



Bis(silylene)-Stabilized Monovalent Nitrogen Complexes

Shenglai Yao, Tibor Szilvási, Yun Xiong, Christian Lorent, Ales Ruzicka, and Matthias Driess*

In memory of Dr. Friedrich Seitz

Abstract: The first series of bis(silylene)-stabilized nitrogen(I) compounds is described. Starting from the 1,2-bis(*N*-heterocyclic silylenyl) 1,2-dicarba-closo-dedecaborane(12) scaffold **1**, [1,2-(*LSi*)₂C₂B₁₀H₁₀; L = PhC(*N*^{*t*}Bu)₂], reaction with adamantyl azide (AdN₃) affords the terminal *N*-μ₂-bridged zwitterionic carborane-1,2-bis(silylium) AdN₃ adduct **2** with an open-cage dianionic nido-C₂B₁₀ cluster core. Remarkably, upon one-electron reduction of **2** with C₈K and liberation of N₂ and adamantane, the two silylene subunits are regenerated to furnish the isolable bis(silylene)-stabilized N^I complex as an anion of **3** with the nido-C₂B₁₀ cluster cage. On the other hand, one-electron oxidation of **2** with silver(I) yields the monocationic bis(silylene) N^I complex **4** with the closo-C₂B₁₀ cluster core. Moreover, the corresponding neutral N^I radical complex **5** results from single-electron transfer from **3** to **4**.

Since the reinterpretation of carbodiphosphorane (Ph₃P)₂C^[1] as a diphosphine carbon(0) complex by Neumüller and Frenking et al. in 2006,^[2] a new class of compounds with the general formula L→:C←L (Scheme 1), termed carbenes, has attracted increasing research interest of both theoretical and experimental chemists.^[3–9] In carbenes, the carbon(0) atom acts as a Lewis acceptor coordinated by two neutral L donors and retains its four valence electrons as two lone pairs.

Striking examples comprise the carbodiphosphorane (NHC)₂C (NHC = *N*-heterocyclic carbene, Scheme 1 A) with two NHC ligands coordinating to C(0).^[5,6] This donor-acceptor concept is not limited to carbon but applicable to its heavy congeners of Group 14. Several interesting tetrelone systems L→:E←L (E = Si, Ge, Sn) have thus been developed.^[10–12] Since nitrogen(I) is isoelectronic to carbon(0), the donor-stabilized N^I in [L→:N←L]⁺, named as nitreones (Scheme 1),^[13] has also gained considerable attention.^[14–16] Akin to the bonding situation of the carbon atom in carbenes, the dicoordinated nitrogen(I) atom in nitreones possesses two lone pairs of electrons. Therefore, nitreones differ significantly from those of nitrenium ions [NR₂]⁺ which are isolobal to carbenes. Featuring a high electron density at the central N^I atom, nitreones have a higher catalytic potential in comparison to [NR₄]⁺ ammonium species in phase-transfer catalysis.^[16] Among the known nitreone complexes, chiral NHC-supported N^I complexes **B** (Pentamidium;^[17] Scheme 1) offer multiple opportunities in enantioselective catalysis.^[17–20]

Currently, we are interested in developing dinucleating NHCs and their heavy congener *N*-heterocyclic silylenes (NHSis) for small molecule activation and coordination chemistry aiming at metal-mediated and metal-free (catalytic) transformations.^[21–23] Utilizing this type of chelating donor ligands, we have successfully synthesized several zero-

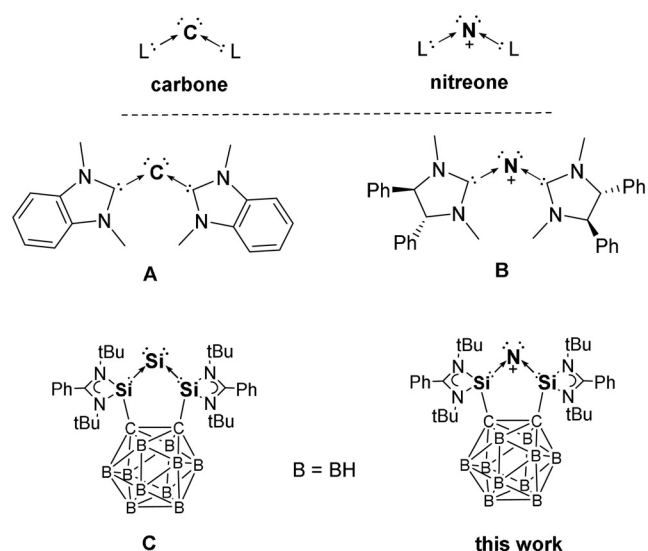
[*] Dr. S. Yao, Dr. Y. Xiong, Prof. Dr. M. Driess
Department of Chemistry: Metalorganics and Inorganic Materials
Technische Universität Berlin
Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin (Germany)
E-mail: matthias.driess@tu-berlin.de

