



Cite this: *Dalton Trans.*, 2019, **48**, 12391

Received 29th March 2019,
Accepted 19th June 2019

DOI: 10.1039/c9dt01359h

rsc.li/dalton

Reactions of hydrazones and hydrazides with Lewis acidic boranes†

Theodore A. Gazis,^a Ayan Dasgupta,^{†a} Michael S. Hill,^b Jeremy M. Rawson,^c Thomas Wirth^d and Rebecca L. Melen^{*,a}

The reaction of (diphenylmethylene)hydrazone or 1,4-bis-hydrazone-ylidene(phenylmethyl)benzene with Lewis acidic boranes $B(2,4,6-F_3C_6H_2)_3$ or $B(3,4,5-F_3C_6H_2)_3$ generates the Lewis acid–base adducts. Alternatively, when (9H-fluoren-9-ylidene)hydrazone is employed several products were isolated including 1,2-di(9H-fluoren-9-ylidene)hydrazone, the 2 : 1 borane adduct of NH_2-NH_2 and the 1-(diarylboraneyl)-2-(9H-fluoren-9-ylidene)hydrazone in which one ArH group has been eliminated. The benz-hydrazide starting material also initially gives an adduct when reacted with Lewis acidic boranes which upon heating eliminates ArH generating a CON_2B heterocycle.

With over a century since the dawn of the Haber–Bosch process, the activation and subsequent functionalisation of dinitrogen remains a challenge. Typically, metal catalysts, such as those based upon Fe or Mo, have been trialled for the reduction of N_2 to NH_3 . The ability of transition metal complexes to bind to N_2 has been attributed to the roles of the metal d-orbitals in bonding and back-bonding interactions with N_2 .¹ Recently however, the activation of nitrogen–nitrogen bonds such as azides, diazo-compounds, hydrazones and dinitrogen using boranes has gained momentum.^{2,3} Both Szymczak⁴ and Simonneau⁵ reported the use of $B(C_6F_5)_3$ to activate $M-N_2$ ($M = Fe, Mo, W$) complexes (Fig. 1) towards protonation or borylation/silylation. A major advance in this area was to remove the transition metal altogether. While $(N_2)BF_3$ has been generated *via* supersonic expansion at 600 Torr and

170 K,⁶ it was only last year that the metal-free activation of N_2 was reported using a cyclic (alkyl)(amino)carbene (CAAC) stabilised borylene (Fig. 1).⁷ Prior to this, Stephan^{3a,8} had shown that the strong Lewis acid $B(C_6F_5)_3$ can be used to release N_2 from Ph_2CN_2 , and can be used in reactions with $Ph_2C=NNH_2$ to form an adduct (Fig. 1). Yamashita⁹ has subsequently shown that a highly Lewis acidic diborane can react with azobenzene and pyridazine *via* diboration and, when phthalazine is employed, $N=N$ bond cleavage occurs. At a similar time, we have been investigating the synthesis and comparative reactivity of new boranes bearing fluorinated aryl groups as an alternative to the archetypical $B(C_6F_5)_3$.¹⁰ In this regard, we were interested in comparing the reactivity of boranes other than $B(C_6F_5)_3$ with a variety of N–N bonded compounds including hydrazones and hydrazides, which are reported herein (Fig. 1). These may provide alternative reactivity and reaction rates depending upon the borane Lewis

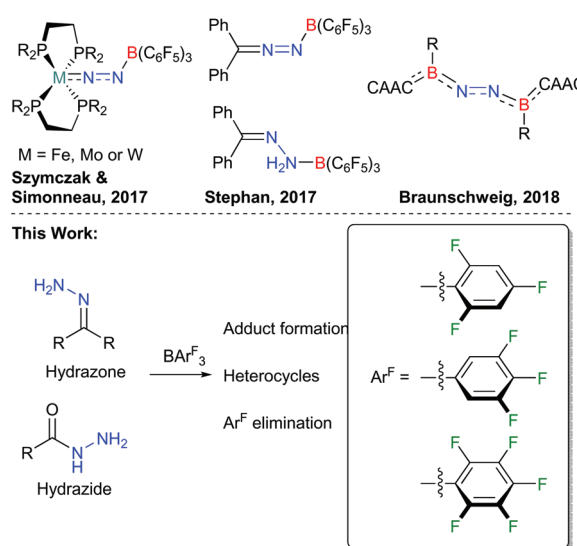


Fig. 1 Previous work on activation of N–N bonds using $B(C_6F_5)_3$ and borylenes, and outline of the work described in this article.

^aCardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, Cymru/Wales, CF10 3AT, UK. E-mail: MelenR@cardiff.ac.uk

^bDepartment of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

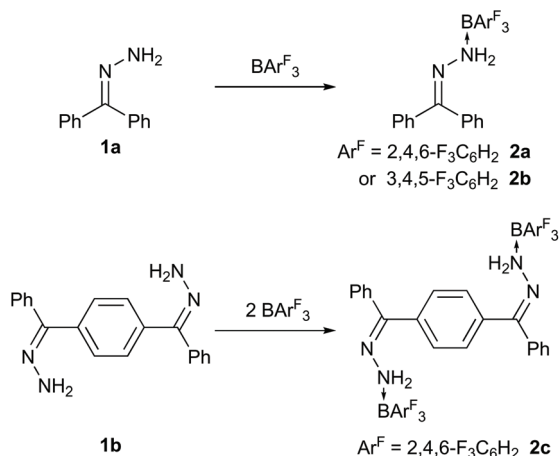
^cDepartment of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario N9B 3P4, Canada

^dSchool of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, Cymru/Wales, CF10 3AT, UK

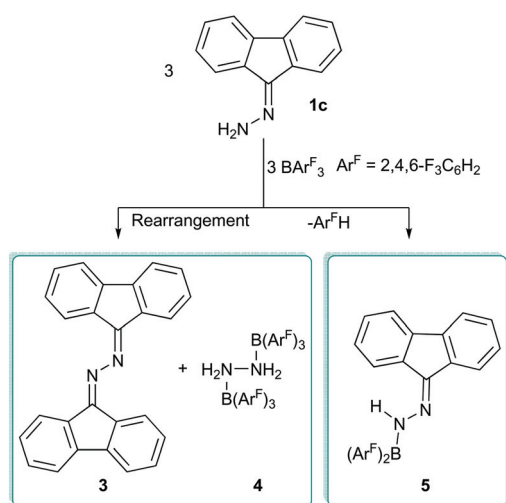
†Electronic supplementary information (ESI) available: Experimental procedures, NMR spectra and details of the X-ray analyses of compounds 2a–c, 4–5, 6a,b, 7. CCDC 1897205–1897211 and 1903201. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt01359h

‡These authors contributed equally.





Scheme 1 Reactions of hydrazones with Lewis acidic boranes.



Scheme 2 Reactions of **1c** with $B(2,4,6-F_3C_6H_2)_3$.

acidity.¹¹ Initially, the hydrazone compounds **1a–c** (Schemes 1 and 2) were prepared from the condensation reaction of the corresponding ketone with hydrazine monohydrate. Upon reaction of **1a** with $B(2,4,6-F_3C_6H_2)_3$ or $B(3,4,5-F_3C_6H_2)_3$ the corresponding N → B adducts **2a** and **2b** were formed in which the $-NH_2$ group of the hydrazone coordinated to the Lewis acidic boron atom analogous to that reported by Stephan when **1a** was combined with $B(C_6F_5)_3$.⁸ Similarly, when bis-hydrazone **1b** was reacted with $B(2,4,6-F_3C_6H_2)_3$ in a 1 : 2 stoichiometric ratio a 1 : 2 adduct (**2c**) was formed. Compounds **2a**, **2b** and **2c** were isolated in 61%, 65% and 56% yield respectively. Adducts **2a–c** all displayed a broad peak ranging between -2.6 and -6.2 ppm in the ^{11}B NMR spectrum. Recrystallisation of the reaction mixtures from a CH_2Cl_2 /pentane solution resulted in single crystals of the adducts whose structures were determined by single crystal X-ray diffraction (Fig. 2). In these structures the boron atom adopted a tetrahedral arrangement with B–N bond lengths ranging from $1.646(5)$ – $1.696(4)$ Å, similar to those observed in previous

