# Easy Access to Silicon(0) and Silicon(II) Compounds

Kartik Chandra Mondal, Prinson P. Samuel, Mykyta Tretiakov, Amit Pratap Singh, Herbert W. Roesky,\* A. Claudia Stückl, Benedikt Niepötter, Elena Carl, Hilke Wolf, Regine Herbst-Irmer, and Dietmar Stalke\*

Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, 37077-Göttingen, Germany

# **Supporting Information**

**ABSTRACT:** Two different synthetic methodologies of silicon dihalide bridged biradicals of the general formula  $(L^n \bullet)_2 SiX_2$  (n = 1, 2) have been developed. First, the metathesis reaction between NHC:SiX<sub>2</sub> and  $L^n$ : ( $L^n$ : = cyclic akyl(amino) carbene in a 1:3 molar ratio leads to the products 2 (n = 1, X = Cl), 4 (n = 2, X = Cl), 6 (n = 1, X = Br), and 7 (n = 2, X = Br). These reactions also produce coupled NHCs (3, 5) under C–C bond formation. The formation of the coupled NHCs ( $L^m$  = cyclic alkyl(amino) carbene substituted N-heterocyclic carbene; m = 3, n = 1 (3) and m = 4, n = 2 (5)) is faster during the metathesis reaction between NHC:SiBr<sub>2</sub> and  $L^n$ : when



compared with that of NHC:SiCl<sub>2</sub>. Second, the reaction of L<sup>1</sup>:SiCl<sub>4</sub> (8) (L<sup>1</sup>: =:C(CH<sub>2</sub>)(CMe<sub>2</sub>)<sub>2</sub>N-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with a nonnucleophilic base LiN(*i*Pr)<sub>2</sub> in a 1:1 molar ratio shows an unprecedented methodology for the synthesis of the biradical (L<sup>1</sup>•)<sub>2</sub>SiCl<sub>2</sub> (2). The blue blocks of silicon dichloride bridged biradicals (2, 4) are stable for more than six months under an inert atmosphere and in air for one week. Compounds 2 and 4 melt in the temperature range of 185 to 195 °C. The dibromide (6, 7) analogue is more prone to decomposition in the solution but comparatively more stable in the solid state than in the solution. Decomposition of the products has been observed in the UV–vis spectra. Moreover, compounds 2 and 4 were further converted to stable singlet biradicaloid dicarbene-coordinated (L<sup>n</sup>:)<sub>2</sub>Si(0) (*n* = 1 (9), 2 (10)) under KC<sub>8</sub> reduction. Compounds 2 and 4 were also reduced to dehalogenated products 9 and 10, respectively when treated with RLi (R = Ph, Me, *t*Bu). Cyclic voltametry measurements show that 10 can irreversibly undergo both one electron oxidation and reduction.

# **1. INTRODUCTION**

Radicals<sup>1</sup> and biradicals<sup>2</sup> are very reactive chemical species which can act as important intermediates in many chemical and biological processes. They are known<sup>1a</sup> as persistent and stable isolable highly reactive species with odd-electron centers which are stabilized by either thermodynamic or kinetic control.<sup>1,2</sup> There are several known stable carbon and silicon centered biradicals.<sup>2b</sup> Among them, carbon centered 1,3-biradicals are sometimes proposed as very important reactive intermediates in some chemical reactions.<sup>3</sup> Unfortunately, isolation and chemical characterization of such species are most often restricted because of their short lifetime and high reactivity.<sup>3,4</sup> Carbon centered 1,3-biradicals were generated under photolysis of azoalkanes below 10 K and were characterized by electron paramagnetic resonance (EPR) spectroscopy in a frozen matrix.<sup>5</sup> These 1,3-biradicals with short lifetime convert into other products depending upon the electronic ground state (singlet or triplet).<sup>5e</sup> The interactions between the radical centers were investigated by ab initio calculations which revealed a complex interplay between through-bond and through-space communication.<sup>5e</sup> The triplet ground state is possible when both effects are similar in magnitude while the singlet ground state can be more stable when one of the effects is significantly dominant over the other.5e Further theoretical investigations'  $Six_2$  (X = H, Me, F, OR, etc.) bridged cyclopentane-1,3-diyls predicted to possess a persistent singlet ground state under conditions without using a trapping agent.<sup>5g</sup>

Few 1,3-biradicals of cyclobutane type were synthesized, isolated, and characterized.<sup>6</sup> However, they suffer from low yield and stability. We have recently developed a unique synthetic route for air stable 1,3-biradical  $(L^1)_2SiCl_2$  (2)<sup>7a</sup> (Scheme 1) and 1,3-biradicaloid  $(L^1)_2Si$  (9)<sup>7b</sup> (Scheme 2) (L<sup>1</sup>: =:C(CH<sub>2</sub>)(CMe<sub>2</sub>)<sub>2</sub>N-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Compound 2 was synthesized by reacting NHC:SiCl<sub>2</sub> (1a) (NHC = N-heterocyclic carbene<sup>8a</sup>) with a cyclic alkyl(amino) carbene<sup>8b</sup> (cAAC: = L<sup>n</sup>:, *n* = 1 and 2) in a 1:3 molar ratio, and 9 was prepared by reducing 2 with 2 equiv of KC<sub>8</sub>. However, the overall syntheses of 2 and 9 involve precursor NHC:SiX<sub>2</sub> (1) and as a result of that more





Received: February 12, 2013 Published: March 25, 2013

Scheme 2. Syntheses of Compounds 9 and 10



laborious and time-consuming work is needed. In this context it is worth mentioning that compounds with low valent silicon were generally synthesized under reduction of siliconhalides with KC<sub>8</sub> by Kira, <sup>9a</sup> Robinson, <sup>9b</sup> Filippou, <sup>9c</sup> and others. <sup>9d</sup> We developed the synthetic procedures of compounds with low valent silicon under NHC<sup>9d,e</sup> or lithium bis(trimethylsilyl)-amide<sup>9e</sup> mediated elimination of HCl from the silicon center. Also sodium and potassium metals can be utilized for the reduction, but they frequently suffer from low yield of the products. <sup>10</sup> Herein we report on some unprecedented synthetic methodologies for biradicals (2, 6, 7, 4) and biradicaloids (9, 10).