Dr. T. Szilvási
Department of Chemical & Biological Engineering
University of Wisconsin-Madison
1415 Engineering Drive, Madison, WI 53706 (USA)
M. Sc. C. Lorent
Department of Chemistry, Physical and Biophysical Chemistry
Technische Universität Berlin
Strasse des 17. Juni 135, Sekr. PC14, 10623 Berlin (Germany)

Prof. Dr. A. Ruzicka
Department of General and Inorganic Chemistry
Faculty of Chemical Technology, University of Pardubice
Studentska 573, 532 10 Pardubice (Czech Republic)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.202011598>.

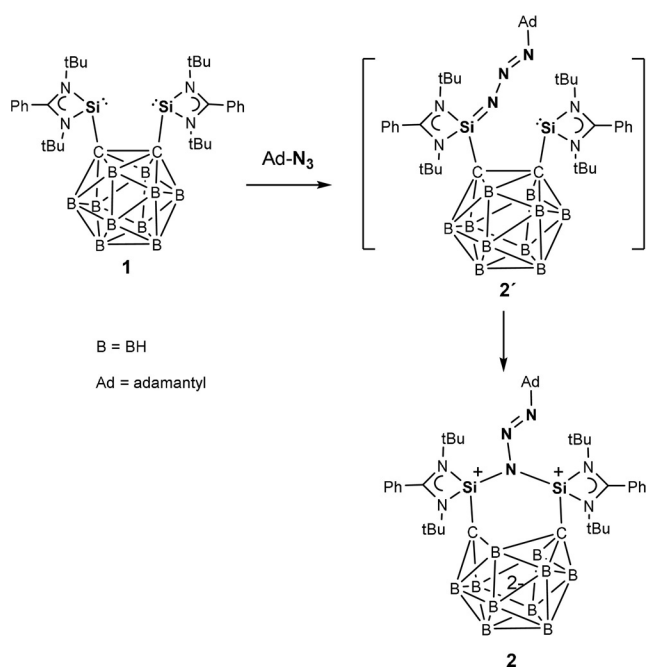
© 2020 The Authors. Published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial, and no modifications or adaptations are made.



Scheme 1. General representation of carbenes and nitreones, and examples of NHC-supported carbene **A** and nitreone **B**, as well as bis(NHSi)-stabilized silicon(0) complex **C** and cationic nitrogen(I) complex reported in this work.

valent Group 14 element complexes (tetrylones) $L \rightarrow E: \leftarrow L$ ($L = \text{NHC}$ or NHSi , $E = \text{Si}$, Ge).^[24–27] The *ortho*-carborane-based bis(silylene) **1** (Scheme 3) with a relatively short Si...Si distance of ca. 3.3 Å, reported by us in 2016,^[28] is reactive towards CO and isocyanides but also suitable as a strong chelating Lewis donor scaffold in coordination chemistry with respect to transition-metals and main group elements.^[29–32] With **1** in hand, we developed very recently the bis(NHSi)-supported Si^0 complex $\text{C}^{[26b]}$ (Scheme 1) and envisioned that bis(NHSi)-supported N^1 complexes could be achievable. Since NHSis have a stronger donor ability than NHCs,^[33] such complexes could, in turn, serve as more nucleophilic N^1 ligands toward metals. Herein, we report the synthesis and structures of the first N^1 complexes supported by a bis(silylene), resulting from the quite unexpected reactivity of **1** towards adamantyl azide.