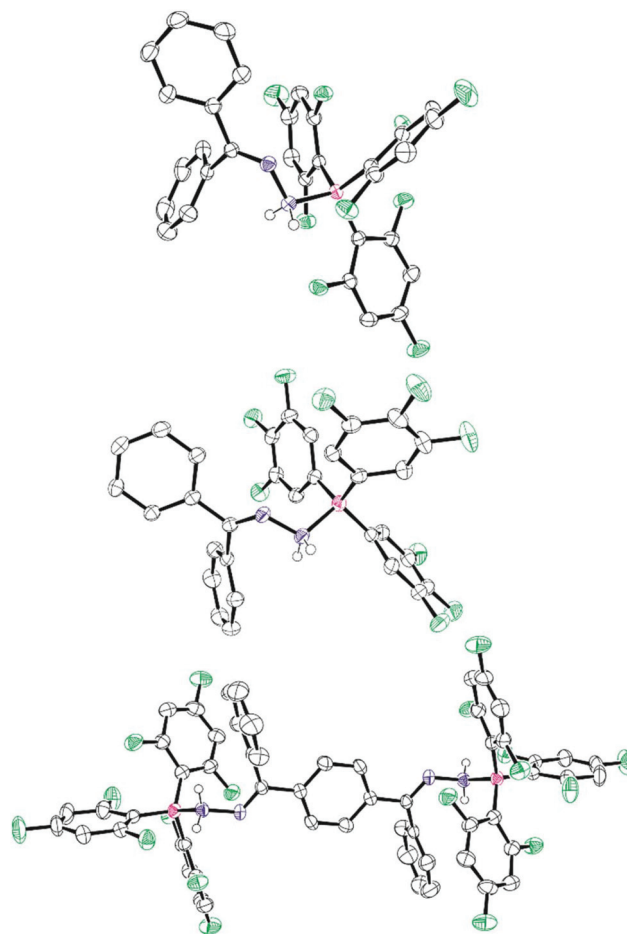


Fig. 2 Solid-state structures of **2a** (top), **2b** (middle) and **2c** (bottom). C: black, N: blue, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. H atoms except N–H omitted for clarity.

reports ($1.631(7)$ Å).⁷ The single N–N bond lengths (range $1.438(4)$ – $1.449(2)$ Å) were also similar to those reported previously.⁸ Likewise, the C=N bond lengths of $1.287(3)$ – $1.294(5)$ Å are typical of C=N double bonds.¹² In all cases, heating adducts **2** resulted in an unidentifiable mixture of compounds and no elimination of $Ar^F H$ was observed, in contrast with previous reports where $B(C_6F_5)_3$ was employed as the Lewis acid.⁸ Alternatively, if the compound **1c** was used in the reactions with boranes BAr^F_3 ($Ar^F = 3,4,5-F_3C_6H_2$, C_6F_5), the reaction gave a complex and inseparable mixture of products. However, if **1c** is reacted with the less Lewis acidic borane $B(2,4,6-F_3C_6H_2)_3$ several products could be selectively crystallised from the reaction mixture to shed light on this reactivity. These could be structurally identified by single crystal X-ray diffraction as the previously reported 1,2-di(9H-fluorene-9-ylidene)hydrazine (**3**),¹³ the bis borane adduct of hydrazone, NH_2NH_2 (**4**) and the 1-(diarylboran-2-yl)-2-(9H-fluorene-9-ylidene)hydrazine (**5**) (Scheme 2 and Fig. 3). It is unclear how the three products are formed from the reaction, but it is likely that initially an adduct is formed between **1c** and the borane. Indeed, *in situ* NMR studies showed that when **1c** is added to the borane in toluene then a



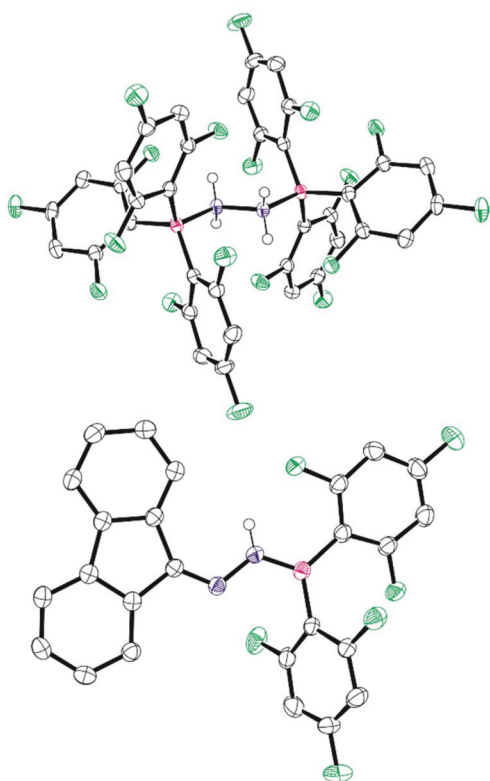


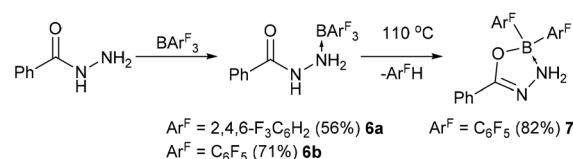
Fig. 3 Solid-state structures of **4** (top) and **5** (bottom). C: black, N: blue, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. H atoms except N–H omitted for clarity.

characteristic broad shift at $\delta = -5.1$ ppm in the ^{11}B NMR spectrum was observed. Two divergent pathways then operate to generate either **3** and **4**, or compound **5**. Elimination of $\text{Ar}^{\text{F}}\text{H}$ generates **5** which is similar to observations made by Stephan for hydrazone $\text{Ph}_2\text{C}=\text{NNH}_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$.⁸ The trigonal planar boron atom in **5** can be observed in the solid-state structure with N–B–C bond angles of $117.8(1)^\circ$ and $119.7(1)^\circ$, and a C–B–C bond angle of $122.5(1)^\circ$. The B–N bond length of $1.397(2)$ Å was also significantly shorter than observed in the adducts **2** indicating some π -donation from $\text{N} \rightarrow \text{B}$ generating a *trans*-diene structure in which the CN_2B atoms lie in the same plane. If the reaction of **1c** with $\text{B}(2,4,6\text{-F}_3\text{C}_6\text{H}_2)_3$ is performed at low temperatures (0°C) in toluene then compound **5** is formed selectively in 46% yield.

