

Unusual nucleophilic reactivity of a  
dithiolene-based N-heterocyclic silane†Phuong M. Tran,<sup>1</sup> Yuzhong Wang,<sup>2</sup> Mitchell E. Lahm, Pingrong Wei,<sup>3</sup>  
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While the dithiolene-based N-heterocyclic silane (**4**) reacts with two equivalents of  $BX_3$  ( $X = Br, I$ ) to give zwitterionic Lewis adducts **5** and **8**, respectively, the parallel reaction of **4** with  $BCl_3$  results in **10**, a dithiolene-substituted N-heterocyclic silane, via the Si–S bond cleavage. Unlike **5**, the labile **8** may be readily converted to **9** via  $BI_3$ -mediated cleavage of the Si–N bond. The formation of **5** and **8** confirms that **4** uniquely possesses dual nucleophilic sites: (a) the terminal sulphur atom of the dithiolene moiety; and (b) the backbone carbon of the N-heterocyclic silane unit.

Silylenes, the silicon analogues of carbenes, have evolved from transient reaction intermediates<sup>1,2</sup> to versatile ligands impacting transition metal coordination chemistry, catalysis, small molecule activation, and the stabilization of novel low-oxidation state main group species.<sup>3–23</sup> A variety of four-, five- and six-membered N-heterocyclic silylenes (NHSis) have been reported<sup>3,8,10,24,25</sup> since the first such molecule was synthesized by the West group three decades ago.<sup>26</sup> N-Heterocyclic silylenes have demonstrated considerably different reactivity toward boron halides than their carbon analogues, N-heterocyclic carbenes (NHCs). N-Heterocyclic carbenes usually form stable Lewis adducts with boron halides.<sup>27–29</sup> Although stable Lewis adducts have been isolated (Scheme 1a),<sup>30,31</sup> reactions between N-heterocyclic silylenes and boron halides often proceed beyond this stage. Braunschweig *et al.* reported that Xyl-substituted NHSi (**A** in Scheme 1b, Xyl = 2,6-dimethylphenyl) may react with organoborane halides to give the corresponding oxidative addition products (**B**), which were subsequently converted to **C** via ring expansion.<sup>32</sup> Subsequently, a series of oxidative additions of the B–X ( $X = \text{halide}$ ) bonds of boron halides at the silylene

centers and silylene ring expansion reactions have been reported.<sup>33–36</sup> When the amidinate-supported four-membered silylene is combined with organoborane halides (Scheme 1c), migration of the amidinate ligand from the silicon atom to the boron atom was reported by Roesky *et al.*<sup>30</sup> In addition, Cui *et al.* recently reported that reaction of the five-membered NHSi (**D**) with  $BBr_3$  produced the N-heterocyclic boryl-substituted silicon bromide **E** via silicon–boron exchange reaction (Scheme 1c).<sup>37</sup> Notably, the literature does not reveal any reports of boron halide-mediated backbone activation of N-heterocyclic silylene rings.

Recently this laboratory investigated the silylene<sup>38,39</sup> (**1**, in Scheme 2a)-mediated sulphur–sulphur bond cleavage of an imidazole-based dithione dimer (**3**),<sup>40</sup> affording a dithiolene-based N-heterocyclic silane (**4**, Scheme 2a).<sup>41</sup> Herein, we report the dual nucleophilic reactivity of the carbon backbone of the N-heterocyclic silyl framework and the terminal sulphur atom of the dithiolene unit in **4** with  $BX_3$  ( $X = Br, I$ )—resulting in the formation of zwitterionic Lewis adducts **5** and **8**, respectively. This discovery is a unique example of Lewis acid-induced charge separation of a five-membered N-heterocyclic silyl ring.

