples are known for Ni.^{54–58} However, the bonding situation and the nature of the silylene is different in those complexes (Scheme 2).

In contrast to the literature known examples, *e.g.* [(η⁵-C₅H₅)Ni(μ-Dipp₂NHSi)]₂ (Dipp₂NHSi = 1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-4-silacyclopent-4-en-2-yliden), where the silylene bridges low valent R_n–Ni–Ni–R_n scaffolds, no metal-to-metal bond is seen in [PhC(NtBu)₂SiNi(C₅Me₅)]₂. This is also reflected in the large Ni–Ni bond distance of 3.8716(13) Å in [PhC(NtBu)₂SiNi(C₅Me₅)]₂ compared to 2.5025(3) Å in [(η⁵-C₅H₅)Ni(μ-Dipp₂NHSi)]₂ and 2.5218(5) Å in [(Ni(CO)₂(μ-Dipp₂NHSi)]₂.^{54,55} The observed large Ni–Ni distance is also in good agreement with the calculated value of 3.624 Å (see below). While Dipp₂NHSi, in which the silicon atom is bound to a dinegatively charged ligand, only acts as a Lewis base, the PhC(NtBu)₂Si-fragment acts as a Lewis base and additionally forms a covalent Ni–Si-bond. Thus, [PhC(NtBu)₂SiNi(C₅Me₅)]₂ can be formally considered as a dimer of [PhC(NtBu)₂SiNi(C₅Me₅)]. The results of quantum chemical calculations of the bonding situation are given below.

The low solubility of [PhC(NtBu)₂SiNi(C₅Me₅)]₂ allowed no conclusive NMR spectroscopic measurements, but ESI and EI mass spectrometry and vibrational spectroscopy (mid and far infrared (IR) as well as Raman) were employed for further characterisation. The mass spectra showed a remarkable stability of the complex as its molecule peak was visible at 904 *m/z*



Scheme 2 Literature known Si₂Ni₂ compounds and the title complex.^{54–57}

in EI mass spectrometry. Vibrational spectroscopic studies, supported by quantum chemical RI-DFT calculations, were carried out to evaluate the bonding properties of the compound.

The calculations were performed using the BP-86 functional,^{59,60} the basis sets were of def2-SV(P) quality for all atoms as given in the program package TURBOMOLE. The symmetry of the molecule was constrained to C_i.⁶¹ The structural and spectroscopic data of the singlet ground state obtained from the quantum chemical calculations are in excellent agreement with the experimental data. Both the ³A_u or ³A_g states are energetically 164 or 140 kJ mol^{–1} higher compared to the singlet ground state. The Si–Si distances related to these structures are 2.99 or 2.58 Å, respectively, so that a triplet ground state can safely be ruled out. After the analytical calculation of the theoretical Hessian matrix with the help of the AOFORCE program module, the eigenvectors are analysed to describe the normal motions of the molecular framework.⁶²

In the IR and Raman spectra given (Fig. 2), the four Si–Ni valence vibrations of the Si₂Ni₂ four-membered ring can be observed in the range between 1000 and 200 cm^{–1} (a_g: exp. 465.3 (calc. 477), 369.2 (396); a_u: 503.0 (515), 423.9 (433) cm^{–1}). The same is true for the two vibrations of the Cp* system against the Ni atom (a_g: exp. 356.6 (365) a_u: 308.5 (330) cm^{–1}) and for the four Si–N valence vibrations (a_g: 765.6 (751) 750.7 (742); a_u 787.1 (785) 744.4 (742) cm^{–1}). The energetic separation observed for the individual SiN₂/Ni₂Si₂/NiCp* bonding systems is within the expected range. Due to the inversion symmetry centre in this molecule, the rule of mutual exclusion applies, and the vibrations of a_g symmetry are only Raman active whereas a_u vibrations are only IR active.