#### 2. RESULTS AND DISCUSSION

We have shown that the reaction of 2 equiv of NHC with 1 equiv of HSiCl<sub>3</sub> produces NHC:SiCl<sub>2</sub> 1a under the precipitation of the NHC·HCl salt.9d We have examined several reactions of 1.<sup>11</sup> It has been shown that cAAC ( $L^n$ :) is more nucleophilic and as well as electrophilic when compared with that of NHC because of the replacement of one  $\sigma$ electron-withdrawing and  $\pi$ -donating N-R group of NHC by a non  $\pi$ -donating and  $\sigma$ -electron-donating carbon.<sup>12</sup> cAAC possesses a singlet spin ground state, and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is smaller when compared with that of NHC. This might play a crucial role between their reactivities. To extend our ongoing chemistry we have reacted a colorless solution of  $L^n$ : (n = 1, n)2) with the light yellow solution of 1a. The color of the solution immediately turned to a dark blue solution of 1,3-biradical  $(L^{n} \cdot)_{2}$ SiCl<sub>2</sub> (n = 1 (2) and 2 (4)). Coupled NHCs (3 (n = 1) and 5 (n = 2)) are formed as side products under C–H bond activation and C-C bond formation. Compounds 3 and 5 are not formed by direct reaction between cAACs and NHCs (Scheme 1). Compounds 2 and 4 are always formed independently of the molar ratio used (1:1 or 2:1 or 3:1) of cAAC and NHC:SiCl<sub>2</sub>. However, the yield depends on the ratio. The yield of 4 is 46% and 81% if the ratio of cAAC and NHC:SiCl<sub>2</sub> is 2:1 and 2.7:1, respectively. Compounds 2 and 4 can be crystallized both from *n*-hexane and tetrahydrofuran (THF). In the solid state 2 does not contain any lattice solvent molecules while 4 crystallizes either as  $4 \cdot n$ -hexane or as  $4 \cdot THF$ depending on the solvent used during the crystallization.

Before it was mentioned that SiX<sub>2</sub> (X = H, Me, F, OR, etc.) bridged carbon centered 1,3-biradicals were theoretically modeled, but they remained experimentally difficult to prepare until recently.<sup>7a</sup> However, to study the stability of silicon dibromide bridged dicarbene (1,3-biradical),  $L^n$ : was reacted with NHC:SiBr<sub>2</sub> (1b)<sup>9c</sup> in a 3:1 molar ratio to obtain  $(L^n \cdot)_2 SiBr_2$  [n = 1 (6) and n = 2 (7)] (Scheme 1). Addition

of THF to the mixture of  $L^n$ : and NHC:SiBr<sub>2</sub> (1b) resulted in a similar blue solution and immediate crystalline blue products 6 and 7 are formed but quickly changed to green and then to light yellow solutions. The properties are different when compared to those of 2 and 4. This shows that compounds 6 and 7 are not as stable as 2 and 4. We tried to recrystallize the blue microcrystalline powder of 6 from THF/*n*-hexane to form single crystals for X-ray diffraction. However, decomposition of 6 was always encountered in solution although it was isolated as a microcrystalline solid which is stable in an inert atmosphere in the solid state. Furthermore, the NMR and UV-vis spectra were recorded before 6 decomposes. Compound 7 is moderately stable, and large blue blocks of 7 were obtained in 6% yield. The reaction is performed in 3.25:1 molar ratio in THF and immediately after the reaction, the solvent was removed under vacuum and extracted with n-hexane from which dark greenish-blue blocks of 7 were formed within 2-3 h. These crystals are stable in solution for a day, but they slowly disappear after one to two days. Meanwhile colorless big blocks of 5 appear which could be manually separated because of their appreciable size and difference in color than those of 7. Blue blocks of 7 are stable in air for about 5 min, and they also decompose to a colorless unidentified solid in an inert atmosphere after 2-3 days.

 $SiX_2$  (X = H, Me, F, OR) bridged cyclopentane-1,3-diyls are theoretically predicted to possess a persistent singlet ground state.<sup>5g</sup> Our experimental results on bis-cyclic alkyl(amino) carbene based SiX<sub>2</sub> 1,3-biradicals (X = Cl (2, 4) and Br (6, 7)) showed that the stability of these biradicals depends on the nature of X on the silicon center. More electronegative chloride substituents on the silicon center provide better stability to the biradical state than does its congener bromide. At this point we wanted to generalize whether the most electronegative fluorine 1,3-biradical analogue is the most stable one. Thus, we chose 2 and 4 as precursor and treated them with Me<sub>3</sub>SnF to replace chlorine by fluorine atoms. In general, the color of the reaction solution changed from dark blue to intense violet which indicated the progress of the reaction. Unfortunately our efforts to isolate the silicon difluoride bridged 1,3-biradical remained elusive. A decomposition was encountered both at room temperature and even at 0  $^{\circ}C$  to -32  $^{\circ}C$ . Finally a colorless solid was obtained after 2 weeks. Our observation is in line to some extent with theoretical prediction.<sup>5g</sup>

Next we investigated the effect of electron donating substituents (aryl or alkyl) on the stability of the 1,3-biradical  $(L^{n}.)_2 SiX_2$  (X = Ph, Me, *t*Bu). To substitute both the chlorine atoms of  $(L^{n}.)_2 SiCl_2$  (2/4), the latter was reacted with 2 equiv of RLi (R = Ph, Me, and 'Bu) in THF. Surprisingly, for each reaction dehalogenated biradicaloid dicarbene-coordinated  $(L^{n}:)_2 Si(0)$  (9/10) was obtained (Scheme 2). The maximum yield of 72% was recorded for 4 when the most basic *t*BuLi was employed. The yields of 58% and 35% were experimentally recorded for MeLi and PhLi. The reaction of 4 with 2 equiv of PhLi produced compound 10 and LiCl and Ph-Ph as byproducts. We assumed that the reaction proceeds via a radical pathway. This was confirmed by elemental and spectroscopy analysis. We did not isolate phenylchloride as one of the byproducts (see Supporting Information).

We have previously reported that  $(L^1\cdot)_2 \operatorname{SiCl}_2(2)$  can be reduced to  $(L^1:)_2 \operatorname{Si}(9)$  in 95% yield when treated with KC<sub>8</sub> in THF within 2–3 h.<sup>7b</sup> Similarly  $(L^2:)_2 \operatorname{Si}(10)$  was synthesized in 85% yield (Scheme 2). To examine the role of the solvent the reduction of 2/4 to 9/10 with KC<sub>8</sub> was performed in *n*-hexane instead of THF. The reaction was found to be extremely slow and did not proceed to completion even after one week. Unreacted KC<sub>8</sub> was recovered, suggesting the more polar THF to be a superior solvent over non polar *n*-hexane for the reduction.

Previously, our theoretical investigations<sup>7b</sup> showed that compound 9 possesses a biradicaloid character because of the low HOMO–LUMO energy gap. The HOMO-1 is a lone pair orbital at the silicon atom where the HOMO is a  $\pi$ -type obital which has the largest extension at the silicon but exhibits significant Si–C  $\pi$ -bonding. The latter distributes 30% on each carbon center and the rest of 40% on the silicon. The NBO value of 0.55 e of silicon was determined from a high level theoretical simulation that suggests a formal oxidation state of zero of the silicon atom in 9 is more likely rather than a Si(II). This value is in good agreement with the difference in the electronegativities of carbon and silicon. On the basis of the structural evidence and theoretical findings, resonance structures 9'/10' of 9/10 can be suggested (Scheme 3).





"The schematic representation drawn in the left formula shows the results of a 3-center two-electron  $\pi$  bond by DFT calculations."

