

A New Disilene with π -Accepting Groups from the Reaction of Disilyne $\text{RSi}\equiv\text{SiR}$ ($\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]$) with Isocyanides

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S Supporting Information

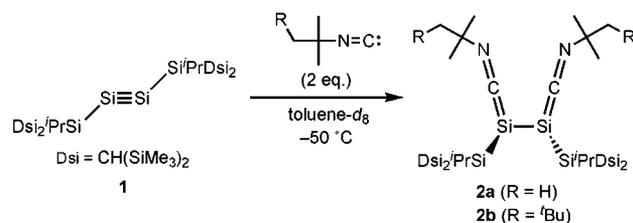
ABSTRACT: The reaction of 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasilene-2-yne (**1**) with *tert*-butylisocyanide or *tert*-octylisocyanide produced the corresponding disilyne–isocyanide adducts $[\text{RSiSiR}(\text{CNR}')_2]$ ($\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]$, $\text{R}' = {}^t\text{Bu}$ (**2a**) or $\text{CMe}_2\text{CH}_2{}^t\text{Bu}$ (**2b**)), which are stable below -30°C and were characterized by spectroscopic data and, in the case of **2a**, X-ray crystallography. Upon warming to room temperature, **2** underwent thermal decomposition to produce 1,2-dicyanodisilene $\text{R}(\text{NC})\text{Si}=\text{Si}(\text{CN})\text{R}$ (**3**) and 1,2-dicyanodisilane $\text{R}(\text{NC})\text{HSiSiH}(\text{CN})\text{R}$ (**4**) via C–N bond cleavage and elimination of an alkane and an alkene. The 1,2-dicyanodisilene derivative **3** was characterized by X-ray crystallography.

During the past 30 years, since West and co-workers synthesized and isolated the first stable disilene, tetramesityldisilene ($\text{Mes}_2\text{Si}=\text{SiMes}_2$, $\text{Mes} = 2,4,6$ -trimethylphenyl),¹ many disilene derivatives have been reported.² However, little is known experimentally about the effects of heteroatom substituents on the properties of the $\text{Si}=\text{Si}$ double bond. Apeloig and Karni investigated substituent effects on the geometry and energy of $\text{H}_2\text{Si}=\text{SiHX}$ systems by theoretical calculations, and they concluded that the structures of the substituted disilenes are strongly dependent on the substituents.³ The general tendencies of the influence of substituents on the configuration of the $\text{Si}=\text{Si}$ bond are as follows: electronegative substituents ($\text{X} = \text{NH}_2, \text{OH}, \text{F}$) increase ΔE_{ST} (the singlet–triplet separation of silylene, SiHX) and the degree of π – σ^* orbital mixing to cause remarkable *trans*-bending at the doubly bonded Si atoms, stretching and weakening the $\text{Si}=\text{Si}$ bond; electropositive groups ($\text{X} = \text{Li}, \text{BeH}, \text{BH}_2, \text{SiH}_3$) reduce both ΔE_{ST} and the degree of π – σ^* interaction, resulting in significant flattening at the doubly bonded Si atoms.^{3,4} Indeed, disilenes with electropositive substituents such as silyl groups,⁵ lithium,^{6,7} sodium,⁷ potassium,⁷ and boranes⁸ were experimentally characterized by X-ray crystallography to show a nearly planar $\text{Si}=\text{Si}$ double bond. In contrast, disilenes with electronegative substituents such as amino groups have pyramidal *trans*-bent geometry at the doubly bonded Si atoms with elongation of the $\text{Si}=\text{Si}$ double bond.^{8b,9} However, to our knowledge, there are no experimental or theoretical studies of a disilene substituted by strong π -accepting groups such as cyano, carbonyl, or nitro groups because of the synthetic difficulty in preparing such molecules.