Treatment of **1** with one molar equivalent of adamantyl azide in diethyl ether at room temperature furnishes the remarkable neutral bis(silylium) carborane adduct **2** with the terminal N-atom of the intact AdN_3 moiety ligated to the two silicon centers in an end-on μ_2 -bridging mode (Scheme 2). Compound **2** is isolated as a pale yellow solid in 89% yields. Perhaps most notable is that the formation of **2** implies an intramolecular two-electron transfer process from the Si^{II} atoms to the C_2B_{10} cluster core, which caused a cage-opening of the neutral *closo*- C_2B_{10} in **1** to the dianionic *nido*- C_2B_{10} cluster core present in **2** (see structural details below). According to the results of Density Functional Theory (DFT) calculations (vide infra), the formation of **2** proceeds via the monosilylene-azide adduct **2'** (see below and Figure S5 in Supporting Information). The formation of **2** designates a very different reactivity compared to that of other silylenes



Scheme 2. Synthesis of the bis(silylium) *nido*-carborane-N-N=N-Ad adduct **2** from bis(silylenyl) *o*-carborane **1** and adamantyl azide via intermediate **2'** as suggested by density function theory (DFT) calculations (at the B97-D/def2-SVP level of theory).

toward organoazides.^[34–38] While most of these reactions yield Staudinger-reaction-type and/or further reaction products, compound **2** represents an isolable intermediate of a so-called “interrupted Staudinger-type” reaction. A related type of organoazide reactivity has recently been observed with frustrated Lewis pairs (FLPs).^[39]

Compound **2** is insoluble in common organic solvents such as hydrocarbons and ethereal solvents, but soluble in dichloromethane. Its ^1H NMR spectrum recorded in CD_2Cl_2 shows a singlet resonance at $\delta = 1.23$ ppm for the *tert*-butyl groups. In line with that, the ^{29}Si NMR spectrum displays only one signal at $\delta = -16.58$ ppm for both silicon atoms. The latter ^{29}Si NMR chemical shift is significantly high-field shifted compared with that of **1** ($\delta = 18.9$ ppm).^[28] Single crystals suitable for an X-ray diffraction analysis were grown in a concentrated solution of **2** in dichloromethane at -30°C .

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with one dichloromethane solvent molecule present in the asymmetric unit (Figure 1). Its molecular structure reveals an open-cage *nido*-carborane backbone with a C...C distance of 2.777 Å and two considerably shortened Si-C distances (1.747(3) and 1.751(3) Å) if compared to the Si-C bonds (1.991(2) and 2.001(2) Å) in the precursor **1**.^[28] The two Si-N bond distances [Si1-N5: 1.765(2) Å, Si2-N5: 1.761(2) Å] of the Si-N-Si bridge in **2** lie in the range of Si-N single bonds. In the N_3 moiety of **2**, the N5-N6 distance of 1.408(3) Å is typical for a N-N single bond and the N6-N7 distance of 1.236(3) Å for a N-N double bond. The latter parameters match well with the N_3 moieties in the FLP-azide adducts mentioned above.^[39] As aforementioned, the structural features of **2** imply that a two-electron reduction of the C_2B_{10} cluster core occurred during the reaction and the neutral *closo*- C_2B_{10} moiety is reduced to *nido*- C_2B_{10} carrying two negative charges (Scheme 2). Apparently, this electron transfer is initiated upon addition of the terminal N-atom of the azide, hence both silicon(II) atoms are oxidized to silicon(IV) centers (silylium-type cations); the zwitterionic nature of **2** could explain its poor solubility in common organic solvents.