As we have mentioned before, syntheses of the important compounds 2/4 and 9/10 involve NHC:SiCl<sub>2</sub> (1) as a precursor of SiCl<sub>2</sub> and thus alternative synthetic pathways are extremely demanding because of time and labor economic reasons. It is well established that  $L^n$ : is more nucleophilic and electrophilic in nature, and  $LiN(iPr)_2$  (LDA) is known as a non nucleophilic base. In this context we reacted the previously isolated  $L^1$ :SiCl<sub>4</sub> (8) with LDA. During the addition of THF to the 1:1 mixture of  $L^1$ :SiCl<sub>4</sub> and  $LiN(iPr)_2$  an immediate formation of a dark blue solution of  $(L^1 \cdot)_2SiCl_2$  (2) was observed (Scheme 4). The reaction was completed within 1 h.





The evaporation of the solvent followed by extraction of 2 with *n*-hexane affords 2 as blue blocks in 48% yield upon slow evaporation of the solvent under vacuum. LDA usually acts as a base or a nucleophile but not as a reducing agent. To the best of our knowledge such a chemical route for the reductive synthesis of 1,3-biradical by LDA is unprecedented in silicon chemistry.

After the reaction was completed, we isolated the volatile  $SiCl_4$  utilizing a cooling trap under vacuum. Based on our observations the following reaction sequence given in Scheme 4 can be proposed. The driving force for this reaction is the

formation of the two electron sharing C–Si single bonds over two C→Si coordinate bonds. Based on our experience biradical 4 could not be prepared following the similar procedure as shown in Scheme 4. When the reaction was carried out with another equivalent of  $\text{LiN}(i\text{Pr})_2$  the formation of  $\text{L}^1$ :2Si (9) was not observed. Compound 2 was smoothly reduced with RLi (Ph, Me, tBu) to 9.

# 3. STABILITY AND DECOMPOSITION STUDIES OF 4, 9, AND 10

Blue plates of 4 retain their blue color for a week in air like 2. But a powder sample of 4 is stable in air for 2 to 3 days and afterwards hydrolyzes to the corresponding  $L^2:H^+Cl^-$  salt and SiO<sub>2</sub>. On exposure to air compounds 9/10 are less stable when compared with their precursor 2/4. The dark blue plates of 9/ 10 retain their blue color for 5 to 6 h and afterwards slowly transform into colorless solids. The time of complete disappearance of the blue color was recorded to be about 24 h for the crystals and 1 h for the powder samples of 9/10.

<sup>1</sup>H and <sup>13</sup>C NMR spectra showed that 9/10 undergo aerial oxidation at the carbene carbon centers to their corresponding N-aryl amide derivatives 11/12 along with the formation of SiO<sub>2</sub>. When N<sub>2</sub>O gas was passed through the THF solution of 9 for 1 h, compound 11 was obtained in 93% yield (Scheme 5).





# 4. SPECTROSCOPIC ANALYSIS

The <sup>13</sup>C NMR spectra of the carbon atoms of cAACs L<sup>*n*</sup>: exhibit resonance at 304.2 ppm (n = 1) and 309.4 ppm (n =2).<sup>8b</sup> Similar resonances for the 1,3-biradicals 4, 6, and 7 were not observed because of the presence of one unpaired electron on each carbene carbon atom. A resonance at  $\delta = 210.8$  ppm was obtained for 10 which is similar to that of  $9.^{7b}$  The  $13^{2}$ C NMR spectra of 11/12 show resonances at  $\delta$  = 179.1 ppm (11) and 178.7 ppm (12) which are corroborated with C=O. Medically and pharmaceutically relevant compounds 1-phenylpyrrolidin-2-one and 4,5-cis-pyrrolidinone show resonances at  $\delta$ = 174.2 and ~176 ppm, respectively.<sup>13a,b</sup> The <sup>29</sup>Si NMR measurements of compounds 4, 6, and 7 are silent, while the corresponding resonances of 9 and 10 were observed at  $\delta$  = 66.71 ppm<sup>7b</sup> and 71.15 ppm. The UV-vis spectra of compounds 2, 4, 6, 7, 9, and 10 were recorded in n-hexane (see Supporting Information). The maxima of absorption bands of 2, 4, 6, and 7 range from 565 to 585 nm while the corresponding maxima of 9 and 10 were observed in the range of 565 to 620 nm.

# 5. CYCLIC VOLTAMMETRY

Since siladicarbene (9/10) contains four electrons on the silicon atom, it was intriguing to investigate whether a dichloromethane solution of 10 undergoes any reversible electronic oxidation/reduction. Consequently a solution of 10

was placed in the cyclic voltammeter in an inert atmosphere. The cyclic voltammetric measurements show that **10** can irreversibly undergo both one electron oxidation (+2.0 V) and reduction (-0.65 V) (see Supporting Information).

# 6. ELECTRONIC GROUND STATE

We have demonstrated that the most stable electronic ground state of 1,3-biradical **2** is a singlet (S = 0, polymorph II).<sup>7a</sup> Magnetic and EPR measurements on **4** showed that **4** also possesses a singlet electronic ground state (see Supporting Information). Compound **10** is EPR silent confirming a singlet ground state like that of biradicaloid **9**.

# 7. CRYSTAL STRUCTURE COMPARISON

Compound  $2^{7a}$  crystallizes in the monoclinic space group C2/c (Figure 1). The central silicon atom exhibits a distorted



Figure 1. Molecular structure of compound 2.

tetrahedral coordination geometry  $(C1-Si1-C21\ 122.99(7)^\circ)$ . The Si- $C_{carbene}$  bonds (1.8455(16)/1.8482(17) Å) in 2 are significantly shorter than in the tricoordinated 1 (1.985(4) Å).<sup>9d</sup> They are also shorter than a Si- $C_{aryl}$  bond (1.879 Å)<sup>14</sup> but longer than a Si=C double bond (1.702-1.775 Å).<sup>15</sup>

In comparison to the  $N-C_{carbene}$  bonds in the similar free carbene<sup>16</sup> the bonds in 2 are slightly elongated (Table 1). This implies that the double bond character of the N-C bond is less pronounced and is further substantiated by the sum of angles of 355.5° and 355.3° in 2 compared to 360.0° and 359.9° in the free carbene (Figure 2).