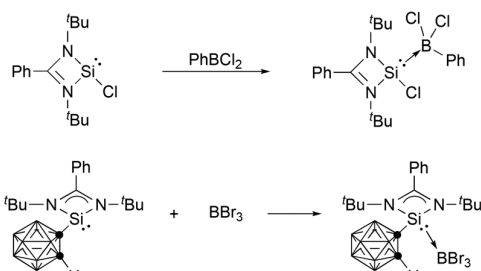
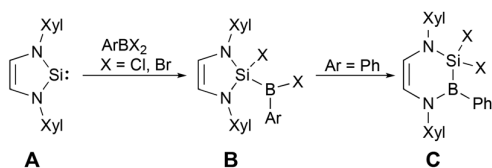
Consistent with the **D**-to-**E** conversion (Scheme 1c),<sup>37</sup> NHSi (**1**) reacts with  $BBr_3$  to give **2** (Scheme 2a). Compound **2** may also be prepared via reaction of the 2-alkoxysilane-1,3,2-diazaborole with  $BBr_3$ .<sup>42</sup> In contrast, room-temperature reaction of **4** with  $BBr_3$  (in a 1 : 2 molar ratio) in toluene gave **5** (81% yield) (Scheme 2b).<sup>43</sup> X-ray quality yellow crystals of **5** were obtained via recrystallization in toluene. While **4** shows one singlet olefin proton resonance at 5.68 ppm,<sup>41</sup> the backbone protons of the N-heterocyclic silyl framework in **5** exhibit two resonances in the <sup>1</sup>H NMR spectrum:<sup>43</sup> a broad singlet at 5.61 ppm (for  $HC:BBR_3$ ) and a singlet at 6.05 ppm (for  $N=CH$ ). The singlet (–6.36 ppm) and doublet (–10.97 ppm, <sup>2</sup> $J_{BH} = 7.8$  Hz) <sup>11</sup>B NMR resonances of **5** correspond to the  $BBr_3$  units bound to the sulphur and carbon atoms, respectively.<sup>43</sup> The 4-to-5 conversion results in the downfield shift of the <sup>29</sup>Si NMR resonance from –4.67 ppm (for **4**, in  $C_6D_6$ )<sup>41</sup> to 8.12 ppm (for **5**, in toluene- $d_8$ ).<sup>43</sup> Compound **5** may be converted back to **4** in

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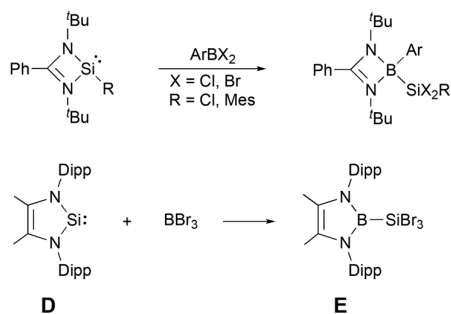
† Electronic supplementary information (ESI) available: Synthetic and computational details and structural and spectral characterization. CCDC 2294615–2294617, 2327747–2327749. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3dt03843b>



## (a) Lewis adduct formation

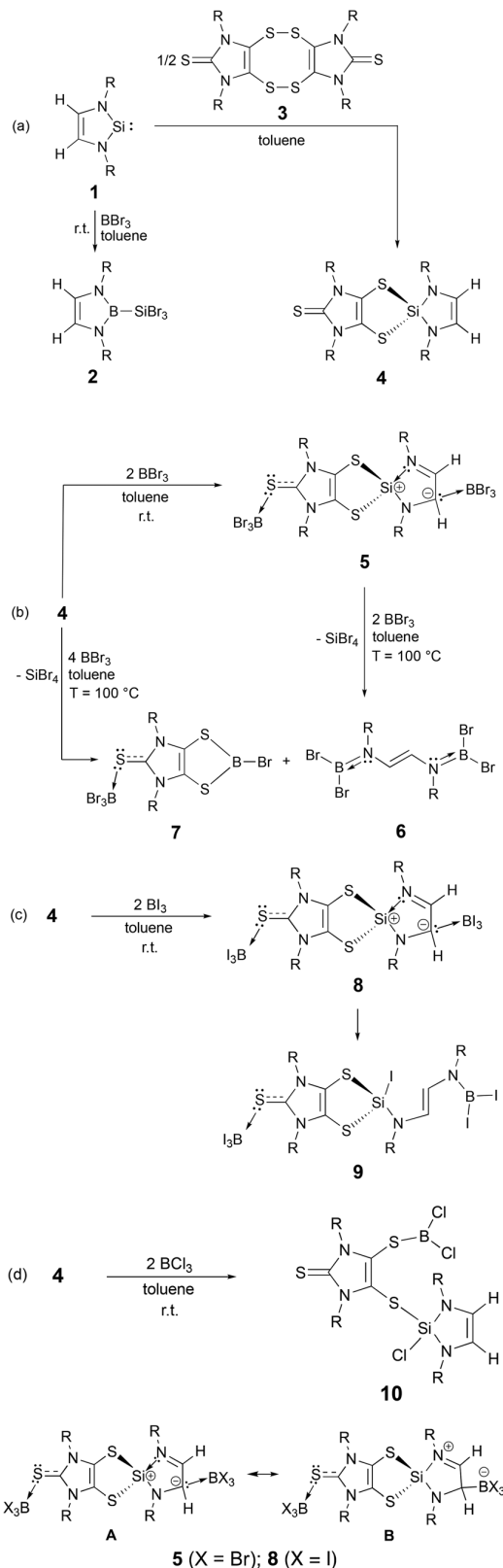
(b) Oxidative addition (A-to-B conversion)  
Ring expansion reaction (B-to-C conversion)