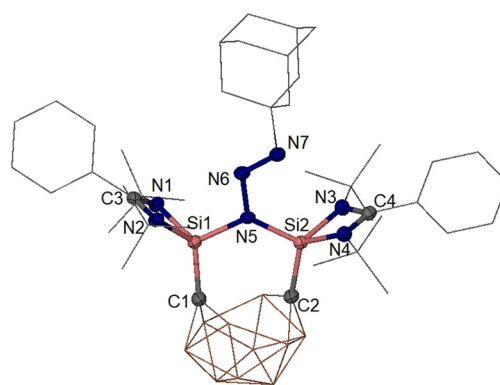
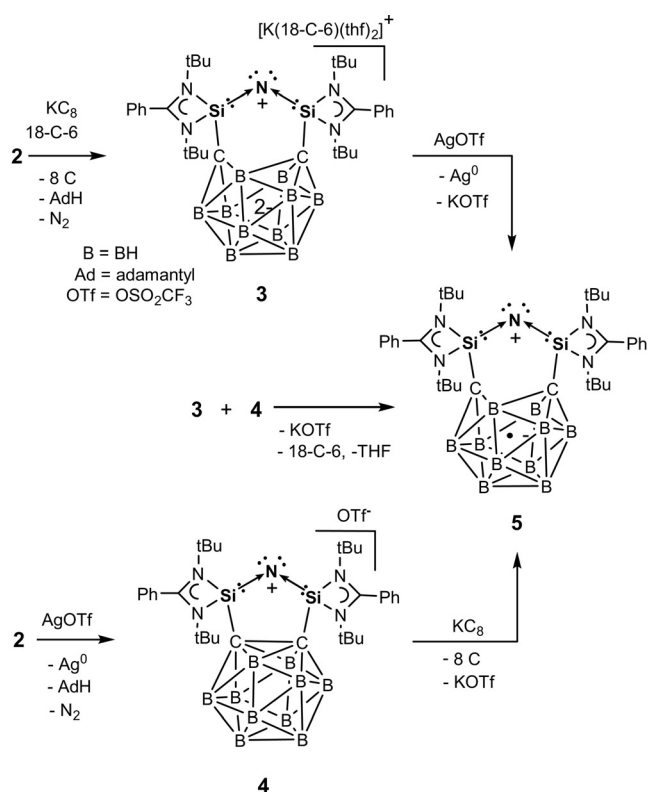


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-C1 1.747(3), Si2-C2 1.751(3), Si1-N1 1.816(2), Si1-N2 1.813(2), Si2-N3 1.796(2), Si2-N4 1.807(2), Si1-N5 1.765(2), Si2-N5 1.761(2), N5-N6 1.408(3), N6-N7 1.236(3), C1...C2 2.777, Si1...Si2 3.170; C1-Si1-N5 111.3(2), C2-Si2-N5 107.0(1), N7-N6-N5 113.2(2), Si2-N5-Si1 128.1(1).

Pristine **2** is quite stable and even survives in boiling dichloromethane. However, it is sensitive towards both reducing and oxidizing reagents. Upon addition of one molar equivalent of potassium graphite to a suspension of **2** in THF results in release of dinitrogen and adamantane as verified by GC-MS analysis (Scheme 3). Further addition of one molar equivalent of 18-crown-6 to the reaction solution allows crystallization of complex in **3** as yellow crystals in 64% yields.

As expected, the ^1H NMR spectrum of diamagnetic **3** recorded in D_8 -THF exhibits only one singlet for the *tert*-butyl groups ($\delta = 1.03$ ppm). The ^{29}Si NMR spectrum shows a resonance at $\delta = -16.50$ ppm, very close to that of **2**. A single-crystal X-ray diffraction analysis revealed that **3** is a separated ion pair. The structure of the anion in **3** is depicted in Figure 2. It comprises an open carborane cage bridged by a Si-N-Si moiety. The Si1-N5 (1.647(3) Å) and Si2-N5 (1.653(3) Å) bonds are shortened by ca. 0.1 Å compared with the corresponding values observed for its precursor **2**, indicating a relatively strong interaction between the NHSi-silicon(II) atoms and the N^1 center. The Si-C distances (Si1-C1 1.779(4) Å and Si2-C2 1.787(4) Å) are similar to those in **2** and the C...C distance of 2.819 Å is close to that of **2** (2.777 Å) as well. Thus the anion in **3** itself can be formally viewed as a zwitterion comprising a *nido*-(C_2B_{10}) $^{2-}$ cage and a positively charged [SiNSi] moiety (Scheme 3).

The facile one-electron reduction-induced N-N bond rupture of the adamantyl azide moiety in compound **2**



Scheme 3. Synthesis of the bis(silylene)-supported nitrogen(I) complexes **3** and **4** from bis(silylene)-azide adduct **2** and the formation of the radical N^1 complex **5** from **3** and/or **4**.

