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Homocoupling of CO and isocyanide mediated by a C,C'-bis(silylenyl)-substituted *ortho*-carborane†

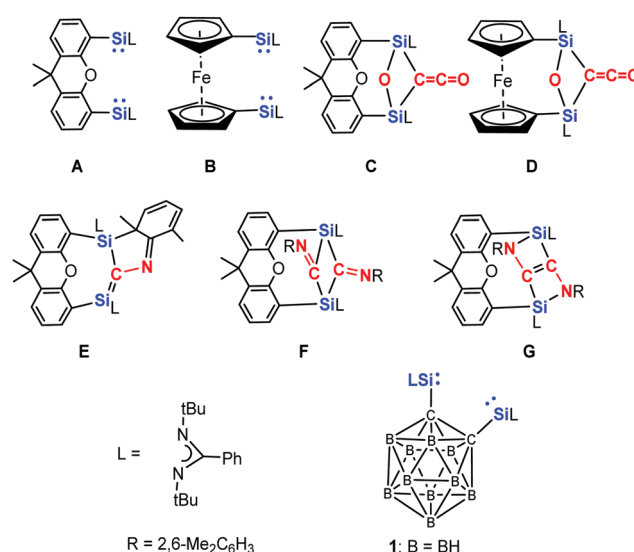
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The unexpected reactivity of the *o*-carborane supported bis-silylene [(LSi)C]₂B₁₀H₁₀ **1** {L = PhC(tBuN)₂} towards carbon monoxide and 2,6-dimethylphenyl isocyanide is reported. While the reaction of **1** with CO leads selectively to the novel head-to-head coupling and C–O cleavage product **2** from two molecules **1** and four molecules CO, the reaction of **1** with 2,6-dimethylphenyl isocyanide affords solely the 1:2 molar head-to-tail coupling product **3** with a Si=C bond.

The activation of important small molecules such as CO, H₂ and N₂ was earlier considered to be a domain of transition metals. However, the last decade witnessed increasing achievements in the chemistry of main-group element (MG) compounds that mediate the cleavage of strong bonds in small molecules.^{1–7} Featuring a lone pair of electrons and a vacant p-orbital at the silicon center, silylenes are particularly reactive species which belong to the rare examples of low-valent MG compounds being suitable for the activation of unreactive bonds and thus represent versatile building blocks for the synthesis of value-added organosilanes. Since the isolation of the first isolable N-heterocyclic silylene (NHSi) by West *et al.* in 1994,⁸ the chemistry of stable silylenes has flourished substantially. Several cyclic^{9–13} and acyclic^{14–18} silylenes have been successfully synthesised and their reactivity towards numerous small molecules such as O₂, N₂O, S₈, P₄, NH₃, CO₂, and even H₂ has been developed.^{5,15–17,19} Nevertheless, the very strong triple bonds of CO cannot be activated easily; one very recent example represents the homocoupling of CO molecules

to OCCO moieties mediated by an acyclic monosilylene reported by Aldridge and co-workers.²⁰

In order to learn whether two silylene (NHSi) moieties could be cooperative in cleaving unreactive bonds, we synthesised several chelating bis-NHSis.^{21–24} To our delight, preliminary investigations revealed that the xanthene and ferrocene supported bis-NHSi **A**^{23a} and **B**^{21b} can even cleave the strong C≡O bond (1072 kJ mol^{−1}) and mediates the deoxygenative coupling of two CO molecules under mild reaction conditions (room temperature, 1 atm) to yield the ketene species **C** and **D**, respectively (Scheme 1).^{23b,c} Moreover, the reaction of bis-silylene **A** with an equimolar amount of the isoelectronic 2,6-dimethylphenyl isocyanide resulted in the dearomatised silene derivative **E**.^{23b} Moreover, the reaction of **A** with two molar equivalents of 2,6-dimethylphenyl isocyanide afforded **F** and **G**.



Scheme 1 Bis-silylenes **A**, **B** and **1** as well as the products **C–G** resulting from the reaction of **A** and **B** with CO and 2,6-dimethylphenyl isocyanide, respectively.