## (c) Silicon-boron exchange reaction



**Scheme 1** Typical reactions of N-heterocyclic silylenes with boron halides (Xyl = 2,6-dimethylphenyl, Dipp = 2,6-diisopropylphenyl).

THF. Compound 5, in the presence of  $\text{BBr}_3$ , readily decomposes at room temperature, giving an acyclic doubly borylated (*E*)-*N,N'*-diaminoethene (6) and other uncharacterized products. Further reaction of 5 with  $\text{BBr}_3$  (in a 1:2 ratio) in toluene at an elevated temperature (100 °C) gave a *ca.* 1:1 mixture of 6 and a dithiolene-based bromoborane complex (7) according to the  $^1\text{H}$  NMR data (Scheme 2b).<sup>43</sup> The mixture of 6 and 7 may also be obtained *via* the 1:4 reaction of 4 with  $\text{BBr}_3$  in toluene at 100 °C (Scheme 2b). Due to the similar solubilities, crystals of 6 (square blocks) and 7 (long rods) were manually separated for NMR measurements. The  $^{11}\text{B}$  NMR resonance of 6 (28.60 ppm) compares well to that of an aminodichloroborane analogue (13) (32.60 ppm),  $\text{Cl}_2\text{B}=\text{N}(\text{Aryl})-\text{CH}=\text{CH}-\text{N}(\text{Aryl})=\text{BCl}_2$  (Aryl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>44</sup> The  $^{11}\text{B}$  NMR spectrum<sup>43</sup> of 7 shows a singlet at -6.36 ppm and a broad singlet at 51.15 ppm, which correspond to the four-coordinated boron (in the  $\text{SBBr}_3$  moiety) and three-coordinated boron (in the five-membered  $\text{C}_2\text{S}_2\text{B}$  ring), respectively. While the mechanistic details of the formation of 6 and 7 from reaction of 5 with  $\text{BBr}_3$  remain unclear, this transformation may



**Scheme 2** Synthesis of 2, 5–10 (R = 2,6-diisopropylphenyl) and canonical forms of 5 and 8.



plausibly involve consecutive insertions of the  $\text{BBr}_3$  species into the Si–N bonds in **5**, accompanied by the migration of one bromide from the boron atom to the silicon atom, rendering to **6** and an intermediate **11** (*i.e.*, the dithiolene-based  $\text{SiBr}_2$  analogue of **7**). The  $\text{BBr}_3$  residing at the backbone carbon in **5** could be released during this process and subsequently react with the intermediate **11** to yield **7** and  $\text{SiBr}_4$  (as a by-product) *via* silicon–boron exchange. However, our repeated attempts to isolate intermediate **11** were unsuccessful.

As a comparison, we also investigated the parallel reactions of **4** with  $\text{BX}_3$  ( $\text{X} = \text{Cl}, \text{I}$ ). The 1 : 2 reaction of **4** with  $\text{BI}_3$  in toluene over 2h resulted in the isolation of **8** (the analogue of **5**) (Scheme 2c). In contrast to **5**, compound **8** may be readily converted to **9** *via* the  $\text{BI}_3$ -mediated silicon–nitrogen bond cleavage (Scheme 2c). While **9** can be isolated as pale-yellow crystalline powder in 72% yield, attempts to obtain pure **8** was unsuccessful due to its high lability. Isolation of **9** further supports our proposed mechanism for the  $\text{BBr}_3$ -mediated decomposition of **5** (Scheme 2b). The formation of **8** has been confirmed by both single crystal X-ray diffraction technique (Fig. 1) and NMR studies. The singlet  $^1\text{H}$  NMR resonances of **8** [5.58 ppm ( $\text{HC:BI}_3$ ) and 6.06 ppm ( $\text{N=CH}$ )] compare well to those for **5** [5.61 ppm ( $\text{HC:BBr}_3$ ) and 6.05 ppm ( $\text{N=CH}$ ), respectively]. The singlet (–82.90 ppm,  $\text{C=SBI}_3$ ) and doublet (–70.43 ppm,  $^2J_{\text{BH}} = 7.0$  Hz,  $\text{C(H)BI}_3$ )  $^{11}\text{B}$  NMR resonances of **8** are shifted highfield compared to those for **5** (–6.36 ppm,  $\text{C=SBBR}_3$  and –10.97 ppm,  $^2J_{\text{BH}} = 7.8$  Hz,  $\text{C(H)BBr}_3$ ). Due to the high lability of **8** (which was converted to **9** during the  $^{29}\text{Si}$  NMR measurement), we only observed the  $^{29}\text{Si}$  NMR resonance for **9** (–18.80 ppm). The singlet  $^{11}\text{B}$  NMR resonances (at 6.02 ppm and –82.85 ppm) of **9** correspond to the three-coordinate  $\text{NBI}_2$  and four-coordinate  $\text{C=SBI}_3$  units, respectively.

