COMMUNICATION
Peter W. Roesky et al.
A square planar silylene nickel four-membered ring
Herein the new nickel silylene \([\text{PhC}({\text{Bu}2} \text{SiNi(C5Me5)})]_2\) is presented. The title compound was obtained by an insertion of the Ni(0) precursor \([\text{Ni}({\text{cod}})_2]\) into the Si–C bond of the silylene \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\). Analytical 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 stabilisation 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 amidate but also another monoanionic ligand attached to the silicon atom. This additional moiety can be varied over a wide range and thus allows for greater 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 \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\). 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 \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\) readily complexes the elements zinc, rhodium and iridium. In all these cases, \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\) acts as a Lewis base. For further reactivity studies, we aimed to treat \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\) with Ni(0) as it is more reactive than the previously used nickel precursors.

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 \([\text{PhC}({\text{Bu}2} \text{Si} \text{C5Me5})]_2\) 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 \([\text{PhC}({\text{Bu}2} \text{Si} \text{Ni} \text{C5Me5})]_2\), 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

**Scheme 1** Synthesis of \([\text{PhC}({\text{Bu}2} \text{Si} \text{Ni} \text{C5Me5})]_2\).
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*centre 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(u)]2-rings (M = transition metal) are rare50–53 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 Rn-Ni-Rn 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 Dipp NHSi, 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) 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 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 C1.61 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 3Au or 3Ag 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 (ag: exp. 465.3 (calc. 477), 369.2 (396); au: 503.0 (515), 423.9 (433) cm−1). The same is true for the two vibrations of the Cpd* system against the Ni atom (ag: exp. 356.6 (365) au: 308.5 (330) cm−1) and for the four Si–N valence vibrations (ag: 765.6 (751) 750.7 (742); au: 787.1 (785) 744.4 (742) cm−1). The energetic separation observed for the individual SiN2/NiSi2/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 ag symmetry are only Raman active whereas au 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
four-membered ring molecules which was intensely investigated, the force constant of the out-of-plane motion is determined according to the method of Wilson, Decius and Cross. Using the $G$-matrix element $G_{oop} = 1/2(\mu_{Si} + \mu_{Ni})$, the unusually large force constant value of 1.92 modyn Å$^{-1}$ is thus obtained, which is indicative of a rather rigid Ni$_2$Si$_2$ framework. In weaker and preferentially ionically bonded four-membered ring molecules such as Si$_2$O$_2$, Ge$_2$O$_2$, or Al$_2$Cl$_2$, the value of the out-of-plane force constant is only 0.61, 0.29 and 0.03 modyn Å$^{-1}$, respectively.

For more detailed investigations, a population analysis based on occupation numbers was carried out according to the method of Ahlrichs and Heinzmann. 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. After a Boys localisation four localized MOs (LMOs) showing pronounced Si–Ni bonding are found for the Ni$_2$Si$_2$ system (see Fig. 3). The strong covalent character is confirmed by the 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. They provide an unconstrained indication of whether a silicon–silicon bond is actually present. 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$_2$X$_2$ (X = N, O) four-membered rings, the formation of a Si–Si bond was ruled out after several theoretical and experimental investigations.

---

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

**Fig. 3** Isosurface plots (values ± 0.10 e) of the localised MOs (LMO 241 to LMO 244) of the Ni$_2$Si$_2$ molecule showing pronounced Ni–Si bonding.

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

The new nickel silylene complex [PhC(NtBu)2SiNi(C5Me5)]2 was synthesized by an oxidative addition of [PhC(NtBu)2Si(C5Me5)] 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. [PhC(NtBu)2SiNi(C5Me5)]2 is fundamentally different compared to other [M–Si[n]]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

Financial support by the German Research Foundation (DFG) funded transregional collaborative research center SFB/TRR 88 “Cooperative Effects in Homo and Heterometallic Complexes (3MET)”, project B3 is gratefully acknowledged. The authors acknowledge computational support by the state of Baden-Württemberg through bwHPC and DFG through grant no. INST 40/467-1 FUGG. We acknowledge Dr S. Schäfer for helpful discussions on the topic of silylenes.