Recently, following reports of the isolation of alkyne analogues of Ge, Sn, and Pb,¹⁰ silicon–silicon triply bonded compounds (disilynes) were synthesized by our group¹¹ and Wiberg's group¹² using bulky silyl groups, and by Tokitoh's group using bulky aryl groups.¹³ To understand the nature of the π -bonding of the silicon–silicon triple bond, we are currently investigating its reactivity toward a variety of reactants, such as alkenes, alkynes, RLi ($\text{R} = \text{Me}, {}^t\text{Bu}$), alkali metals, nitriles, silylcyanides, amines, hydroboranes, 1,3,4,5-tetramethylimidazol-2-ylidene (NHC), and 4-dimethylamino-pyridine.^{8b,c,14} Herein, we report that the reaction of disilyne **1** with *tert*-butylisocyanide or *tert*-octylisocyanide produces disilyne–isocyanide adducts $[\text{RSiSiR}(\text{CNR}')_2]$ ($\text{R} = \text{Si}^i\text{Pr}[\text{CH}(\text{SiMe}_3)_2]$, $\text{R}' = {}^t\text{Bu}$ (**2a**) or $\text{CMe}_2\text{CH}_2{}^t\text{Bu}$ (**2b**)), which are stable at low temperature and were characterized by NMR spectroscopy and, in the case of **2a**, X-ray crystallography. However, these compounds undergo thermal decomposition upon warming above -30°C . In both cases, decomposition yields the 1,2-dicyanodisilene derivative $\text{R}(\text{NC})\text{Si}=\text{Si}(\text{CN})\text{R}$ (**3**), accompanied by elimination of isobutene and isobutane for **2a** and 2,4,4-trimethylpentene and 2,2,4-trimethylpentane for **2b**. Compound **3** is the first example of a disilene with π -accepting groups.

Disilyne **1** was allowed to react with 2 equiv of *tert*-butylisocyanide or *tert*-octylisocyanide in toluene- d_8 in a sealed NMR tube at -50°C to give disilyne–isocyanide adducts **2a,b** quantitatively (by NMR analysis), which were stable at temperatures below -30°C for over 1 month (Scheme 1).¹⁵

Scheme 1. Reaction of Disilyne 1 with *tert*-Butylisocyanide or *tert*-Octylisocyanide, Giving Disilyne–Isocyanide Adduct 2



The low-temperature NMR spectra of deep-red crystals of **2a,b** (260 K for **2a**, 220 K for **2b**) were recorded in toluene- d_8 . The ^{29}Si NMR spectra have broad signals at high field (-146.9 ppm for **2a**, -142.5 ppm for **2b**), which correspond to the Si

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centers coordinated by isocyanide. The quaternary carbon is observed in the ^{13}C NMR spectrum at low field (184.3 ppm for **2a**, 182.3 ppm for **2b**). These results are very similar to those of disilyne–trimethylsilylisocyanide adduct $[\text{RSiSiR}(\text{CNSiMe}_3)_2]$ (**2c**) (−172.0 ppm for skeletal Si atoms, 193.9 ppm for skeletal C atoms), which we reported recently.^{14c}

As shown in Figure 1, the molecular structure of **2a** was definitively determined by X-ray crystallographic analysis.¹⁵ The

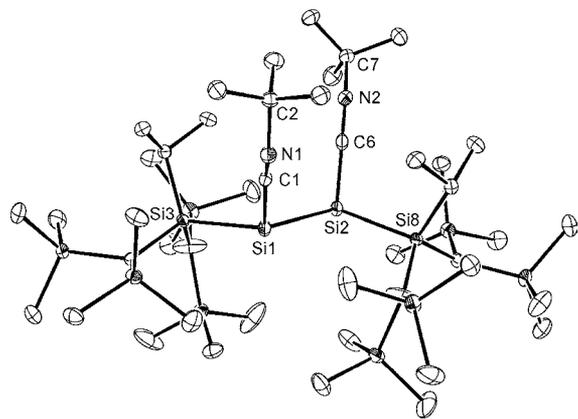
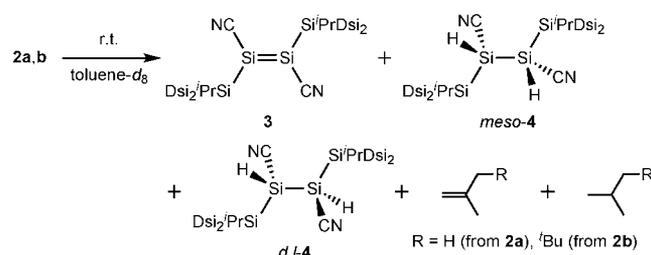