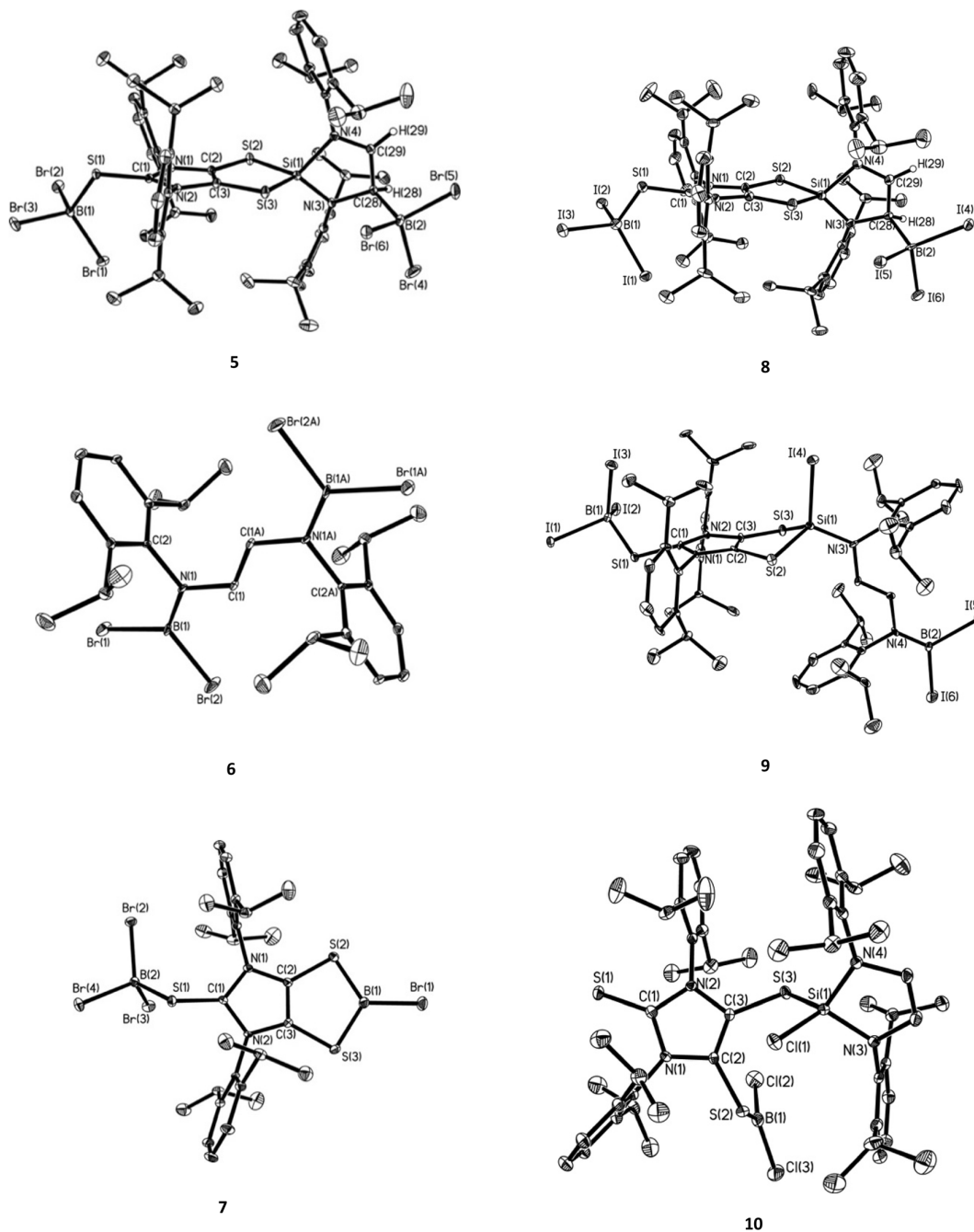
Interestingly, the parallel reaction of **4** with  $\text{BCl}_3$  gave **10** as colourless crystalline powder (in 19% yield) (Scheme 2d) *via*  $\text{BCl}_3$ -mediated cleavage of the Si–S bond in **4**. Formation of the zwitterionic analogue of **5** and **8** was not observed in terms of the  $^1\text{H}$  NMR tube experiments. **10** exhibits singlet  $^{11}\text{B}$  NMR (53.28 ppm) and  $^{29}\text{Si}$  NMR (–33.47 ppm) resonances, revealing the presence of three-coordinate boron atom and four-coordinate silicon atom. Compound **10** is labile in solution, which may gradually decompose to give **12**, the analogue of **6**, in benzene. Compound **12** can be directly synthesized *via* 1 : 5 reaction of **4** with  $\text{BCl}_3$  (in 58% yield). The  $^{11}\text{B}$  NMR resonance of **12** (32.27 ppm) compares to that of **6** (28.60 ppm).