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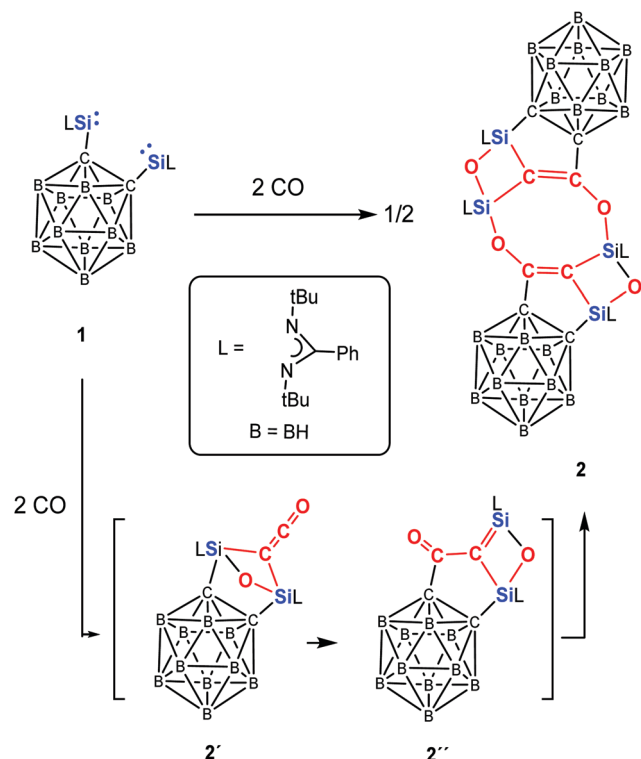
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Scheme 2 Reaction of bis-silylene **1** with CO to afford **2** via **2'** and **2''**.

Compared to the bis-silylene **A**,^{23a} the *ortho*-carborane supported bis-NHSi **1**²⁴ is more rigid, and we wondered its reactivity towards CO and the isoelectronic 2,6-dimethylphenyl isocyanide furnishes similar or different coupling products. Herein, we report the unexpected novel coupling products from CO and 2,6-dimethylphenyl isocyanide mediated by the bis(NHSi) **1**.

Exposure of the yellow solution of **1** in toluene to CO (1 atm) at $-20\text{ }^{\circ}\text{C}$ leads to a colour change from yellow to brown. The reaction mixture was allowed to warm to room temperature to give a brown solution, from which the unprecedented coupling compound **2** could be crystallised after one day at ambient temperature in the form of colourless crystals in 62% yields (Scheme 2). In contrast to the reaction of **A** and **B** with CO, the corresponding disilaketene could even not be observed as intermediates, presumably owing to the rigidity and steric hindrance of the *o*-carborane backbone.

In compound **2**, the two different sorts of ^{29}Si nuclei give rise to different ^{29}Si NMR resonances. The resonance at $\delta = -62.27$ ppm can be assigned to the Si atoms of the CSiO_2 moiety, whereas that at $\delta = -108.44$ ppm corresponds to the C_2SiO units; the latter value is close to the ^{29}Si NMR resonance of **C** ($\delta = -91.4$ ppm).^{23b} Interestingly, the $\text{C}=\text{C}-\text{O}$ moieties in **2** resonate at 22.34 and 173.78 ppm in the ^{13}C NMR spectrum, which are reminiscent of those observed for the ketene moiety in **C** (19.7 and 165.5 ppm).

A single crystal X-ray diffraction analysis revealed a polycyclic skeleton in **2** as depicted in Fig. 1. Compound **2** crystallises in the triclinic space group $P\bar{1}$. Its molecular structure