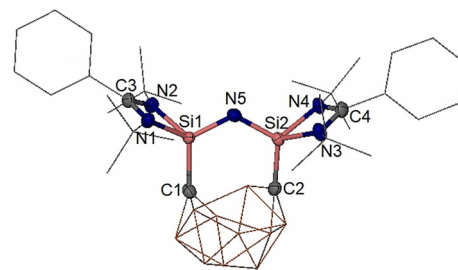


Figure 2. Molecular structure of the anion in **3**. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-N5 1.647(3), Si2-N5 1.653(3), Si1-C1 1.779(4), Si2-C2 1.787(4), Si1-N1 1.842(3), Si1-N2 1.861(3), Si2-N3 1.854(3), Si2-N4 1.851(3), C1...C2 2.819, Si1...Si2 2.897; N5-Si1-C1 116.7(2), N5-Si2-C2 117.1(2), Si1-N5-Si2 122.8(2).

prompted us to investigate its oxidation with $\text{AgOSO}_2\text{CF}_3$ (AgOTf). Accordingly, treatment of **2** with one molar equivalent of AgOTf in dichloromethane at room temperature results in an immediate precipitation of elemental silver and N_2 gas evolution (Scheme 3). From the reaction mixture, complex **4** could be isolated as pale yellow crystals in 88% yields. According to GC-MS analysis, adamantane was obtained from the latter oxidation as a side product. The same side product was also detected along with the formation of **3** described above. To figure out the H atom sources of the thus-formed adamantane, D_8 -THF and D_2 -dichloromethane were used as solvents, respectively. However, no deuterated adamantane was formed in both reactions, implying that the H atom of the adamantane did not originate from the solvents, but from compound **2**, presumably, the carborane backbones. Akin to **2**, compound **4** is insoluble in common hydrocarbon and etheral solvents, but soluble in dichloromethane. The ^1H NMR spectrum recorded in CD_2Cl_2 shows a singlet at $\delta = 1.27$ ppm, slightly low-field shifted with respect to that of the anionic species **3** ($\delta = 1.03$ ppm, D_8 -THF). In contrast, the ^{29}Si NMR spectrum of **4** exhibits a signal at $\delta = -22.38$ ppm, slightly high-field shifted compared to that of the anion in **3** ($\delta = -16.50$ ppm, D_8 -THF).

A single-crystal X-ray diffraction analysis of **4** revealed also a separated ion-pair structure. Surprisingly, the cation of **4** features a *closo*-carborane backbone as depicted in Figure 3. The C1-C2 distance of 1.706(4) Å in **4** is much shorter than those observed in **3** (2.819 Å) and in **2** (2.777 Å), but almost identical to the C-C distance in **1** (1.71 Å).^[28] In line with that, the Si1-C1 [1.922(3) Å] and Si2-C2 distances [1.913(3) Å] in **4** are much longer than the corresponding values [1.779(4) and 1.787(4) Å] in **3**, but similar to those values in **1**. The Si1-N5 [1.639(3) Å] and Si2-N5 distances [1.645(3) Å] in **4** are quite close to those in **3** [1.647(3) and 1.653(3) Å], suggesting that the SiNSi moiety in **4** resembles well that of **3**, despite of the significant difference in the carborane cluster cores.

With both cationic and anionic bis(NHSi) N^1 complexes **3** and **4** in hand, we attempted to conduct a metathesis reaction between them in THF at room temperature, expecting the formation of an ion pair in one compound. To our surprise, the reaction leads to the formation of the radical complex **5** as

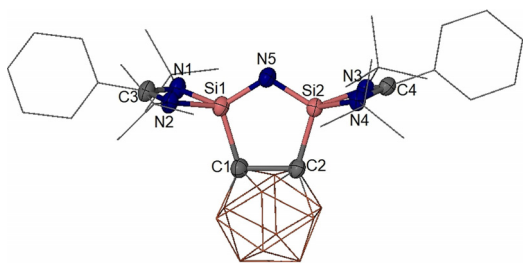
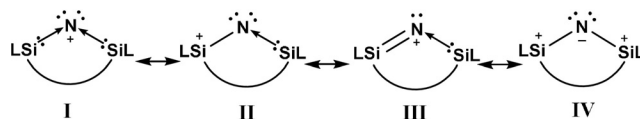


Figure 3. Molecular structure of the cation in **4**. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1–N1 1.791(3), Si1–N2 1.794(3), Si2–N3 1.798(3), Si2–N4 1.807(3), Si1–N5 1.639(3), Si2–N5 1.645(3), Si1–C1 1.922(3), Si2–C2 1.913(3), C2–C1 1.706(4); Si1–Si2 2.782, N5–Si1–C1 106.0(1), N5–Si2–C2 105.6(1), Si1–N5–Si2 115.8(2).