The molecular structures of **5**–**10** were determined by single crystal X-ray diffraction and supported by DFT computations (**5-Ph**, **7**, and **10-Ph** models, B3LYP/6-311G\*\* level; **8-Ph** and **9-Ph** models, mPW1PW91/LANL2DZ level).<sup>43</sup> The crystal unit cell contains an enantiomeric pair of **5** (with identical bonding parameters) (Fig. 1). The formation of **5** reveals that **4** can serve as a double donor ligand to bind two equivalents of  $\text{BBr}_3$  at two nucleophilic sites: the terminal sulphur atom of the dithiolene unit and the backbone carbon of the  $\text{C}_2\text{N}_2\text{Si}$  ring in **4**. Each boron atom in **5** is four-coordinate and adopting a dis-

torted tetrahedral geometry. The backbone protons of the  $\text{C}_2\text{N}_2\text{Si}$  ring [*i.e.*, H(28) and H(29)] were located from difference Fourier map.<sup>43</sup> With the  $\text{BBr}_3$  coordination, the C(1)–S(1) bond is elongated from 1.6638(9) Å (as observed in **4**)<sup>41</sup> to 1.725(2) Å, which compares well to that [1.7256(18) Å] of the zwitterionic boron dithiolene complex with a terminal SR group ( $\text{R} = \text{cyclohexyl}$ ) residing at the C2 carbon.<sup>45</sup> Accordingly, the Wiberg bond index (WBI) of the C(1)–S(1) bond in **5** (1.17) is somewhat lower than that in **4** (1.49),<sup>41</sup> indicating its modest multiple bond character. The S–B bond in **5** [1.932(2) Å] is shorter than that in  $\text{C}_4\text{H}_8\text{S}\cdot\text{BBr}_3$  [1.966(13) Å].<sup>46</sup> The C–B bond in **5** [1.656(3) Å] is similar to that [1.660(2) Å] in  $[\{\text{Ph}_2(\text{S}=\text{P})(\text{H})(\text{Ph}_3\text{SiC}(\text{BH}_3))\}[\text{Li}(\text{THF})_3]$ .<sup>47</sup> The structural features of the  $\text{C}_2\text{N}_2\text{Si}$  ring in **5** are remarkably different from those of **4**.<sup>41</sup> While the C=C double bond [1.3375(15) Å] in the  $\text{C}_2\text{N}_2\text{Si}$  ring of **4** is elongated to the C(28)–C(29) single bond in **5** [1.462(3) Å], one of the two C–N single bonds in the  $\text{C}_2\text{N}_2\text{Si}$  ring of **4** [1.414 Å, *av*] is concomitantly shortened to the N(4)–C(29) double bond in **5** [1.293(3) Å]. The Si(1)–N(3) bond in **5** [1.6797(18) Å (experimental value), 1.703 Å (theoretical value)] compares to the covalent Si–N single bonds in **4** [1.713 Å, *av*].<sup>41</sup> The obviously elongated Si(1)–N(4) bond in **5** [1.8197(18) Å (experimental value), 1.829 Å (computed value)] is comparable with the reported dative Si–N single bonds (such as that [1.858(9) Å] in  $[\text{Me}_3\text{Si}(\text{py})]^+[\text{I}]^-$ <sup>48</sup> and those [1.8290(18) Å and 1.8617(18) Å] in a chlorosilyliumylidene complex).<sup>49</sup> Accordingly, the WBI of the Si(1)–N(4) bond in **5** (0.49) is considerably smaller than that (0.70) of the Si(1)–N(3) bond in **5**. However, there have no obvious changes for the structural parameters of the  $\text{C}_2\text{S}_2\text{Si}$  rings in both **4** and **5**. Compound **5** may be regarded as an intramolecular base-stabilized dithiolene-based silylium species. Natural bond orbital (NBO) analysis of **5-Ph** model supports its zwitterionic feature (as shown in Scheme 2)—the silicon atom has a positive charge of +1.57, whereas the carbon atom [*i.e.*, C(28)] bound to the  $\text{BBr}_3$  unit bears a negative charge of –0.37. The electrostatic potential map of **4** (Fig. S22†) reveals the negative potential resides predominately in the region around the terminal sulphur atom of the dithiolene unit, while the region of the backbone carbon atoms of the N-heterocyclic silyl unit has a very weak negative electrostatic potential. Thus, it is somewhat surprising to observe the nucleophilic behaviour of the backbone carbon atom of the N-heterocyclic silyl ring in **4**.