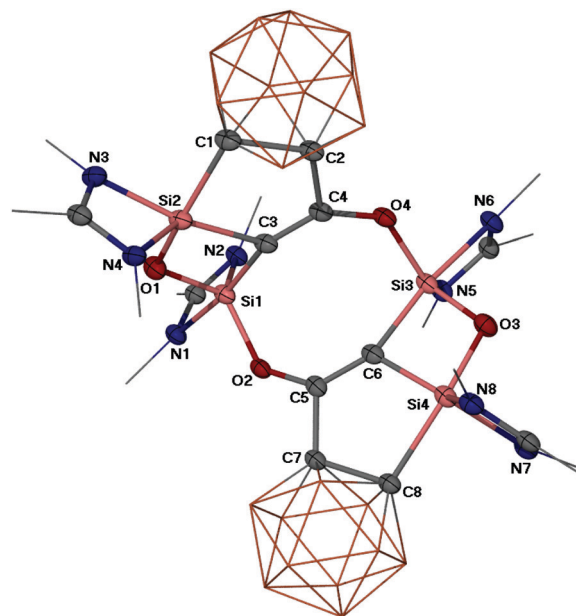
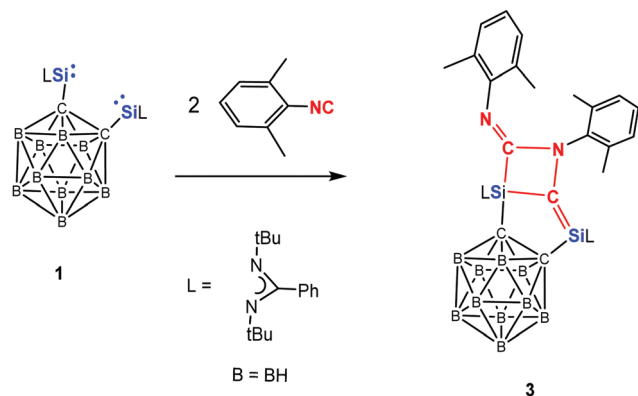


Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and Ph as well as *t*-Bu groups are omitted for clarity. Selected bond distances (\AA) and angles ($^{\circ}$): Si1–O1 1.690(1), Si2–O1 1.698(2), Si1–O2 1.728(2), Si3–O3 1.683(3), Si4–O3 1.705(2), Si3–O4 1.724(2), Si1–C3 1.876(3), Si2–C3 1.905(3), C3–C4 1.324(4), C4–C2 1.537(3), O4–C4 1.361(3), Si3–C6 1.878(3), Si4–C6 1.905(4), C5–C6 1.337(4), C5–O2 1.346(4), C5–C7 1.536(4), Si2–C1 2.042(3), Si4–C8 2.070(3); Si1–O1–Si2 104.1(1), Si1–C3–Si2 89.9(1), Si3–O3–Si4 103.9(1), Si3–C6–Si4 89.7(1), C3–C4–O4 132.0(2), C6–C5–O2 132.2(3), C3–Si1–N1 172.2(1), C3–Si2–N3 161.3(1), N6–Si3–C6 170.6(1), C8–Si4–O3 162.1(1).

consists of an eight-membered $\text{Si}_2\text{C}_4\text{O}_2$ ring and two four-membered SiOSiC rings. The penta-coordinate Si1 and Si3 atoms in the eight-membered ring feature a distorted trigonal bipyramidal coordination geometry with the N1–Si1–C3 angle of $172.2(1)^{\circ}$ and the N6–Si3–C6 angle of $170.6(1)^{\circ}$ in the axial direction, respectively. In comparison, the Si2 and Si4 atoms are also penta-coordinated (ON_2C_2), but adopt a stronger distorted trigonal bipyramidal geometry with the C8–Si4–O3 angle of $162.1(1)^{\circ}$ and N3–Si2–C3 of $161.3(1)^{\circ}$, respectively. The Si–O distances, ranging from 1.683(3) to 1.728(2) \AA , are in the common range of Si–O bonds. The Si–C distances with the carborane C atoms (Si2–C1 2.042(3) and Si4–C8 2.070(3) \AA) are significantly longer than those of the C atoms in the eight-membered $\text{Si}_2\text{C}_4\text{O}_2$ ring (1.876(3) to 1.905(3) \AA). The C4–C2 (1.537(3) \AA) and C5–C7 (1.536(4) \AA) interactions, bridging the eight-membered ring and the two carborane clusters, represent C–C single bonds. However, the C–C distances within the eight-membered ring C3–C4 (1.324(4) \AA) and C5–C6 (1.337(4) \AA) are significantly shorter and indicative of $\text{C}=\text{C}$ bonds. It is worthy of note that the C4–O4 (1.361(3) \AA) and C5–O2 (1.346(4) \AA) are much shorter than a C–O bond in ethers, implying considerable electron delocalisation in those C–C–O moieties.