indicated by disappearance of the *tert*-butyl resonance signal in the ^1H NMR spectrum (Scheme 3). Accordingly, the electron paramagnetic resonance spectrum of **5** (Figure S14 in *Supporting Information*) exhibits an isotropic signal at $g = 2.004$ (line width = 24.8 G) very similar to the spectral signature of known anionic carborane radicals.^[40–43] Apparently, a one-electron transfer from the anion of complex in **3** to the cation in **4** occurs during the salt metathesis. This is consistent with cyclic voltammometric (CV) measurements of **3**, which revealed two irreversible redox events at $E = 0.16$ V and $E = 0.57$ V (vs. Fc/Fc^+), corresponding to oxidations of the anion of **3** via radical **5** to the cation of **4**, respectively (see Figure S15 in *Supporting Information*). The reversibility of the latter redox events in CV may be owing to the rebound of the carborane-carbon atoms along with the corresponding structural change of the cage. In fact, the formation of **5** can be alternatively achieved by treating **3** with one molar equivalent of AgOTf or **4** with one molar equivalent of KC_8 (Scheme 3). Unfortunately, attempts to crystallize **5** from the resulting solution failed.

To gain insight into the mechanism of **2** and the electronic structures of **3–5**, we performed DFT calculations (for details see *Supporting Information*). The formation of **2** occurs stepwise, starting with the initial reaction of adamantyl azide with one silylene moiety of **1** with an activation barrier of 6.7 kcal mol $^{-1}$, via the transient $\text{Si}=\text{N}$ doubly bonded species **2'** with high energy gain (-17.4 kcal mol $^{-1}$, Scheme 2, Figure S19). The subsequent intramolecular reaction step with a relatively small barrier (-10.8 kcal mol $^{-1}$) affords **2** (-36.9 kcal mol $^{-1}$) that shows high stability explaining the experimentally observed high yields and mild reaction conditions. We analyzed the electronic structures of **3–5** using Natural Bond Orbital (NBO) analysis, Natural Population Analysis, Wiberg Bond Indices, and calculated frontier molecular orbitals. Interestingly, we have found that the central Si_2N moiety features the same bonding pattern in all three compounds but bearing different charge in the C_2B_{10} cluster backbone (Tables S7–S10). According to NBO analysis, the latter Si_2N moiety possesses Si–N single bonds and bears two lone pairs at the N^{I} center (see representative resonance structures in Scheme 4) resembling the situation of those NHCs supported nitreones mentioned above.^[13] We



Scheme 4. Representative resonance structures I–IV of the bis(silylene) supported N^{I} cations ($\text{L} = \text{PhC}(\text{N}^t\text{Bu})_2$, linker = $o\text{-C}_2\text{B}_{10}\text{H}_{10}$).

note that Natural Resonance Theory calculations could not locate a covalent reference structure pointing to the importance of resonance structure **I**, which is thus solely featured in Scheme 3, but we think other resonance structures such as **II–IV** shown in Scheme 4 may also have significant contributions. The oxidation and reduction occur on the two carbon atoms of the carborane backbone and result in the change of the C–C distances of the carborane cages in **3** (2.841 Å), **4** (1.670 Å), and **5** (2.354 Å) as observed in the X-ray crystal structures of **3** and **4** (Figure S6–S8). Moreover, the extra electrons of the anionic complex **3** and the unpaired electron in **5** are largely located at the carborane-carbon atoms as clearly suggested by the HOMO of **3** (Figure S20) and the Singly Occupied Molecular Orbital (SOMO) of the neutral radical **5**, respectively (Figure S22), which is reminiscent of the electronic situation in the reduction products of the 1,2-diaryl-*ortho*-carboranes.^[43]