Notes and references

1 P. Jutzi, D. Kanne and C. Krüger, Angew. Chem., Int. Ed. Engl., 1986, 98, 163–164.
2 B. Marcinièc, Hydroisilylation: A comprehensive review on recent advances, Springer, Dordrecht, 2009.
3 M. Asay, C. Jones and M. Driess, Chem. Rev., 2011, 111, 354–396.
4 J. Y. Corey and J. Braddock-Wilking, Chem. Rev., 1999, 99, 175–292.
5 A. Staubitz, A. P. Robertson, M. E. Sloan and I. Manners, Chem. Rev., 2010, 110, 4023–4078.
6 N. J. Hill and R. West, J. Organomet. Chem., 2004, 689, 4165–4183.
7 A. J. Arduengo, R. L. Harlow and M. Kline, J. Am. Chem. Soc., 1991, 113, 361–363.
8 R. West, A. F. Hill and M. J. Fink, Advances in organometallic chemistry, Elsevier, Oxford, 2008.
9 M. Haaf, T. A. Schmedake and R. West, Acc. Chem. Res., 2000, 33, 704–714.
10 M. Driess, S. Yao, M. Brym, C. van Wullen and D. Lentz, J. Am. Chem. Soc., 2006, 128, 9628–9629.
11 C. W. So, H. W. Roesky, J. Magull and R. B. Oswald, Angew. Chem., Int. Ed., 2006, 45, 3948–3950.
12 S. S. Sen, H. W. Roesky, D. Stern, J. Henn and D. Stalke, J. Am. Chem. Soc., 2010, 132, 1123–1126.
13 C. W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones and S. Blaurock, J. Am. Chem. Soc., 2007, 129, 12049–12054.
14 C. W. So, H. W. Roesky, R. B. Oswald, A. Pal and P. G. Jones, Dalton Trans., 2007, 5241–5244.
15 S. Nagendran and H. W. Roesky, Organometallics, 2008, 27, 437–492.
16 A. Jana, D. Leusser, I. Objartel, H. W. Roesky and D. Stalke, Dalton Trans., 2011, 40, 5458–5463.
17 S. Khan, S. S. Sen, D. Kratzert, G. Tavcar, H. W. Roesky and D. Stalke, Chem. – Eur. J., 2011, 17, 4283–4290.
18 S. Khan, S. S. Sen, R. Michel, D. Kratzert, H. W. Roesky and D. Stalke, Organometallics, 2011, 30, 2643–2645.
19 R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf and D. Stalke, Organometallics, 2012, 31, 4588–4592.
20 S. Schäfer, R. Köppe, M. T. Gamer and P. W. Roesky, Chem. Commun., 2014, 50, 11401–11403.
21 S. Schäfer, R. Köppe and P. W. Roesky, Chem. – Eur. J., 2016, 22, 7127–7133.
22 S. Kaufmann, S. Schäfer, M. T. Gamer and P. W. Roesky, Dalton Trans., 2017, 46, 8861–8867.
23 S. Li, Y. Wang, W. Yang, K. Li, H. Sun, X. Li, O. Fuhr and D. Fenske, Organometallics, 2020, 39, 757–766.
24 W. Yang, Y. Dong, H. Sun and X. Li, Dalton Trans., 2021, 50, 6766–6772.
25 X. Sun, T. Simler, R. Yadav, R. Köppe and P. W. Roesky, J. Am. Chem. Soc., 2019, 141, 14987–14990.
26 B. Blom, G. Klett, D. Gallego, G. Tan and M. Driess, Dalton Trans., 2015, 44, 639–644.
27 K. Junold, J. A. Baus, C. Burschka, D. Auerhammer and R. Tacke, Chem. – Eur. J., 2012, 18, 16288–16291.
28 K. Junold, J. A. Baus, C. Burschka and R. Tacke, Angew. Chem., Int. Ed., 2012, 51, 7020–7023.
29 K. Junold, M. Nutz, J. A. Baus, C. Burschka, C. Fonseca Guerra, F. M. Bickelhaupt and R. Tacke, Chem. – Eur. J., 2014, 20, 9319–9329.
30 S. Z. Tasker, E. A. Standley and T. F. Jamison, Nature, 2014, 509, 299–309.
31 R. Jana, T. P. Pathak and M. S. Sigman, Chem. Rev., 2011, 111, 1417–1492.
32 L. Ackermann, R. Vicente and A. R. Kapdi, Angew. Chem., Int. Ed., 2009, 48, 9792–9826.
33 W. Xu, H. Sun, Z. Xiong and X. Li, Organometallics, 2013, 32, 7122–7132.
34 U. S. D. Paul and U. Radius, Eur. J. Inorg. Chem., 2017, 2017, 3362–3375.
35 T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius and A. Mix, J. Am. Chem. Soc., 2008, 130, 9304–9317.