The X-ray structural analysis<sup>43</sup> of **6** (Fig. 1) reveals a planar  $\text{Br}_2\text{B–N–C–C–N–BBr}_2$  framework, while the two 2,6-diisopropylphenyl substituents are nearly perpendicular to this plane. The structural parameters of the  $\text{C}_2\text{N}_2\text{B}_2(\text{BBr}_2)_2$  core in **6** [ $d_{\text{C–C}} = 1.310(9)$  Å;  $d_{\text{N=B}} = 1.387(6)$  Å] compare well to those for **13** [ $d_{\text{C=C}} = 1.333(2)$  Å;  $d_{\text{N=B}} = 1.395(1)$  Å].<sup>44</sup> In the solid state<sup>43</sup> (Fig. 1), the terminal S(1) atom of **7**, as that in **5**, is capped by a boron tribromide species. The  $\text{C}_2\text{S}_2\text{B}$  ring in **7** is nearly planar [bend angle ( $\eta$ ) between the  $\text{BS}_2$  plane and the  $\text{C}_2\text{S}_2$  plane = 1.7°]. The three-coordinate boron atom, involved in the five-membered dithiolene ring, adopts a trigonal planar geometry. In **7**, the B(1)–S bonds [1.809(4) Å, *av*; WBI = 1.24, *av*] are somewhat shorter than the B(2)–S(1) bond [1.935(4) Å, *av*; WBI =





**Fig. 1** Molecular structures of 5–10. Thermal ellipsoids represent 30% probability. All hydrogen atoms (except H(28) and H(29) in 5 and 8) have been omitted for clarity.

0.83], which should be due to  $\pi$ -donation of the S-lone pairs into the empty p orbital of the B(1) atom. The C–S bonds (1.737 Å, av) in the  $C_2S_2$  unit of 7 are longer than those (1.710 Å, av) for the reported four-coordinate boron-based dithiolate complex,<sup>45</sup> which may be attributed to the electron donation from the sulphur atoms to the three-coordinate boron in 7.

X-ray structural analysis (Fig. 1) shows that 8 is isostructural with 5. The  $BI_3$  bound to the backbone carbon of the N-heterocyclic silyl unit in 8 was released and subsequently cleaved one of the two Si–N bonds to give the NHSi-ring opened product 9. The solid-state structure of 9 (Fig. 1) shows that while a  $BI_2$  species is bonded to a nitrogen atom [ $d_{N=B} = 1.393(11)$  Å], one iodine atom is attached to the central four-



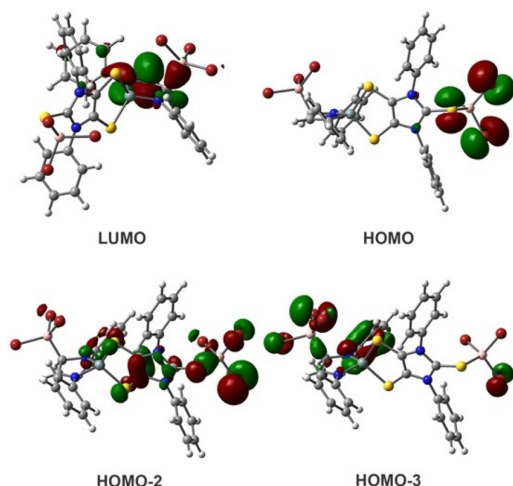


Fig. 2 Molecular orbitals of the simplified 5-Ph model.