In summary, the unexpected reactivity of the 1,2-dicarba-*ortho*-dodecaborane(12)-based 1,2-bis(silylene) **1** towards adamantyl azide furnishes the bis(silylium) N^{I} complex **2**, which is an isolable intermediate of a “interrupted Staudinger-type” reaction. Concomitantly, the closo- C_2B_{10} cluster core of **1** is cage-opened to the nido- C_2B_{10} core by intramolecular two-electron reduction with the Si^{II} atoms. The one-electron reduction of **2** with C_8K regenerates the two Si^{II} moieties to yield the first isolable anionic bis(silylene)-supported N^{I} complex in **3**. Further, the one-electron oxidation of **2** with AgOTf results (under concomitant nido-to-closo C_2B_{10} cluster core oxidation) in the isolable cationic bis(silylene) N^{I} complex in **4**, while the neutral N^{I} radical complex **5** is formed via redox reaction of **3** and **4**. DFT calculations of **3–5** revealed a similar bonding pattern with two lone pairs at the N^{I} center and Si–N–Si single bonds in the Si_2N moieties. Investigations on the ligand abilities of **3–5** towards transition metals and their use in metal-mediated catalytic transformations are currently in progress.

Acknowledgements

This work was funded by DFG (German Research Foundation) under Germany’s Excellence Strategy—EXC 2008—390540038—UniSysCat and DR-226-19/2. We thank Jan Seliger (TU Berlin) for GC-MS analysis, Dr. Biswarup Chakraborty and Rodrigo Beltran Suito (TU Berlin) for CV measurement. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: azides · carboranes · nitrogen complexes · redox non-innocent ligands · silylenes