The isostructural compounds 4 (Figure 3a) and 7 (Figure 3b) crystallize both in the monoclinic space group  $P2_1/n$  with half a molecule of *n*-hexane in the asymmetric unit as lattice solvent (see Supporting Information). The Si- $C_{carbene}$  bond



**Figure 2.** Superimposed cAACs of **2** (blue) and a free carbene (red).<sup>16</sup>.



Figure 3. Molecular structures of compounds (a) 4.0.5 *n*-hexane and (b) 7.0.5 *n*-hexane.

distances in 4.0.5 *n*-hexane/7.0.5 *n*-hexane are 1.854(2)/1.8585(18) Å and 1.843(2)/1.8497(18) Å.<sup>7a</sup> Similarly Si–Cl/Si–Br bond distances of 4/7 are 2.0701(8)/2.2405(6) Å and 2.0663(8)/2.2375(6) Å. These values are in good agreement with the data reported in the literature.<sup>7a,9c</sup> The only significant

# Table 1. Selected Bond Lengths of Compounds 2, 4, 7, 9, 10, L<sup>2</sup><sub>2</sub>BH, and the Free Carbenes (L<sup>1</sup>: and L<sup>2</sup>:)<sup>a</sup>

	2	4·0.5 S	7·0.5 S	9/2nd molecule	10	L <sup>1</sup> : <sup>16</sup>	L <sup>2</sup> : <sup>16</sup>	$L_{2}^{2}BH^{17}$
N1–C1 [Å]	1.3994(19)	1.400(2)	1.399(2)	1.378(2)/ 1.374(2)	1.3819(16)	1.312	1.315	1.377
N2-C21/C24 [Å]	1.395(2)	1.403(2)	1.398(2)	1.378(2)/ 1.378(2)	1.3726(16)			1.390
C1-N1-C4 [deg]	111.81(12)	112.04(15)	112.17(14)	115.89(13)/ 115.99(13)	116.04(10)	118.74	118.41	116.39
C21/24–N2–C24/C27 [deg]	112.14(12)	111.9(2)	111.87(14)	115.97(13)/ 115.87(13)	115.25(10)			115.63
sum of angles at N1 [deg]	355.5	355.7	355.6	359.9/359.9	359.9	360.0	359.9	359.1
sum of angles at N2 [deg]	355.3	354.8	354.7	360.0/359.9	359.9			359.1
angle between C5 and C1–N1–C4	19.8	19.3	19.6	2.3/2.9	2.9	1.8	2.1	5.0
angle between C25/C28 and C21/C24–N1–C24/27	20.3	21.2	21.6	1.6/2.2	3.0			5.3

 $a^{\prime}S = n$ -hexane. The tables of bond lengths and bond angles of compounds 4, 5, 7, and 10 are given in the Supporting Information.

difference to 2 is a slightly bigger C21/C24-Si1-C1-N1 torsion angle of 106.71(18) (4) and 107.03(16) (7), respectively, compared to 2 (96.12(14)° (Figure 4).



Figure 4. Superimposed molecular structure of compounds 2 (red) and 4 (blue).

When compounds 2, 4, and 7 are compared, the angle between the two cAAC as well as the geometry at the nitrogen atoms is completely different. The N1-C1-Si1-C21/C24 torsion angle in 9 is 163.12(11)° and in 10 167.15(9)° while the torsion angle in 2 is much smaller  $(96.13(14)^{\circ})$ . The geometry at the nitrogen atom in the cAAC in 9 and 10 is nearly planar. The sum of angles is in good agreement with the sum in the similarly built free carbenes (Table 1). This leads to a deviation of the C25/C28 atom of just 1.6 to  $3.0^{\circ}$  from the C21/C24-N1-C24/C27 plane. In 2 this is 20.3°. Following this the nitrogen carbene carbon bonds are no longer elongated like in 2. They are more similar to the shorter bonds in the free carbenes or in  $L^2_2BH^{17}$  for which Bertrand et al. assumed a donor-acceptor bond. Thus the bonding situation in 9 and 10 has to be considered also as a donor-acceptor bond between the cAACs and a silicon atom of formal oxidation state zero. A complete list of the crystallographic data and all bond lengths and angles is given in the Supporting Information.

Compound  $9^{7b}$  crystallizes in the triclinic space group  $P\overline{1}$  with two molecules and one *n*-hexane lattice solvent molecule in the asymmetric unit (Figure 5a). Compound 10 also crystallizes in the triclinic space group  $P\overline{1}$  but with only one molecule in the asymmetric unit and without any lattice solvent (Figure 5b). However, the molecular structures of both are similar (Figure 5c).

The Si-C<sub>carbene</sub> bond distances of 9 (C1-Si1 1.8411(18) Å, C21-Si1 1.8417(17) Å, C41-Si2 1.8471(17) Å, and C61-Si2 1.8482(17) Å) and 10 (C1-Si1 1.8407(13) Å and C24-Si1 1.8531(14) Å) are quite similar to the bond lengths found in 2 (C1-Si1 1.8455(16) Å and C21-Si1 1.848(2) Å), but slightly shorter than the calculated bond length for the (NHC)<sub>2</sub>Si  $(1.869\ \text{\AA}).^{18a,b}$  This could be explained by the fact that the cAAC is a much better  $\pi$ -acceptor than the NHC. The C–Si– C angles are  $117.70(8)^{\circ}$  and  $117.18(8)^{\circ}$  for **9** and  $118.16(6)^{\circ}$ for 10. Thus the C-Si-C backbone is significantly bent, which indicates that 9 and 10 should not be rationalized as allene type structures. This is also supported by the angle between the fivemembered rings (26.3° and 26.7°) that clearly differs from  $90^{\circ}$ , expected for that type of structure. Theoretical calculations on  $R_2C$  = Si =  $CR_2$  showed that 2-silaallenes have a linear structure in contrast to 9 and 10.18b,c

# 8. CONCLUSION

We have developed novel methodologies for the synthesis of silicondihalide bridged dicarbene biradicals. The base stabilized



Article



Figure 5. Molecular structures of (a) 9 and (b) 10. (c) Superposition of the molecular structures of 9 (blue) and 10 (red).

 $SiX_2$  (X = Cl (2, 4), Br(6, 7)) was reacted with L<sup>n</sup>: to produce  $(L^n \cdot)SiX_2$ . Yields of compound 2 (91%) and 4 (85%) are very high when compared with those of 6 (20%) and 7 (6%). The chlorine substituents on the silicon atom induced high stability when compared with that of the two other congeners bromine (6, 7) and fluorine. The blue blocks of biradicals 2 and 4 are stable in air for 1 week. The powder samples are stable for 2-3days and hydrolyze to the  $L^n:H^+Cl^-$  salt. Compound 2 was also synthesized reacting the  $L^1$ :SiCl<sub>4</sub> adduct with LiN(*i*Pr)<sub>2</sub> in moderate yield.  $L^n$  of compounds 2 and 4 can activate a C-H bond and undergo C-C coupling reaction to produce the coupled L<sup>n</sup>-NHC (3,5) carbenes at room temperature. Dehalogenated singlet siladicarbene biradicaloids  $(L^n:)_2$ Si (9, 10) were obtained when the singlet biradical  $(L^{n} \bullet)_{2}SiCl_{2}(2, 4)$ was reacted with RLi (R = Ph, Me, tBu). The highest yield of 72% was obtained when tBuLi was used. Compounds 2 and 4 were also conventionally reduced to 9 and 10 when reacted with 2 equiv of KC<sub>8</sub>. Cyclic voltammetry measurements show that 10 can irreversibly undergo both one electron oxidation and reduction. Compounds 9 and 10 were oxidized to N-aryl amides 11 and 12, respectively when N<sub>2</sub>O gas was passed

through the solution of 9 and 10. Compounds 9 and 10 exposed to air also produced the same products 11 and 12, respectively.