coordinate silicon atom. The Si(1)–I(4) bond distance in **9** [2.406(3) Å] is somewhat shorter than the computed value (2.492 Å). The  $B_{sp^2}$ –I bonds (2.128 Å, av) in **9** is shorter than those  $B_{sp^3}$ –I bonds in **8** and **9** (2.236 Å, av). NBO analysis shows that while the silicon atom in **9-Ph** bears a positive charge of +1.10, the silicon atom and the carbon atom (next to  $BI_3$ ) in zwitterionic **8** have a charge of +1.56 and –0.39, respectively. These results, coupled with the elongated Si(1)–N(4) bonds in **5** and **8**, suggest that the canonical form A (Scheme 2) represents the predominant formulation of both **5** and **8**. The X-ray structure of **10** (Fig. 1) indicates that one Si–S bond in **4** is cleaved by  $BCl_3$  via the formation of a Si–Cl bond and a B–S bond. The Si–Cl bond distance in **10** [2.0522(11) Å] is marginally shorter than the computed value (2.088 Å). The B–S bond in **10** [1.793(4) Å] compares well to those (involving the three-coordinate boron atom) in **7** [1.809(4) Å, av].

Computations of the simplified 5-Ph model<sup>43</sup> (Fig. 2) show that while the LUMO involves both C–B bonding and C–N  $\pi$ -anti-bonding character, the HOMO is dominated by the sulphur- and bromine-based lone pair character of the terminal  $SBBR_3$  unit. HOMO–2 and HOMO–3 contain the S–B and C–B  $\sigma$ -bonding character, respectively. According to natural bond orbital (NBO) analysis, the C–B  $\sigma$  bond polarization is 28.2% toward boron and 71.8% toward carbon that has 28.90% s-, 71.08% p-, and 0.02% d-character.

## Conclusions

Dithiolene-based N-heterocyclic silane (**4**) reacts with two equivalents of  $BX_3$  (X = Br, I) to give zwitterionic Lewis adducts **5** and **8**, respectively, whereas the parallel reaction of **4** with  $BCl_3$  gives **10** via the Si–S bond cleavage. Further reaction of **5** with  $BBr_3$  (in a 1 : 2 ratio) in toluene at an elevated temperature (100 °C) resulted in its decomposition, giving a mixture of **6**

and **7**. In contrast to **5**, the labile zwitterion (**8**) may be readily converted to **9** via  $BI_3$ -mediated Si–N bond cleavage. The 4-to-(**5** and **8**) conversions reveal that both the terminal sulphur atom of the dithiolene unit and the backbone carbon of the N-heterocyclic silyl moiety in **4** may serve as nucleophilic sites to bind  $BX_3$  (X = Br and I) moieties. The potential broad utility of **4** as a species with dual nucleophilic sites is being investigated in this laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, 1964, **86**, 1442–1443.
- W. H. Atwell and D. R. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 469–477.
- M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.*, 2000, **33**, 704–714.
- S. S. Sen, S. Khan, P. P. Samuel and H. W. Roesky, *Chem. Sci.*, 2012, **3**, 659–682.
- Y. Xiong, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2013, **52**, 4302–4311.
- R. Waterman, P. G. Hayes and T. D. Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719.
- B. Blom, D. Gallego and M. Driess, *Inorg. Chem. Front.*, 2014, **1**, 134–148.
- M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354–396.
- B. Blom, M. Stoelzel and M. Driess, *Chem. – Eur. J.*, 2013, **19**, 40–62.
- S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767.
- L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1–28.
- S. Yao, A. Saddington, Y. Xiong and M. Driess, *Acc. Chem. Res.*, 2023, **56**, 475–488.
- W. J. Yang, Y. H. Dong, H. J. Sun and X. Y. Li, *Dalton Trans.*, 2021, **50**, 6766–6772.
- M. J. Krahfuss and U. Radius, *Dalton Trans.*, 2021, **50**, 6752–6765.
- M. Ghosh and S. Khan, *Dalton Trans.*, 2021, **50**, 10674–10688.
- S. Fujimori and S. Inoue, *Eur. J. Inorg. Chem.*, 2020, **2020**, 3131–3142.