36 M. Denk, R. K. Hayashi and R. West, Chem. Commun., 1994, 33–34.
37 B. Gehrh us, P. B. Hitchcock, M. F. Lappert and H. Maciejewski, Organometallics, 1998, 17, 5599–5601.
38 L. Kong, J. Zhang, H. Song and C. Cui, Dalton Trans., 2009, 5444–5446.
39 A. Meltzer, C. Prasang, C. Milsmann and M. Driess, Angew. Chem., Int. Ed., 2009, 48, 3170–3173.
40 G. Tavcar, S. S. Sen, R. Azhakar, A. Thorn and H. W. Roesky, Inorg. Chem., 2010, 49, 10199–10202.
41 W. Wang, S. Inoue, S. Yao and M. Driess, J. Am. Chem. Soc., 2010, 132, 15890–15892.
42 M. Stoelzel, C. Prasang, S. Inoue, S. Enthaler and M. Driess, Angew. Chem., Int. Ed., 2012, 51, 399–403.
43 N. C. Breit, T. Szilvasi, T. Suzuki, D. Gallego and S. Inoue, J. Am. Chem. Soc., 2013, 135, 17958–17968.
44 D. Gallego, A. Bruck, E. Irran, F. Meier, M. Kaupp, M. Driess and J. F. Hartwig, J. Am. Chem. Soc., 2013, 135, 15617–15626.
45 Y. Wang, A. Kostenko, S. Yao and M. Driess, J. Am. Chem. Soc., 2017, 139, 13499–13506.
46 A. Kostenko and M. Driess, J. Am. Chem. Soc., 2018, 140, 16962–16966.
47 M. D. Walter, C. J. Burns, P. T. Matsunaga, M. E. Smith and R. A. Andersen, Organometallics, 2016, 35, 3488–3497.
48 D. V. Fomitchev, T. R. Furlani and P. Coppens, Inorg. Chem., 1998, 37, 1519–1526.
49 S. Pelties, D. Herrmann, B. de Bruin, F. Hartl and R. Wolf, Chem. Commun., 2014, 50, 7014–7016.
50 M. Stoelzel, C. Prasang, B. Blom and M. Driess, Aust. J. Chem., 2013, 66, 1163–1170.
51 A. Furstner, H. Krause and C. W. Lehmann, Chem. Commun., 2001, 2372–2373.
52 S. Khoo, J. Cao, M. C. Yang, Y. L. Shan, M. D. Su and C. W. So, Chem. – Eur. J., 2018, 24, 14329–14334.
53 W. A. Herrmann, P. Härter, C. W. K. Gstöttmayr, F. Bielet, N. Seeboth and P. Sirsch, J. Organomet. Chem., 2002, 649, 141–146.
54 M. J. Krahfuss and U. Radius, Inorg. Chem., 2020, 59, 10976–10985.
55 M. J. Krahfuss, J. Nitsch, F. M. Bickelhaupt, T. B. Marder and U. Radius, Chem. – Eur. J., 2020, 26, 11276–11292.
56 B. J. Frohley, A. F. Hill, M. Sharma, A. Sinha and J. S. Ward, Chem. Commun., 2020, 56, 3532–3535.
57 A. Nova, H. W. Suh, T. J. Schmeier, L. M. Guard, O. Eisenstein, N. Hazari and F. Maseras, Angew. Chem., Int. Ed., 2014, 53, 1103–1108.
58 R. Beck and S. A. Johnson, Organometallics, 2012, 31, 3599–3609.
59 A. D. Becke, Phys. Rev. A: At., Mol., Opt. Phys., 1988, 38, 3098–3100.
60 J. F. Hartwig, Phys. Rev. B: Condens. Matter, 1986, 33, 8822–8824.
61 A development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
62 P. Deglmann, K. May, F. Furche and R. Ahlrichs, Chem. Phys. Lett., 2004, 384, 103–107.
63 R. Evans, A. J. Downs, R. Köppe and S. C. Peake, J. Phys. Chem. A, 2011, 115, 5127–5137.
64 E. B. Wilson, J. C. Decius and P. C. Cross, Molecular vibrations: the theory of infrared and Raman vibrational spectra, Courier Corporation, 1980.
65 R. Heinzmann and R. Ahlrichs, Theor. Chem. Acc., 1976, 42, 33–45.
66 R. Ahlrichs and C. Ehrhardt, Chem. Unserer Zeit, 1985, 19, 120–124.
67 T. Lu and F. Chen, J. Comput. Chem., 2012, 33, 580–592.
68 F. Richard and R. Bader, Atoms in molecules: a quantum theory, Oxford University Press, Oxford, 1990.
69 S. S. Sen, G. Tavéar, H. W. Roesky, D. Kratzertz, J. Hey and D. Stalke, Organometallics, 2010, 29, 2343–2347.
70 D. Gau, R. Nougué, N. Saffon-Merceron, A. Baceiredo, A. De Cózar, F. P. Cossio, D. Hashizume and T. Kato, Angew. Chem., Int. Ed., 2016, 55, 14673–14677.