# 9. EXPERIMENTAL SECTION

All reactions and handling of reagents were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or a glovebox where the  $O_2$  and  $H_2O$  levels were usually kept below 1 ppm. Ligand L<sup>n</sup>: and NHC:SiCl<sub>2</sub> were prepared according to literature methods.<sup>8a,b,9a</sup> LiN(*i*Pr)<sub>2</sub>, SiCl<sub>4</sub>, MeLi, PhLi, and tBuLi were purchased from Sigma Aldrich and used as received. KC8 was prepared by reacting K metal with graphite in argon atmosphere at 200 °C. Solvents were purified with the M-Braun solvent drying system. Solution NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers. Deuterated NMR solvent C<sub>6</sub>D<sub>6</sub> was dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus. See reference 7a for the synthesis of  $(L^1 \cdot)_2 SiCl_2$  (2) and  $L^{3}$ : (3).

Alternative synthetic method of  $(L^1 \cdot)_2 SiCl_2$  (2): A molar mixture (1:1) of L<sup>1</sup>:SiCl<sub>4</sub> (8) (455 mg, 1 mmol) and LiN(*i*Pr)<sub>2</sub> (107 mg, 1 mmol) was placed into a 50 mL round-bottom flask. After addition of THF (50 mL) at room temperature to the colorless mixture, an immediate color change to dark blue was observed. Stirring continued for 1 h, and THF was evaporated applying a vacuum. The resulting blue solid was extracted with n-hexane (30 mL) to obtain a dark blue solution which was stored at 0 °C in a refrigerator to form blue blocks of 2 in 48% yield (based on carbene) after 2-3 days. <sup>1</sup>H NMR (298 °C, THF-d<sub>8</sub>, δ ppm, 500.133 MHz): 7.12 (m, 2H, m-H<sub>ar</sub>), 7.09 (m, 2H, m-H<sub>ar</sub>), 7.04 (m, 2H, p-H<sub>ar</sub>), 3.59 (m, 2H, CHMe<sub>2</sub>), 3.43 (m, 2H, CHMe<sub>2</sub>), 1.89 (s, 6H, NCMe<sub>2</sub>), 1.85 (d, 2H, CH<sub>2</sub>, J = 12.38 Hz), 1.69 (s, 6H, NCMe<sub>2</sub>), 1.65 (d, 2H, CH<sub>2</sub>, J = 12.40 Hz), 1.57 (s, 6H, CMe<sub>2</sub>), 1.50 (d, 6H, CHMe<sub>2</sub>, J = 6.66 Hz), 1.39 (d, 6H, CHMe<sub>2</sub>, J = 6.67 Hz), 1.29 (d, 6H, CHMe<sub>2</sub>, J = 6.62 Hz), 1.14 (d, 6H, CHMe<sub>2</sub>, J = 6.80 Hz), 0.85 (s, 6H, CMe<sub>2</sub>); <sup>13</sup>C NMR (δ ppm): 210.0 (C), 143.3, 127.5, 127.1, 125.5, 124.1, 73.5, 67.7, 58.4, 30.2, 29.1, 28.5, 27.7, 27.3, 26.3, 26.0, 25.4, 25.1.

Synthesis of 4: Compound 4 was synthesized following the previously mentioned procedure of 2.7ª A 3:1 mixture of 1a (1.630 g, 3.34 mmol) and  $L^2$ : (3.25 g, 10 mmol) was placed in a 100 mL round-bottom flask. THF (20 mL) was added at room temperature. The color of the solution immediately turned to dark blue. On stirring the solution for 10 min dark blue crystalline precipitate of 4 was obtained, which was separated by filtration. The yield of the 4 is 85%. Compound 4 was further purified by recrystallization from *n*-hexane. Single crystals of 4 were formed from THF or *n*-hexane. The yield of 4 decreased to 81% and 46% when the reaction was performed in 2.7:1 and 2:1 molar ratio, respectively. Elemental analysis found % (calcd) for C<sub>46</sub>H<sub>70</sub>Cl<sub>2</sub>N<sub>2</sub>Si; C 73.58 (73.66), H 9.30 (9.40), N 3.78 (3.73). Mp 189–191 °C, decom. point 195 °C, UV  $\lambda_{ab} = 582$  nm. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>) 500.133 MHz,  $\delta$  ppm): 7.15–7.05 (m, 6H, H<sub>ar</sub>), 3.75 (m, 2H, CHMe<sub>2</sub>), 3.56 (m, 2H, CHMe<sub>2</sub>), 2.52-2.44 (m, 4H, CH<sub>2</sub> (cyclohexane)), 2.11-2.09 (m, 2H, CH<sub>2</sub>(cyclohexane)), 2.01-1.99 (d, 2H, CH<sub>2</sub>, J = 12.44 Hz), 1.86-1.72 (m, 8H, CH<sub>2</sub>(cyclohexane)), 1.67-1.65(d, 2H, CH<sub>2</sub>, J = 11.98 Hz), 1.60-1.43 (m, 6H, CH<sub>2</sub>(cyclohexane)), 1.51 (d, 6H, CHMe<sub>2</sub>, J = 6.67 Hz), 1.40 (d, 6H, CHMe<sub>2</sub>, J = 7.39 Hz), 1.37 (s, 6H, NCMe<sub>2</sub>), 1.35 (d, 6H, CHMe<sub>2</sub>), 1.17 (d, 6H, CHMe<sub>2</sub>, J = 6.43 Hz), 0.78 (s, 6H, NCMe<sub>2</sub>);  $^{13}\text{C}$  NMR ( $\delta$  ppm): 143.8, 126.8, 125.3, 124.4, 67.7, 51.0, 44.0, 32.0, 30.5, 29.3, 27.9, 26.9, 26.7, 26.3, 25.9, 25.7, 25.0, 24.9 and 23.0; <sup>29</sup>Si NMR ( $\delta$  ppm): no resonance signal was recorded.

Synthesis of  $L^4$ : (5): A 3:1 molar mixture of 1 (1.630, 3.34 mmol) and  $L^2$ : (3.25g, 10 mmol) was placed in a 100 mL round-bottom flask. THF (20 mL) was added at room temperature to form an immediate

dark blue solution which was stirred for 12 h. The dark blue crystalline precipitate of **4** was separated by filtration. The filtrate was dried and extracted with *n*-hexane (60 mL). The volume of *n*-hexane solution was reduced to 10 mL and stored at 0 °C in a refrigerator to form colorless blocks of **5** in 50% yield after 1 week. Elemental analysis found % (calcd) for  $C_{50}H_{71}N_3$ ; C 84.15 (84.09), H 10.20 (10.02), N 5.75 (5.88). <sup>1</sup>H NMR (298 °C, THF-d<sub>s</sub>,  $\delta$  ppm, 200.13 MHz): 7.37–6.99 (m, 9H, H<sub>ar</sub>), 4.20 (s, 0.5H, H), 3.70 (s, 0.5H, H), 3.97 (m, 2H, CHMe<sub>2</sub>), 3.10 (m, 2H, CHMe<sub>2</sub>), 2.95 (m, 2H, CHMe<sub>2</sub>), 2.40–1.72 (m, 4H, cyclohexyl), 1.54–0.75 (m, 51H); EI MS: 713.