Figure 1. ORTEP drawing of **2a**- C_5H_{12} (30% thermal ellipsoids). Hydrogen atoms and pentane molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si2, 2.3575(17); Si1–Si3, 2.4070(16); Si1–C1, 1.809(4); Si2–Si8, 2.4220(16); Si2–C6, 1.803(5); N1–C1, 1.185(6); N1–C2, 1.476(5); N2–C6, 1.190(6); N2–C7, 1.485(6); Si2–Si1–Si3, 120.18(7); Si2–Si1–C1, 102.71(14); Si3–Si1–C1, 105.11(14); Si1–Si2–Si8, 114.65(7); Si1–Si2–C6, 104.36(15); Si8–Si2–C6, 103.90(14); C1–N1–C2, 144.0(4); C6–N2–C7, 143.5(4); Si1–C1–N1, 166.0(4); Si2–C6–N2, 176.5(4).

two isocyanide molecules bound to each of the skeletal silicon atoms, Si1 and Si2, are oriented on the same side. The central Si1 and Si2 atoms are significantly pyramidalized (sum of the bond angles: 328.0° for Si1 and 322.9° for Si2), which suggests substantial lone-pair character at both Si1 and Si2. The Si1–Si2 bond length [2.3575(17) Å] is in the typical range of Si–Si single bonds.¹⁶ The Si1–C1 and Si2–C6 bond lengths are 1.809(4) and 1.803(5) Å, respectively, which are shorter than the normal Si–C single bond (1.860 Å).¹⁶ The N1–C1 [1.185(6) Å] and N2–C6 [1.190(6) Å] bond lengths are longer than that of the C–N triple bond of *meso*-**4** [1.151(3) Å],^{14c} and the C1–N1–C2 [$144.0(4)^\circ$] and C6–N2–C7 [$143.5(4)^\circ$] angles are not linear. These structural parameters are similar to those of disilyne–silylisocyanide adduct **2c**; this indicates that **2a**, like **2c**, has silaketenimine character with contributions from the zwitterionic form, which has anionic character on the central Si atoms and cationic character on the nitrogen atoms.^{14c}

The disilyne–silylisocyanide adduct **2c** is stable;^{14c} however, the corresponding **2a** and **2b** are thermally labile compounds. These compounds readily underwent thermal decomposition upon warming above -30°C . At room temperature, the toluene solution of **2a** changed from dark red to yellow over 5 h, accompanied by the formation of 1,2-dicyanodisilene **3** as a yellow powder, which was isolated in 21% yield.^{15,17} Monitoring of the reaction in toluene- d_6 by NMR spectroscopy showed the disappearance of **2a** and the formation of **3** as well as *meso*-**4** (21%), *d,l*-**4** (7%), isobutene (22%), and isobutane (10%) (Scheme 2). Similarly, thermal decomposition of **2b** at

Scheme 2. Thermal Decomposition of **2**, Giving 1,2-Dicyanodisilene **3**



-10°C in a sealed NMR tube also produced **3** (24%), *meso*-**4** (16%), *d,l*-**4** (20%), 2,4,4-trimethylpentene (68%), and 2,4,4-trimethylpentane (29%). Compound **2b** completely decomposed at -10°C within 1 h; thus, **2b** is more labile than **2a** (Scheme 2).

Unfortunately, **3** is insoluble in organic solvents, which makes it difficult to measure NMR spectra. However, single crystals of **3** were obtained from a THF suspension of **3**, and the molecular structure of **3** was determined by X-ray diffraction analysis.¹⁵ According to the X-ray structure of **3**, shown in Figure 2, the skeletal Si1 atom is slightly

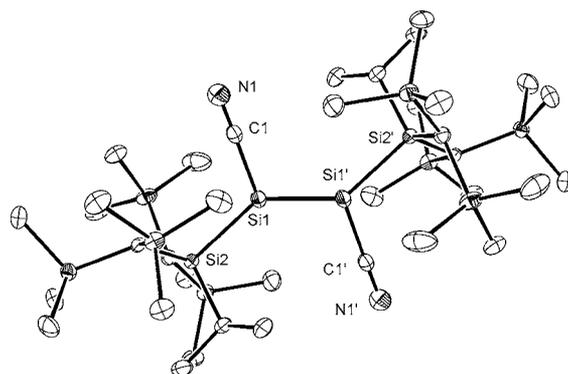


Figure 2. ORTEP drawing of **3** (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si1', 2.213(2); Si1–Si2, 2.3989(15); Si1–C1, 1.860(4); N1–C1, 1.120(4); Si1'–Si1–Si2, 136.48(9); Si1'–Si1–C1, 107.96(13); Si2–Si1–C1, 111.93(12); Si1–C1–N1, 178.6(4).