In the IR spectrum, a shoulder is found at 293 cm^{–1} (calc. 316 cm^{–1}) which is assigned to the butterfly-like out-of-plane motion of the Ni₂Si₂ ring. In analogy to the procedure in small

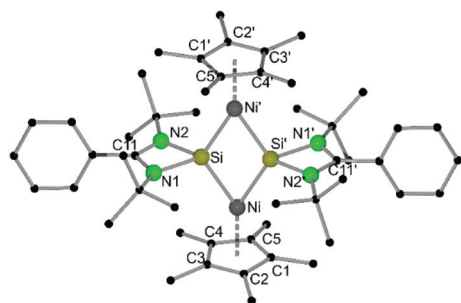


Fig. 1 Molecular structure of [PhC(NtBu)₂SiNi(C₅Me₅)]₂ in the solid state. Hydrogen atoms were omitted for better clarity. The symmetry generated atoms were labelled with an apostrophe. Selected bond lengths [Å] and angles [°]: Ni–Si 2.2579(12), Ni'–Si or Ni–Si' 2.2632(13), Ni–Cp*_{ctr} 1.8992(8), Si–N1 1.857(3), Si–N2 1.793(3), N1–C11 1.278(4), N2–C11 1.332(5), Si–Ni–Si' 62.18(5), Ni–Si–Ni' 117.82(5), N1–C11–N2 109.7(3). (Distance between the two Ni-atoms in [Å]: Ni–Ni' 3.8716(13).)



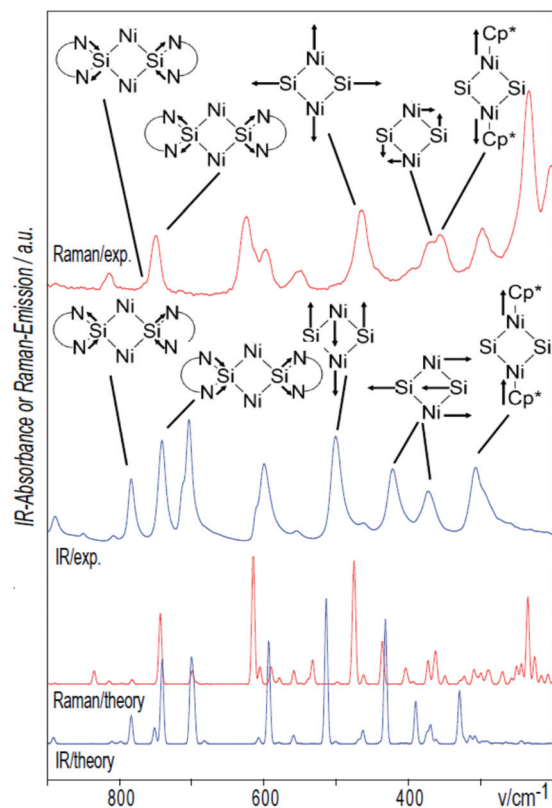


Fig. 2 Experimental and theoretical IR and Raman spectra of the title compound. The normal modes of the molecular framework are given.

four-membered ring molecules which was intensely investigated,⁶³ the force constant of the out-of-plane motion is determined according to the method of Wilson, Decius and Cross.⁶⁴ Using the *G*-matrix element $G_{oop} = 1/2(\mu_{Si} + \mu_{Ni})$,⁶³ the unusually large force constant value of $1.92 \text{ mdy}\cdot\text{\AA}^{-1}$ is thus obtained, which is indicative of a rather rigid Ni_2Si_2 framework. In weaker and preferentially ionically bonded four-membered ring molecules such as Si_2O_2 , Ge_2O_2 , or Al_2Cl_2 , the value of the out-of-plane force constant is only 0.61, 0.29 and $0.03 \text{ mdy}\cdot\text{\AA}^{-1}$, respectively.⁶³

For more detailed investigations, a population analysis based on occupation numbers was carried out according to the method of Ahlrichs and Heinzmann.^{65,66} The atomic partial charges determined for Si and Ni are +0.49 and +0.37, respectively, and confirm the expected covalent bonding forces. For the shared electron number (SEN) as a measure for the covalent bond strength a value of 1.05 is obtained, which is in good agreement with a covalent Ni–Si single bond. Furthermore, a SEN between the silicon atoms of 0.93 is found, which could be indicative of a Si–Si bond. However, this high value results as an artefact based on a three-centre SEN(Si–Ni–Si) of 0.19. This behaviour has been discussed before in four-membered ring molecules like diborane.⁶⁶ After a Boys localisation four localized MOs (LMOs) showing pronounced Si–Ni bonding are found for the Ni_2Si_2 system (see Fig. 3). The strong covalent character is confirmed by the