Synthesis of  $(L^1 \cdot)_2$ SiBr<sub>2</sub> (6): Compound 6 was synthesized following the procedure of 4. A molar mixture (4:1) of L<sup>1</sup>: (1.3 g, 4 mmol) and L:SiBr<sub>2</sub>  $(1b)^{9c}$  (0.576 g, 1 mmol) was placed into a 50 mL round-bottom flask. After addition of THF (10 mL) at room temperature to the colorless mixture, an immediate color change to blue was observed. The blue product 6 was separated by immediate filtration in 20% yield. Elemental analysis found % (calcd) for  $C_{40}H_{62}Br_2N_2Si$ , 6; C 63.15 (63.31), H 8.30 (8.23), N 3.65 (3.69). Mp 180–182 °C, decomp. point 190 °C, UV  $\lambda_{ab}$  = 583 nm. <sup>1</sup>H (298 °C, THF-d<sub>8</sub>, δ ppm, 500.130 MHz): 7.12 (m, 2H, m-H<sub>ar</sub>), 7.09 (m, 2H, m-H<sub>ar</sub>), 7.04 (m, 2H, p-H<sub>ar</sub>), 3.59 (m, 2H, CHMe<sub>2</sub>), 3.48 (m, 2H, CHMe<sub>2</sub>), 1.93 (s, 6H, NCMe<sub>2</sub>), 1.87 (s, 4H, CH<sub>2</sub>), 1.77 (s, 6H, NCMe<sub>2</sub>), 1.57 (s, 6H, CMe<sub>2</sub>), 1.55 (d, 6H, CHMe<sub>2</sub>, J = 6.66 Hz<sub>1</sub>), 1.47 (d, 6H, CHMe<sub>2</sub>, J = 6.66 Hz), 1.30 (d, 6H, CHMe<sub>2</sub>, J = 6.53 Hz), 1.14 (d, 6H, CHMe<sub>2</sub>, J = 6.65 Hz,), 0.79 (s, 6H, CMe<sub>2</sub>); <sup>13</sup>C ( $\delta$  ppm): 143.3, 127.3, 125.7, 124.2, 78.5, 67.4, 58.6, 29.1, 28.5, 27.7, 27.4, 26.8, 26.3, 25.3, 24.8.  $^{29}\text{Si}$  NMR ( $\delta$  ppm); no resonance was observed.

Synthesis of  $(L^2:)_2$ SiBr<sub>2</sub> (7): Compound 7 was synthesized following a similar procedure to that used for 6. A molar mixture (3.25:1) of L<sup>2</sup>: (1.056 g, 3.25 mmol) and L:SiBr<sub>2</sub> (1b) (0.576 g, 1 mmol) was placed into a 50 mL round-bottom flask. After addition of THF (10 mL) at room temperature to the colorless mixture, an immediate color change to dark green-blue was observed. The mixture was immediately dried under vacuum and extracted with *n*-hexane (20 mL) and filtered. The green-blue filtrate produced greenish blue plates of 5 in 6% yield. The large dark green-blue plates of 7 were manually separated inside the glovebox. Elemental analysis found % (calcd) for C<sub>46</sub>H<sub>70</sub>Br<sub>2</sub>N<sub>2</sub>Si; C 65.76 (65.85), H 8.48 (8.41), N 3.45 (3.34). Mp 183–185 °C, decomp. point 192 °C, UV  $\lambda_{ab}$  = 583 nm. <sup>1</sup>H NMR (THF-d\_8, 200 MHz, 298 K) 7.22–7.08 (m, 6H,  $H_{ar}$ ), 3.07 (m, 2H, CHMe2), 2.81 (m, 2H, CHMe2), 2.40-1.80 (m, 4H, CH2 (cyclohexane)), 1.75-1.57 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.67 (d, 2H, CH<sub>2</sub>, J = 12.34 Hz), 1.42-1.20 (m, 8H, CH<sub>2</sub>(cyclohexane)), 1.21 (d, 2H, CH<sub>2</sub>, J = 12.20 Hz), 1.23-1.27 (m, 6H, CH<sub>2</sub>(cyclohexane)), 1.28 (d, 6H, CHMe<sub>2</sub>, J = 6.66 Hz,), 1.20 (d, 6H, CHMe<sub>2</sub>, J = 6.64 Hz), 1.17 (s, 6H, NCMe<sub>2</sub>), 1.13 (d, 6H, CHMe<sub>2</sub>, J = 6.66 Hz), 1.09 (d, 6H, CHMe<sub>2</sub>, J = 6.54 Hz,), 0.82 (s, 6H, NCMe<sub>2</sub>); <sup>13</sup>C NMR ( $\delta$  ppm): 141.2, 125.5, 124.9, 124.2, 66.3, 51.2, 45.0, 31.8, 30.5, 29.5, 28.1, 26.8, 26.5, 26.2, 25.9, 25.6, 25.1, 24.8 and 22.6;  $^{29}\mathrm{Si}$  NMR ( $\delta$  ppm): no resonance signal was recorded.

Synthesis of  $L^1$ :SiCl<sub>4</sub> (8): It was prepared following a similar procedure  $^{9b}$  using THF as a solvent.

Synthesis of  $(L^1:)_2$ Si (9): See reference 7a for the synthesis.

Synthesis of  $(L^2:)_2$ Si 10: The 1:2 mixture of  $(L^2:)_2$ SiCl<sub>2</sub> (4) (585 mg, 0.78 mmol) and KC<sub>8</sub> (112 mg, 1.57 mmol) was placed into a 100 mL round-bottom flask. THF (50 mL) was cooled to -78 °C and added to the mixture which was stirred for 6 h at room temperature and filtered. The dark blue filtrate was dried under vacuum to obtain a solid mass which was extracted with *n*-hexane (60 mL). The volume of the final solution was reduced to 5–7 mL and stored at 0  $^\circ C$  in a refrigerator to form dark blue plates of 10 in 85% yield after 3-4 days. Mp (range) 194–195 °C, decomp. point 215 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.130 MHz,  $\delta$  ppm): 7.21–7.07 (m, 6H, H<sub>ar</sub>), 3.18 (m, 2H, CHMe<sub>2</sub>), 2.93-2.85 (m, 2H, CH<sub>2</sub>(cyclohexane)), 2.66 (m, 2H, CHMe<sub>2</sub>), 2.55–2.50 (m, 2H, CH<sub>2</sub>(cyclohexane)), 2.19–2.16 (d, 2H, CH<sub>2</sub>, J = 12.57 Hz), 1.88–1.86 (d, 2H, CH<sub>2</sub>, J = 12.66 Hz), 1.81–1.70 (m, 10H, CH<sub>2</sub>(cyclohexane)), 1.65–1.55 (m, 2H, CH<sub>2</sub>(cyclohexane)), 1.49 (d, 6H, CHMe<sub>2</sub>, J = 6.41 Hz), 1.40–1.32 (m, 4H, CH<sub>2</sub>(cyclohexane)), 1.31 (d, 6H, CHMe<sub>2</sub>, J = 6.67 Hz), 1.22 (d, 6H, CHMe<sub>2</sub>, J = 6.64 Hz), 1.16 (s, 6H, NCMe<sub>2</sub>), 1.01 (d, 12H,