pyramidalized (the sum of the bond angles around Si1 being 356.4°). The Si=Si bond length of 2.213(2) Å is typical for disilenes.² This demonstrates that π -accepting cyano groups have a negligible effect on the molecular structure of disilenes. This is in contrast to π -donating groups, which induce significant pyramidalization of the central Si atoms and elongation of the Si=Si double bond.^{8b,9,14h}

The π -electron-withdrawing cyano groups on the central silicon atoms are expected to influence the energy of the HOMO and LUMO of **3**, which directly affects the UV–vis absorptions (π – π^* transitions) of the Si=Si double bond. The UV–vis spectrum of **3** in THF shows an absorption maximum assigned to the π – π^* transition at 414 nm ($\epsilon = 3900 \text{ M}^{-1} \text{ cm}^{-1}$), occurring in the region for tetraaryldisilenes (400–430 nm).^{2a} To understand the UV–vis of **3**, computational studies of the model compounds $\text{Me}_3\text{Si}(\text{NC})\text{Si}=\text{Si}(\text{CN})\text{SiMe}_3$ (**3'**) and $\text{Me}_3\text{Si}(\text{Me})\text{Si}=\text{Si}(\text{Me})\text{SiMe}_3$ (**3''**) were performed at the B3LYP/6-31G(d) level. Both the HOMO and LUMO levels of **3'** (−4.95 and −2.27 eV, respectively) are considerably lower than those of **3''** (−3.96 and −0.94 eV, respectively). The

HOMO energy level is lowered by the electronegative cyano groups, and the LUMO energy level also is greatly lowered by the π -conjugation between the cyano groups and the Si=Si π -bond. This energy difference clearly corresponds to the observed red shift in the π - π^* transition of **3**. This π -conjugation is also supported by the decrease of the Wiberg bond index of the Si=Si double bond in **3'** (1.883) compared to that in **3''** (1.944).

To understand the C–N bond cleavage of **2a** and **2b** at low temperature, the bond dissociation energies (BDEs) relevant for the cleavage of the nitrogen substituent were estimated (see the Supporting Information).¹⁸ The BDE of the nitrogen–*tert*-butyl N–C bond of **2a** is smaller than that of a typical C–N single bond (35.9 kcal/mol for **2a** and 77.4 kcal for Me₂N–CMe₃ at the B3LYP/6-31G(d) level). The low BDE for the bis(silaketenimine) system in **2a** can be understood on the basis of resonance stabilization of the radical intermediate, in which the radical spin density is delocalized over the Si–C–N π -system (Chart 1, Figure 3).

Chart 1. Resonance Stabilization of the Radical Intermediate over the Si–C–N π -System

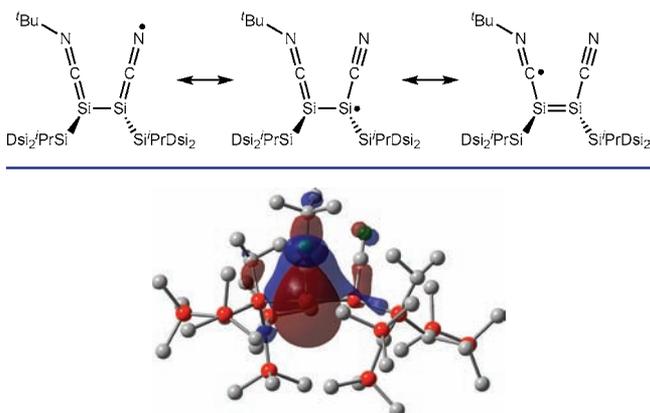


Figure 3. SOMO of [(Dsi₂ⁱPrSi)SiSi(SiⁱPrDsi₂)(CN^tBu)(CN)][•] at HF/6-31G(d).