The reactivity of **1** towards the isoelectronic 2,6-dimethylphenyl isocyanide has also been investigated (Scheme 3). ^1H NMR measurements showed that compound **3** is formed as sole product independent of the molar ratio of the starting





Scheme 3 Reaction of **1** with 2,6-dimethylphenylisocyanide to form **3**.

materials chosen. Thus reaction of **1** with two molar equivalents of isocyanide at $-20\text{ }^{\circ}\text{C}$ in toluene affords **3** in 78% isolated yields. This is in stark contrast to the reactions of bis-NHSi **A** with the same isocyanide,^{23b} which led to **E**, **F**, and **G** (Scheme 1) as products depending on the molar ratio of the starting materials and the reaction conditions.

The ^{29}Si NMR spectrum of **3** shows two resonances at $\delta = -32.3$ ppm (Si=C) and -60.0 ppm (SiC_3N_2), assignable to the four- and five-coordinate Si atoms, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a signal at $\delta = 181.7$ ppm for Si=C-Si and 190.4 ppm for R=N=C-Si (R = 2,6-dimethylphenyl), respectively. A single-crystal X-ray diffraction analysis revealed that **3** crystallises in the monoclinic space group $P2_1/n$. The molecular structure of **3** (Fig. 2) shows that the two molecules isocyanide underwent N=C-N-C coupling and concomitantly Si-C bond formation. While the four-coordinate Si2 atom features a distorted tetrahedral coordination environment, the five-coordinate Si1 atom adopts a distorted trigonal bipyramidal coordination geometry with the axial C2-Si1-C5 angle of 165° .

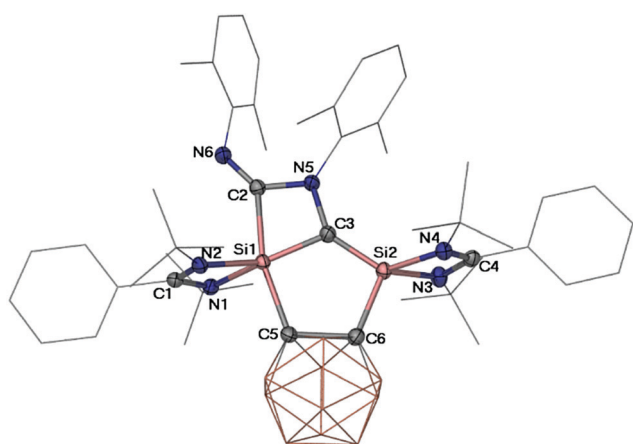


Fig. 2 Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (\AA) and angles ($^{\circ}$): Si1-C3 1.822(2), Si1-C2 2.027(2), Si1-C5 2.054(2), Si2-C3 1.724(2), Si2-C6 1.905(2), C2-N6 1.281(2), C2-N5 1.413(2), C3-N5 1.474(2); C3-Si1-C2 70.7(1), C3-Si1-C5 94.3(1), C2-Si1-C5 165.0(1), C3-Si2-C6 101.6(1), N5-C3-Si2 139.9(1), N5-C3-Si1 97.3(1), Si2-C3-Si1 22.3(1).

Both of the four-membered SiC_2N and the five-membered Si_2C_3 rings are planar. Along the axial direction, the Si1-C2 (2.027(2) \AA) and Si1-C5 (2.054(2) \AA) distances are significantly longer than that of Si1-C3 (1.822(2) \AA) in the equatorial direction. Moreover, the five-coordinate Si1 atom features also a longer Si1-C5 distance (2.054(2) \AA) than that of the four-coordinate Si2 atom in the Si2-C6 bond (1.905(2) \AA). The shortest Si2-C3 distance (1.724(2) \AA) among all Si-C distances in **3** lies even in the range of Si=C bond distances of silaethylene.²⁵ Similarly, the relatively short C2-N6 (1.281(2) \AA) distance compared with that of C3-N5 (1.474(2) \AA) suggests C=N bond character. It is noteworthy that compound **3** represents an unique example of head-to-tail coupling product of isocyanide compared to those usual head-to-head coupling products.²⁶