NCMe<sub>2</sub> plus CHMe<sub>2</sub>). <sup>13</sup>C NMR ( $\delta$  ppm): 210.8, 148.7, 148.4, 136.2, 125.4, 124.9, 68.7, 53.4, 50.0, 44.0, 35.6, 30.2, 30.1, 29.5, 28.3, 27.9, 27.5, 25.3, 25.2, 24.4, 24.3, 23.6, 22.9; <sup>29</sup>Si NMR ( $\delta$  ppm): 71.15.

Alternative methods for the synthesis of 10.7b

To a solution of 4 (150 mg, 0.2 mmol) in THF (20 mL), *tert*-butyl lithium in pentane (1.7 M, 0.29 mL, 0.5 mmol) was added slowly at -78 °C. The solution was slowly warmed to room temperature and stirred again for 6 h. THF was removed under vacuum, and the product was extracted with *n*-hexane and stored at -18 °C to obtain **10** as a crystalline product in 72%.

10 was synthesized in 58% yield following the similar procedure as mentioned above utilizing 4 (150 mg, 0.2 mmol) in THF (20 mL), methyl lithium in diethyl ether (1.6 M, 0.31 mL, 0.5 mmol).

10 was synthesized in 35% yield following the similar procedure as mentioned above utilizing 4 (150 mg, 0.2 mmol) in THF (20 mL), phenyl lithium in dibutyl ether (1.9 M, 0.26 mL, 0.5 mmol).

Decomposition of 9 and 10: The dark blue powders of compounds 9 and 10 undergo oxidation to the corresponding colorless cyclic N-aryl amides (11 and 12) and  $SiO_2$  on exposure to air for 1 h. Compounds 11 and 12 are extracted with *n*-hexane and characterized by NMR spectroscopy. The  $SiO_2$  was separated by filtration.

Synthesis of 11: Compound 9 (0.2 mmol, 120 mg) was placed into a 50 mL round-bottom flash, and THF (30 mL) was added to obtain a blue solution. N<sub>2</sub>O gas was bubbled through the solution for 1.5 h to obtain a colorless solution which was dried under vacuum and extracted with *n*-hexane (30 mL) and concentrated to 1–2 mL. The solution was stored at 0 °C in a refrigerator for 1 week to obtain needles of 11 in 93% yield: Mp 118–119 °C; C, H, and N found % (calcd) for C<sub>20</sub>H<sub>31</sub>NO, 80.65 (79.86), H 10.12 (10.36), N 4.51 (4.65); IR (KBr, cm<sup>-1</sup>) 3040, 2964, 2924, 2868, 1681 (C=O), 1460, 1388, 1365, 1261, 1095, 1061, 801; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.130 MHz,  $\delta$  ppm): 7.20–7.12 (m, 3H, H<sub>ar</sub>), 3.11 (m, 2H, CHMe<sub>2</sub>), 1.72 (s, 2H, CH<sub>2</sub>), 1.29 (s, 6H, NCMe<sub>2</sub>), 1.26 (d, 6H, CHMe<sub>2</sub>) *J* = 6.78 Hz), 1.22 (d, 6H, CHMe<sub>2</sub>, *J* = 5.55 Hz), 0.97 (s, 6H, CMe<sub>2</sub>) ; <sup>13</sup>C NMR ( $\delta$  ppm): 179.1, 149.2, 131.7, 128.8, 124.1, 59.6, 54.6, 50.6, 39.9, 29.5, 29.2, 27.9, 26.4, 22.6; EI MS 301.

Compound **12** was synthesized following a similar procedure like that of **11**. Yield 85%. Mp 122–123 °C; C, H, and N found % (calcd) for C<sub>23</sub>H<sub>35</sub>NO, C 79.91 (80.88), H 10.10 (10.33), N 4.05 (4.10); IR (KBr, cm<sup>-1</sup>) 3035, 2966, 2920, 2829, 2868, 1682 (C=O), 1461, 1387, 1364, 1262, 1095, 1062, 800; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300.132 MHz,  $\delta$  ppm): 7.25–7.19 (m, 3H, H<sub>ar</sub>), 3.11 (m, 2H, CHMe<sub>2</sub>), 1.75 (s, 2H, CH<sub>2</sub>) 2.10–1.95 (m, 2H, cyhexane), 1.65–1.56 (m, 4H, cyclohexane), 1.55–139 (m, 4H, cyclohexane), 1.25 (d, 6H, CHMe<sub>2</sub>), J = 9.16 Hz), 1.20 (d, 6H, CHMe<sub>2</sub>), J = 6.27 Hz), 0.99 (s, 6H, NCMe<sub>2</sub>); <sup>13</sup>C NMR ( $\delta$  ppm): 178.7, 149.2, 131.5, 128.8, 124.6, 124.1, 62.1, 60.0, 53.5, 47.1, 38.8, 29.6, 29.01, 28.2, 27.8, 22.6; EI MS 341.

Crystal Structure Determination. Suitable single crystals for Xray structural analysis of compounds 4, 5, 7, and 10 were mounted at low temperature in inert oil under argon atmosphere by applying the X-Temp2 device.<sup>19</sup> The data were collected on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microfocus source with INCOATEC Quazar mirror optics (7) and a Bruker TXS Mo rotating anode with INCOATEC Helios mirror optics (4, 10).<sup>20</sup> The data were integrated with SAINT,<sup>21</sup> and a semiempirical absorption correction with SADABS<sup>22</sup> was applied. The structure was solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on  $F^2$  (SHELXL-2012).<sup>23</sup> All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their  $U_{iso}$  values constrained to 1.5  $U_{eq}$  of their pivot atoms for terminal sp<sup>3</sup> carbon atoms and 1.2 times for all other carbon atoms. Compound 4 showed disorder of one of the cAACs substituents. This disorder was also observed in 4•THF (4a). 7 showed a disordered hexane lattice solvent molecule. The disordered residues and molecules were resolved and modeled successfully using distance restraints and restraints for the anisotropic displacement parameters. For details of the crystal structure determination of  $(L^1 \cdot)_2 SiCl_2(2)$  and  $L^3$ : (3) see reference 7a and for  $(L^1 \cdot)_2 Si$  (9) see reference 7b.