In summary, we report a new synthetic strategy for the 1,2-dicyanodisilene derivative **3**, the first example of a disilene with a π -accepting group, by the reaction of disilyne **1** with *tert*-butylisocyanide or *tert*-octylisocyanide. This reaction involved the formation of disilyne–isocyanide adducts [RSiSiR(CNR)₂] (R = SiⁱPr[CH(SiMe₃)₂]₂, R' = ^tBu (**2a**) or CMe₂CH₂^tBu (**2b**)) stable below –30 °C. Upon warming to room temperature, **2** underwent thermal decomposition to give the unexpected 1,2-dicyanodisilene R(NC)Si=Si(CN)R **3** via C–N bond cleavage and elimination of an alkane and an alkene. The 1,2-dicyanodisilene derivative **3** was characterized by X-ray crystallography, revealing that the doubly bonded Si atoms have a slightly pyramidalized geometry with the Si=Si bond length of 2.213(2) Å, in contrast to the highly pyramidal structure of disilenes with electronegative substituents such as amino groups.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures for **2a**, **2b**, and **3**; computational results on model compounds **3'** and **3''**; calculated BDEs of **2a**, **2c**, Me₂N–CMe₃, Me₂N–SiMe₃, and model compound **2d**; and crystallographic data including atomic positional and

thermal parameters for **2a** and **3** (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.
- (a) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 2001; Vol. 3, Chapter 5. (b) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (c) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (d) Lee, V. Ya.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*; Wiley: Chichester, UK, 2010; Chapter 5.
- Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589.
- For the second-order Jahn–Teller effect on the heavy alkenes by π - σ^* orbital mixing, see: (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (c) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 1039.
- Kira, M.; Maruyama, T.; Kabuto, C.; Ebata, K.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1489.
- (a) Scheschke, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 2965. (b) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. *Organometallics* **2004**, *23*, 3088.
- (a) Inoue, S.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2005**, *34*, 1564. (b) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. *Silicon Chem.* **2005**, *3*, 111.
- (a) Inoue, S.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2008**, *37*, 1044. (b) Takeuchi, K.; Ikoshi, M.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 930. (c) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *Organometallics* **2011**, *30*, 2044.
- (a) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479. (b) Müller, T.; Apeloig, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3457.
- Pb analogue: (a) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524. Ge analogue: (b) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930. (c) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023. Sn analogue: (d) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.
- (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755. Also see: (b) Kravchenko, V.; Kinjo, R.; Sekiguchi, A.; Ichinohe, M.; West, R.; Balazs, Y. S.; Schmidt, A.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2006**, *128*, 14472. (c) Sekiguchi, A. *Pure Appl. Chem.* **2008**, *80*, 447. (d) Murata, Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2010**, *132*, 16768.
- Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823.
- (a) Sasamori, T.; Hironaka, K.; Sugiyama, Y.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2008**, *130*, 13856. (b) Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N. *J. Am. Chem. Soc.* **2010**, *132*, 2546. (c) Han, J. S.; Sasamori, T.; Mizuhata, Y.; Tokitoh, N. *Dalton Trans.* **2010**, *39*, 9238.

- (14) (a) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. *J. Am. Chem. Soc.* **2007**, *129*, 7766. (b) Kinjo, R.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 26. (c) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2008**, *130*, 16848. (d) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Synth. Met.* **2009**, *159*, 773. (e) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A.; Guo, J.-D.; Nagase, S. *Organometallics* **2009**, *28*, 2658. (f) Yamaguchi, T.; Ichinohe, M.; Sekiguchi, A. *New J. Chem.* **2010**, *34*, 1544. (g) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A.; Guo, J.-D.; Nagase, S. *J. Phys. Org. Chem.* **2010**, *23*, 390. (h) Takeuchi, K.; Ikoshi, M.; Ichinohe, M.; Sekiguchi, A. *J. Organomet. Chem.* **2011**, *696*, 1156. (i) Yamaguchi, T.; Sekiguchi, A.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 14061. (j) Yamaguchi, T.; Sekiguchi, A. *J. Am. Chem. Soc.* **2011**, *133*, 7352.
- (15) For experimental procedures and spectral data for **2a**, **2b**, and **3** as well as crystal data for **2a** and **3**, see the Supporting Information.
- (16) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, UK, 1989; Part 1, Chapter 5.
- (17) Power et al. reported that the reaction of the digermene ArGeGeAr (Ar = C₆H₃-2,6(C₆H₃-2,6-ⁱPr₂) with *tert*-butylisocyanide yielded the adduct [ArGeGeAr(CN^tBu)]; however, no cleavage reaction between Ge and isocyanide C was observed: (a) Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85. (b) Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530.
- (18) For the C–N bond cleavage of **2a** and **2b**, homolytic cleavage is more likely than heterolytic cleavage because the reaction proceeds in nonpolar solvents such as toluene, benzene, hexane, and pentane.