- 17 Y. P. Zhou and M. Driess, *Angew. Chem., Int. Ed.*, 2019, **58**, 3715–3728.
- 18 C. Shan, S. Yao and M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733–6754.
- 19 S. Raoufnoghaddam, Y. P. Zhou, Y. Wang and M. Driess, *J. Organomet. Chem.*, 2017, **829**, 2–10.
- 20 R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444–456.
- 21 M. Driess, *Nat. Chem.*, 2012, **4**, 525–526.
- 22 S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578–587.
- 23 N. Muthukumar, K. Velappan, K. Gour and G. Prabusankar, *Coord. Chem. Rev.*, 2018, **377**, 1–43.
- 24 Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511.
- 25 Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2010, **110**, 3850–3850.
- 26 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691–2692.
- 27 A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall and R. Schmutzler, *Monatsh. Chem.*, 2000, **131**, 251–265.
- 28 Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2007, **129**, 12412–12413.
- 29 P. Bissinger, H. Braunschweig, K. Kraft and T. Kupfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 4704–4707.
- 30 J. C. Li, Y. S. Liu, S. Kundu, H. Keil, H. P. Zhu, R. Herbst-Irmer, D. Stalke and H. W. Roesky, *Inorg. Chem.*, 2020, **59**, 7910–7914.
- 31 H. Wang and Z. Xie, *Organometallics*, 2021, **40**, 3819–3824.
- 32 A. Gackstatter, H. Braunschweig, T. Kupfer, C. Voigt and N. Arnold, *Chem. – Eur. J.*, 2016, **22**, 16415–16419.
- 33 H. Braunschweig, T. Brückner, A. Deifsenberger, R. D. Dewhurst, A. Gackstatter, A. Gärtner, A. Hofmann, T. Kupfer, D. Prieschl, T. Thiess and S. R. Wang, *Chem. – Eur. J.*, 2017, **23**, 9491–9494.
- 34 S. Khoo, Y.-L. Shan, M.-C. Yang, Y. Li, M.-D. Su and C.-W. So, *Inorg. Chem.*, 2018, **57**, 5879–5887.
- 35 L. Zhu, J. Zhang and C. Cui, *Inorg. Chem.*, 2019, **58**, 12007–12010.
- 36 M. K. Bisai, V. S. V. S. N. Swamy, K. V. Raj, K. Vanka and S. S. Sen, *Inorg. Chem.*, 2021, **60**, 1654–1663.
- 37 Y. Ding, Y. Li, J. Zhang and C. Cui, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205785.
- 38 L. Kong, J. Zhang, H. Song and C. Cui, *Dalton Trans.*, 2009, 5444–5446.
- 39 P. Zark, A. Schäfer, A. Mitra, D. Haase, W. Saak, R. West and T. Müller, *J. Organomet. Chem.*, 2010, **695**, 398–408.
- 40 Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III and G. H. Robinson, *Dalton Trans.*, 2019, **48**, 3543–3546.
- 41 Y. Wang, P. M. Tran, Y. Xie, P. Wei, J. N. Glushka, H. F. Schaefer III and G. H. Robinson, *Angew. Chem., Int. Ed.*, 2021, **60**, 22706–22710.
- 42 Z. Liu and C. Cui, *J. Organomet. Chem.*, 2020, **906**, 121041.
- 43 See the ESI† for synthetic, computational, and crystallographic details.
- 44 L. Weber, J. Forster, H. G. Stammer and B. Neumann, *Eur. J. Inorg. Chem.*, 2006, 5048–5056.
- 45 Y. Wang, Y. Xie, P. Wei, S. A. Blair, D. Cui, M. K. Johnson, H. F. Schaefer III and G. H. Robinson, *Angew. Chem., Int. Ed.*, 2018, **57**, 7865–7868.
- 46 B. Krebs, G. Schwetlik and M. Wienkenhöver, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1989, **45**, 257–261.
- 47 S. Molitor and V. H. Gessner, *Chem. – Eur. J.*, 2013, **19**, 11858–11862.
- 48 K. Hensen, T. Zengerly, P. Pickel and G. Klebe, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 725–726.
- 49 F. Hanusch, D. Munz, J. Sutter, K. Meyer and S. Inoue, *Angew. Chem., Int. Ed.*, 2021, **60**, 23274–23280.