ASSOCIATED CONTENT

# **S** Supporting Information

Crystallographic data (CIF), UV-visible spectra, magnetic properties, EPR spectra, cyclic voltammetry. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: hroesky@gwdg.de (H.W.R.), dstalke@chemie.uni-goettingen.de (D.S.).

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was funded by the Deutsche Forschungsgemeinschaft (RO 224/60-1). We thank Prof. F. Meyer and Dr. S. Demeshko for magnetic and CV investigations and T. Bayer, K. Dalle ,and F. Klinke for UV–visible measurements. This work is dedicated to Professor Oliver Reiser on the occasion of his 50th birthday.

#### ABBREVIATIONS

NHC, *N*-heterocyclic carbene; cAAC:, cyclic alkyl(amino) carbene; LDA, lithium diisopropylamide

#### REFERENCES

(1) (a) Griller, D.; Ingold, K. U. Acc. Chem. Res. 1976, 9, 13–19.
(b) Hicks, R. G. Org. Biomol. Chem. 2007, 5, 1321–1338.

(2) (a) Rajca. Chem. Rev. **1994**, *94*, 871–893. (b) Abe, M.; Ye, J.; Mishima, M. Chem. Soc. Rev. **2012**, *41*, 3808–3820, and references herein. (c) Kamada, K.; Fuku-en, S.-i.; Minamide, S.; Ohta, K.; Kishi, R.; Nakano, M.; Matsuzaki, H.; Okamoto, H.; Higashikawa, H.; Katsuya, I.; Kojima, S.; Yamamoto, Y. J. Am. Chem. Soc. **2013**, *135* (1), 232–241.

(3) (a) Bentrude, W. G.; Lee, S.-G.; Akutagawa, K.; Ye, W.-Z.; Charbonnel, Y. J. Am. Chem. Soc. **1987**, 109, 1577–1579. (b) Kyler, K. S.; Watt, D. S. J. Am. Chem. Soc. **1983**, 105, 619–621.

(4) (a) Sakamoto, M.; Kawanishi, H.; Mino, T.; Kasashima, Y.; Fujita, T. *Chem. Commun.* **2006**, 4608–4610. (b) Alawode, O. E.; Robinson, C.; Rayat, S. J. Org. *Chem.* **2011**, *76*, 216–222.

(5) (a) Dowd, P. J. Am. Chem. Soc. 1966, 88, 2587–2589. (b) Closs,
G. L.; Kaplan, L. R.; Bendall, V. I. J. Am. Chem. Soc. 1967, 89, 3376–3377. (c) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. J. Am. Chem. Soc. 1971, 93, 1544–1546. (d) Buchwalter, S. L.; Closs, G. L. J. Am. Chem. Soc. 1979, 101, 4688–4694. (e) Goldberg, A. H.; Dougherty, D. A. J. Am. Chem. Soc. 1983, 105, 284–290. (f) Ma, J.; Ding, Y.; Hattori, K.; Inagaki, S. J. Org. Chem. 2004, 69, 4245–4255. (g) Abe, M.; Ishihara, C.; Takegami, A. J. Org. Chem. 2004, 69, 7250–7255.

(6) (a) Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. Angew. Chem., Int. Ed. Engl. **1995**, 34, 555–557; Angew. Chem. **1995**, 107, 640–642. (b) Baumgartner, T.; Gudat, D.; Nieger, M.; Niecke, E.; Schiffer, T. J. J. Am. Chem. Soc. **1999**, 121, 5953–5960. (c) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. Science **2002**, 295, 1880–1881. (d) Cui, C.; Brynda, M.; Olmstead, M. M.; Power, P. P. J. Am. Chem. Soc. **2004**, 126, 6510–6511. (e) Cox, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. Angew. Chem., Int. Ed. **2004**, 43, 4500–4504. (f) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. J. Am. Chem. Soc. **2011**, 133, 12478–12481.

(7) (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Niepötter, B.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 1801–1805. (b) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.;

Wolf, H.; Herbst-Irmer, R.; Stalke, D. Angew. Chem., Int. Ed. 2013, 52 (10), 2963–2967 ; Angew. Chem. 2013, 125, 3036–3040.

(8) (a) Jafarpou, L.; Stevens, E. D.; Nolan, S. P. J. Org. Chem. 2000, 606, 49–54. (b) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. Angew. Chem., Int. Ed. 2005, 44, 5705–5709; Angew. Chem., Int. Ed. 2005, 117, 5851–5855.

(9) (a) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. Nature 2003, 421, 725-727. (b) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. Science 2008, 321, 1069-1071. (c) Filippou, A. C.; Chernov, O.; Schnakenburg, G. Angew. Chem., Int. Ed. 2009, 48, 5687-5690; Angew. Chem. 2009, 121, 5797-5800. (d) Ghadval, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. Angew. Chem., Int. Ed. 2009, 48, 5683-5686; Angew. Chem. 2009, 121, 5793-5796. (e) Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. J. Am. Chem. Soc. 2010, 132, 1123-1126.

(10) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. Angew. Chem. **2006**, 118, 4052–4054; Angew. Chem., Int. Ed. **2006**, 45, 3948–3950.

(11) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. Chem. Sci. 2012, 3, 659-682.

(12) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Organometallics 2011, 30, 5304–5313.

(13) (a) Yang, Y.-H.; Shi, M. J. Org. Chem. 2005, 70, 8645–8648.
(b) Roy, S.; Reiser, O. Angew. Chem., Int. Ed. 2012, 51, 4722–4725; Angew. Chem. 2012, 124, 4801–4804.

(14) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2.

(15) Lee, V. Y.; Sekiguchi, A. In Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds; Wiley: Chichester, U.K., 2010.

(16) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. Angew. Chem. **2005**, 117, 5851–5855; Angew. Chem., Int. Ed. **2005**, 44, 5705–5709.

(17) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610–613.

(18) (a) Takagi, N.; Shimizu, T.; Frenking, G. Chem.—Eur. J. 2009, 15, 3448–3456. (b) Takagi, N.; Shimizu, T.; Frenking, G. Chem.— Eur. J. 2009, 15, 8593–8604. (c) Takagi, N.; Tonner, R.; Frenking, G. Chem.—Eur. J. 2012, 18, 1772–1780.

(19) (a) Stalke, D. Chem. Soc. Rev. **1998**, 27, 171–178. (b) Kottke, T.; Stalke, D. J. Appl. Crystallogr. **1993**, 26, 615–619.

(20) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. J. Appl. Crystallogr. 2009, 42, 885–891.

(21) SAINT; Bruker AXS Inc.: Madison, WI, 2000.

(22) Sheldrick, G. M. SADABS; Universität Göttingen: Göttingen, Germany, 2000.

(23) (a) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112–122.
(b) Müller, P.; Herbst-Irmer, R..; Spek, A. L.; Schneider, T. R.; Sawaya, M. R. In Crystal Structure Refinement - A Crystallographer's Guide to SHELXL; Müller, P., Ed.; Oxford University Press: Oxford, U.K., 2006; IUCr Texts on Crystallography, Vol. 8.