Because all attempts to detect an intermediate even at $-78\text{ }^{\circ}\text{C}$ by means of multi nuclear NMR spectroscopy were unsuccessful, Density Functional Theory (DFT) calculations were performed to gain insight into the mechanism of the formation of **2** and **3**. The DFT-derived mechanism leading to **2** (Scheme 2 and Fig. S3 in ESI[†]) follows initially similar reaction steps that have been uncovered previously for the reaction of CO and bis-NHSi **A** to give **C** (Scheme 1).^{23b} In contrast to the former case, however, the disilaketene analogue of **C** (compound **2'**, Scheme 2) is a reactive intermediate which undergoes migration of one of the carbons of the carborane from Si to the central carbon of the ketene moiety to afford another intermediate (compound **2''**) with a Si=C-C=O moiety; head-to-tail dimerisation of the latter furnishes the final product **2**. We think that the newly observed cleavage of the $\text{C}_{\text{carborane}}\text{-Si}$ bond is the consequence of the weaker and more polar nature of the C-Si bond as indicated by the lower Wiberg Bond Index (WBI, 0.53 in **1**) compared to the WBI of 0.69 in both **A** and **B**. In addition, the proposed ketene intermediate **2'** is energetically 32.5 kcal mol $^{-1}$ less stable than its dimer **2** in part owing to the steric congestion of **2'** caused by both bridged $\mu\text{-C}=\text{C}=\text{O}$ and $\mu\text{-O}$. In case of the reaction of **1** with 2,6-dimethylphenyl isocyanide, the isocyanide moiety reacts rapidly with **1** to form **3'** which is attacked by an additional 2,6-dimethylphenyl isocyanide molecule to give **3** (Fig. 3). The latter reaction step shows a very small energy barrier of 1.9 kcal mol $^{-1}$ that is consistent with the experimental fact that the conversion proceeds at $-20\text{ }^{\circ}\text{C}$. NBO analysis (Tables S5-S7, ESI[†]) reveals the zwitterionic nature of **3'** (Fig. 3) that enables the reactivity of **3'** towards an additional isocyanide.

In conclusion, the *o*-carborane supported bis-NHSi **1** is more reactive towards CO and 2,6-dimethylphenyl isocyanide than the previously reported bis-NHSis **A** and **B**.^{23b} Owing to the different steric and electronic effects of the *o*-carborane backbone, the outcome of the reaction of **1** with CO affords solely, *via* a cascade of cleavage and coupling reactions, the new bis-silylene-mediated polycyclic CO coupling product **2** as the final product. The reaction of **1** with 2,6-dimethylphenyl isocyanide furnishes the new Si=C containing coupling product **3**, irrespective of the chosen molar ratio of **1** to isocyanide. The unexpected head-to-head of CO and head-to-tail of isocyanide homocoupling products represent new reactivity features of a



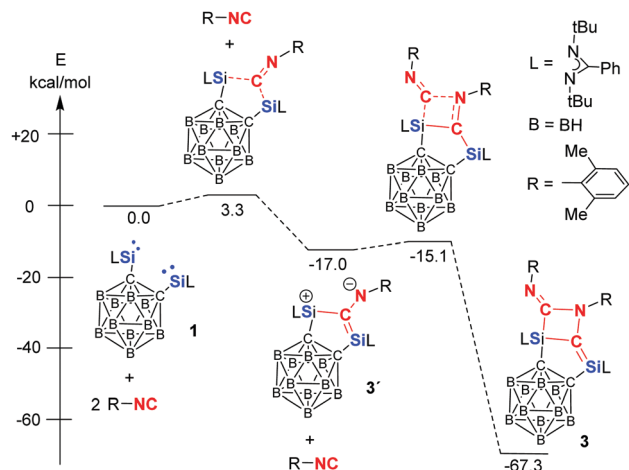


Fig. 3 DFT-derived mechanism for the formation **3** from **1** via **3'**.

bis-NHSi towards small molecules. More investigations concerning the remarkable reactivity of bis-NHSi **1** to furnish new classes of organosilicon compounds are currently in progress.