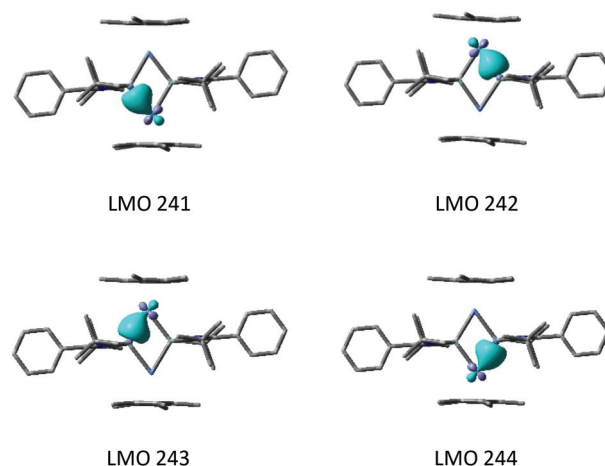


Fig. 3 Isosurface plots (values $\pm 0.10 \text{ e}$) of the localised MOs (LMO 241 to LMO 244) of the Ni_2Si_2 molecule showing pronounced Ni–Si bonding.

results of a Mulliken population analysis for each LMO (LMOs 241 and 242: Ni 0.98, Si 1.01; LMOs 243 and 244: Ni 0.88, Si 1.11).

The electron density contour plot and the gradient vector field (Fig. 4) according to Bader's Theory of Atoms in Molecules were determined using the program Multiwfn 3.6.⁶⁷ They provide an unconstrained indication of whether a silicon–silicon bond is actually present.⁶⁸ Bond critical points are found between Ni and Si, but not between both Si or Ni atoms. Based on this orienting consideration, both a Si–Si bond as well as a Ni–Ni bond can be safely excluded. A small Si–Si distance in four-membered ring compounds is not a compelling indication of a bond. For instance, in molecules containing Si_2X_2 ($\text{X} = \text{N}, \text{O}$) four-membered rings, the formation of a Si–Si bond was ruled out after several theoretical and experimental investigations.^{69,70}

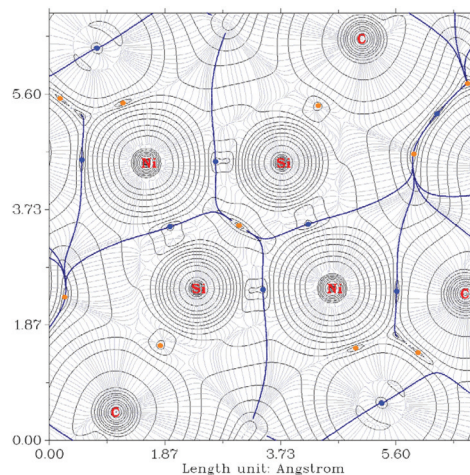


Fig. 4 Contour plot of the electronic charge density and its corresponding gradient vector field of the molecule $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)_2]$. Critical bond points are depicted in blue, ring critical points in orange.



Conclusions

The new nickel silylene complex $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)]_2$ was synthesized by an oxidative addition of $[\text{PhC}(\text{NtBu})_2\text{Si}(\text{C}_5\text{Me}_5)]$ to a Ni(0) precursor. The compound features a four-membered planar ring consisting of two nickel and two silylenes. This motif shows a surprising stability and rigidity. Furthermore, vibrational spectroscopy confirmed by quantum chemical calculations was employed to gain more insight into the bonding situation. The results indicate covalent bonds within the four-membered ring. $[\text{PhC}(\text{NtBu})_2\text{SiNi}(\text{C}_5\text{Me}_5)]_2$ is fundamentally different compared to other $[\text{M}-\text{Si}(\text{u})]_2$ -rings as neither Si-Si nor Ni-Ni bonds through the ring are observed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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