- [1] F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540.
- [2] R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem. Int. Ed.* **2006**, *45*, 8038–8042; *Angew. Chem.* **2006**, *118*, 8206–8211.
- [3] G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597–614.
- [4] N. Takagi, R. Tonner, G. Frenking, *Chem. Eur. J.* **2012**, *18*, 1772–1780.
- [5] R. Tonner, G. Frenking, *Angew. Chem. Int. Ed.* **2007**, *46*, 8695–8698; *Angew. Chem.* **2007**, *119*, 8850–8853.
- [6] C. A. Dyker, V. Lavallo, B. Donnadiou, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206–3209; *Angew. Chem.* **2008**, *120*, 3250–3253.
- [7] C. Prankevičius, L. Liu, G. Bertrand, D. W. Stephan, *Angew. Chem. Int. Ed.* **2016**, *55*, 5536–5540; *Angew. Chem.* **2016**, *128*, 5626–5630.
- [8] C. A. Dyker, G. Bertrand, *Nat. Chem.* **2009**, *1*, 265–266.
- [9] M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fu, *Nat. Chem.* **2009**, *1*, 295–301.
- [10] G. Frenking, M. Hermann, D. M. Andrada, N. Holzmann, *Chem. Soc. Rev.* **2016**, *45*, 1129–1144.
- [11] S. Yao, Y. Xiong, M. Driess, *Acc. Chem. Res.* **2017**, *50*, 2026–2037.
- [12] P. K. Majhi, T. Sasamori, *Chem. Eur. J.* **2018**, *24*, 9441–9455.
- [13] D. S. Patel, P. V. Bharatam, *J. Phys. Chem. A* **2011**, *115*, 7645–7655.
- [14] a) I. Bernhardt, T. Drews, K. Seppelt, *Angew. Chem. Int. Ed.* **1999**, *38*, 2232–2233; *Angew. Chem.* **1999**, *111*, 2370–2372; b) R. A. Kunetskiy, I. Císařová, D. Šaman, I. M. Lyapkalo, *Chem. Eur. J.* **2009**, *15*, 9477–9485; c) H. Bruns, M. Patil, J. Carreras, A. Vázquez, W. Thiel, R. Goddard, M. Alcarazo, *Angew. Chem. Int. Ed.* **2010**, *49*, 3680–3683; *Angew. Chem.* **2010**, *122*, 3762–3766.
- [15] D. Kathuria, M. Arfeen, A. A. Bankar, P. V. Bharatam, *J. Chem. Sci.* **2016**, *128*, 1607–1614.
- [16] N. Patel, R. Sood, P. V. Bharatam, *Chem. Rev.* **2018**, *118*, 8770–8785.
- [17] T. Ma, X. Fu, C. W. Kee, L. Zong, Y. Pan, K. W. Huang, C. H. Tan, *J. Am. Chem. Soc.* **2011**, *133*, 2828–2831.
- [18] L. Zong, X. Ban, C. W. Kee, C. H. Tan, *Angew. Chem. Int. Ed.* **2014**, *53*, 11849–11853; *Angew. Chem.* **2014**, *126*, 12043–12047.
- [19] B. Teng, W. Chen, S. Dong, C. W. Kee, D. A. Gandamana, L. Zong, C. H. Tan, *J. Am. Chem. Soc.* **2016**, *138*, 9935–9940.
- [20] Y. Yang, F. Moinodeen, W. Chin, T. Ma, Z. Jiang, C. H. Tan, *Org. Lett.* **2012**, *14*, 4762–4765.
- [21] B. Blom, D. Gallego, M. Driess, *Inorg. Chem. Front.* **2014**, *1*, 134–148.
- [22] S. Raoufoghaddam, Y. P. Zhou, Y. Wang, M. Driess, *J. Organomet. Chem.* **2017**, *829*, 2–10.
- [23] Y.-P. Zhou, M. Driess, *Angew. Chem. Int. Ed.* **2019**, *58*, 3715–3728; *Angew. Chem.* **2019**, *131*, 3753–3766.
- [24] Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147–7150; *Angew. Chem.* **2013**, *125*, 7287–7291.
- [25] Y. Xiong, S. Yao, G. Tan, S. Inoue, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 5004–5007.
- [26] a) Y. Wang, M. Karni, S. Yao, A. Kaushansky, Y. Apeloig, M. Driess, *J. Am. Chem. Soc.* **2019**, *141*, 12916–12927; b) S. Yao, A. Kostenko, Y. Xiong, A. Ruzicka, M. Driess, *J. Am. Chem. Soc.* **2020**, *142*, 12608–12612.
- [27] Y. Wang, M. Karni, S. Yao, Y. Apeloig, M. Driess, *J. Am. Chem. Soc.* **2019**, *141*, 1655–1664.
- [28] Y.-P. Zhou, S. Raoufoghaddam, T. Szilvási, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 12868–12872; *Angew. Chem.* **2016**, *128*, 13060–13064.
- [29] Y. Xiong, S. Yao, T. Szilva, A. Ruzicka, M. Driess, *Chem. Commun.* **2020**, *56*, 747–750.
- [30] H. Wang, L. Wu, Z. Lin, Z. Xie, *J. Am. Chem. Soc.* **2017**, *139*, 13680–13683.
- [31] H. Wang, J. Zhang, H. K. Lee, Z. Xie, *J. Am. Chem. Soc.* **2018**, *140*, 3888–3891.
- [32] H. Wang, L. Wu, Z. Lin, Z. Xie, *Angew. Chem. Int. Ed.* **2018**, *57*, 8708–8713; *Angew. Chem.* **2018**, *130*, 8844–8849.
- [33] Z. Benedek, T. Szilvási, *RSC Adv.* **2015**, *5*, 5077–5086.
- [34] N. J. Hill, D. F. Moser, I. A. Guzei, R. West, *Organometallics* **2005**, *24*, 3346–3349.
- [35] Y. Xiong, S. Yao, M. Driess, *Chem. Eur. J.* **2009**, *15*, 8542–8547.
- [36] R. Azhakar, H. W. Roesky, J. J. Holstein, K. Pröpper, B. Dittrich, *Organometallics* **2013**, *32*, 358–361.
- [37] P. P. Samuel, R. Azhakar, R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, J. Matussek, R. Herbst-irmer, D. Stalke, *Inorg. Chem.* **2012**, *51*, 11049–11054.
- [38] T. Iwamoto, N. Ohnishi, Z. Gui, S. Ishida, H. Isobe, S. Maeda, K. Ohno, M. Kira, *New J. Chem.* **2010**, *34*, 1637–1645.
- [39] D. H. A. Boom, A. R. Jupp, M. Nieger, A. W. Ehlers, J. C. Slootweg, *Chem. Eur. J.* **2019**, *25*, 13299–13308.
- [40] M. A. Fox, C. Nervi, A. Crivello, P. J. Low, *Chem. Commun.* **2007**, 2372–2374.
- [41] X. Fu, H. S. Chan, Z. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 8964–8965.
- [42] J. Zhang, X. Fu, Z. Lin, Z. Xie, *Inorg. Chem.* **2015**, *54*, 1965–1973.
- [43] N. C. D. Patel, J. M. Oliva-Enrich, M. A. Fox, *Eur. J. Inorg. Chem.* **2017**, 4568–4574.

Manuscript received: August 24, 2020

Accepted manuscript online: August 25, 2020

Version of record online: September 28, 2020