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Conflicts of interest

There are no conflicts to declare.

References

- P. P. Power, *Nature*, 2010, **463**, 171–177.
- S. Yadav, S. Saha and S. S. Sen, *ChemCatChem*, 2016, **8**, 486–501.
- D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.*, 2011, **2**, 389–399.
- P. P. Power, *Chem. Rev.*, 2012, **12**, 238–255.
- T. Chu and G. I. Nikonov, *Chem. Rev.*, 2018, **118**, 3608–3680.
- (a) M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels and H. Braunschweig, *Science*, 2018, **359**, 896–900; (b) M.-A. Légaré, M. Rang, G. Bélanger-Chabot, J. I. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. C. Holthausen and H. Braunschweig, *Science*, 2019, **363**, 1329–1332.
- (a) X. Wang, Z. Zhu, Y. Peng, H. Lei, J. C. Fettingner and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 6912–6913; (b) H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan and A. Vargas, *Nat. Chem.*, 2013, **5**, 1025–1028.
- 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.
- B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boesec and D. Bläser, *J. Chem. Soc., Chem. Commun.*, 1995, 1931–1932.
- M. Kira, S. Ishida, T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.*, 1999, **121**, 9721–9723.
- M. Driess, S. Yao, M. Brym, C. Van Wüllen and D. Lentz, *J. Am. Chem. Soc.*, 2006, **128**, 9628–9629.
- C.-W. So, H. W. Roesky, J. Magull and R. B. Oswald, *Angew. Chem., Int. Ed.*, 2006, **45**, 3948–3950.
- M. Asay, S. Inoue and M. Driess, *Angew. Chem., Int. Ed.*, 2011, **50**, 9589–9592.
- B. D. Reinken, T. M. Brown, J. C. Fettingner, H. M. Tuononen and P. P. Power, *J. Am. Chem. Soc.*, 2012, **134**, 6504–6507.
- A. V. Protchenko, K. H. Birj Kumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503.
- A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem., Int. Ed.*, 2013, **52**, 568–571.
- T. J. Hadlington, J. A. B. Abdalla, R. Tirfoin, S. Aldridge and C. Jones, *Chem. Commun.*, 2016, **52**, 1717–1720.
- S. Inoue and K. Leszczyńska, *Angew. Chem., Int. Ed.*, 2012, **51**, 8589–8593.
- S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767.
- A. Protchenko, P. Vasko, D. C. H. Do, J. Hicks, M. Á. Fuentes, C. Jones and S. Aldridge, *Angew. Chem., Int. Ed.*, 2019, **58**, 1808–1812.
- (a) W. Wang, S. Inoue, E. Irran and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 3691–3694; (b) W. Wang, S. Inoue, S. Enthaler and M. Driess, *Angew. Chem., Int. Ed.*, 2012, **51**, 6167–6171.
- D. Gallego, S. Inoue, B. Blom and M. Driess, *Organometallics*, 2014, **33**, 6885–6897.
- (a) Y. Wang, A. Kostenko, S. Yao and M. Driess, *J. Am. Chem. Soc.*, 2017, **139**, 13499–13506; (b) Y. Wang, A. Kostenko, T. J. Hadlington, M.-P. Luecke, S. Yao and M. Driess, *J. Am. Chem. Soc.*, 2019, **141**, 626–634; (c) M.-P. Luecke, A. Kostenko, Y. Wang, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2019, **58**, 12940–12944.
- Y.-P. Zhou, S. Raoufmoghaddam, T. Szilvási and M. Driess, *Angew. Chem., Int. Ed.*, 2016, **55**, 12868–12872.
- H. F. Schaefer III, *Acc. Chem. Res.*, 1982, **15**, 283–290.
- See for examples: (a) M. Ma, A. Stasch and C. Jones, *Chem. – Eur. J.*, 2012, **18**, 10669–10676; (b) W. Uhl, U. Schütz, W. Hiller and M. Heckel, *Chem. Ber.*, 1994, **127**, 1587–1592; (c) Y. Xiong, S. Yao and M. Driess, *Chem. – Eur. J.*, 2009, **15**, 8542–8547.