Alternatively, another reaction can take place when **1c** is reacted with $\text{B}(2,4,6\text{-F}_3\text{C}_6\text{H}_2)_3$. Here a hydrazone metathesis reaction occurs to yield the azine (**3**) and borane adduct of hydrazone (**4**). This reaction is more predominant when the reaction is performed at elevated temperatures (e.g. r.t. to 50°C). N–N-linked diimines (azines) are an important class of compounds isoelectronic to 1,3-butadiene. These compounds have a variety of uses including applications as chromophores in optoelectronic devices.¹⁴ Previously, **3** has been reported to have been synthesised by the decomposition of diazo compounds catalysed by $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$.¹⁵ Similar reactions which generate a diazine from hydrazones have been reported

and involve harsh conditions and long time periods e.g. refluxing in ethanolic hydrogen chloride for several hours.¹⁶ More interesting is that, in our case, the borane adduct of hydrazone **4** is also generated in the reaction. Previously, the hydrazine bisborane $\text{N}_2\text{H}_4(\text{BH}_3)_2$ has been postulated as a good hydrogen storage material containing 16.9 wt% hydrogen. Additionally, coordinated hydrazine has been identified as a potential intermediate in nitrogen fixation reactions.^{17–19} While $\text{N}_2\text{H}_4(\text{BH}_3)_2$ is easily prepared from the reaction of hydrazine sulfate with sodium borohydride, other borane adducts are more challenging to synthesise and a search of the literature reveals that generally intramolecular bis boranes are employed. Previously, Gabbaï²⁰ and Szymczak¹⁷ have reported that intramolecular bisboranes can react with hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). In these reactions, the use of a bisborane appears key to trapping and activating the hydrazone unit. We attempted to generate **4** independently from the reaction BAr^{F}_3 ($\text{Ar} = 2,4,6\text{-F}_3\text{C}_6\text{H}_2$) and hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) in a 2 : 1 ratio with the use of molecular sieves to trap the water by-product. Pleasingly, this led to the formation of compound **4** as observed by *in situ* multinuclear NMR spectroscopy. The structure of **4** displays a B–N bond length of $1.673(2)$ Å which is longer than that in hydrazine bisborane (1.609 Å)²¹ and slightly shorter than that reported by Gabbaï ($1.688(2)$ Å) and Szymczak ($1.697(2)$ Å and $1.698(2)$ Å) for the chelating bisborane complexes.^{17,20} The N–N distance of $1.461(2)$ Å is similar to that reported for other hydrazine bisborane complexes (range $1.356(2)$ Å– $1.469(2)$ Å).^{17,20,22}

Finally, we turned our attention to other N–N bonded substrates, namely hydrazides (Scheme 3). When commercially available benzhydrazide was reacted with BAr^{F}_3 an adduct was formed initially between the NH_2 group and the borane. In the case of the boranes where $\text{Ar} = 2,4,6\text{-F}_3\text{C}_6\text{H}_2$ or C_6F_5 the adducts **6a–b** could be isolated in 56% and 71% yield, respectively. Recrystallisation of the solutions afforded crystals of the adducts which could be structurally determined (Fig. 4 and ESI†). The ^{11}B NMR spectra showed a broad peak at $\delta = -6.1$ ppm (**6a**) and -6.2 ppm (**6b**) similar to that observed with the hydrazone borane adducts. In the case of **6b** *in situ* heating of the BAr^{F}_3 adduct of benzhydrazide to 110°C in toluene led to loss of $\text{Ar}^{\text{F}}\text{H}$ and generation of a CON_2B heterocycle (**7**). Recrystallisation of the reaction mixture afforded pink crystals of the product in 82% yield. Compound **7** crystallised in the $P\bar{1}$ space group with two molecules in the asymmetric unit. The N–H hydrogen atoms were identified in the difference map. X-ray diffraction analysis revealed the CON_2B rings to be planar with r.m.s.d. of 0.010 Å and 0.023 Å. The B–N bond



Scheme 3 Reaction of hydrazides with BAr^{F}_3 .



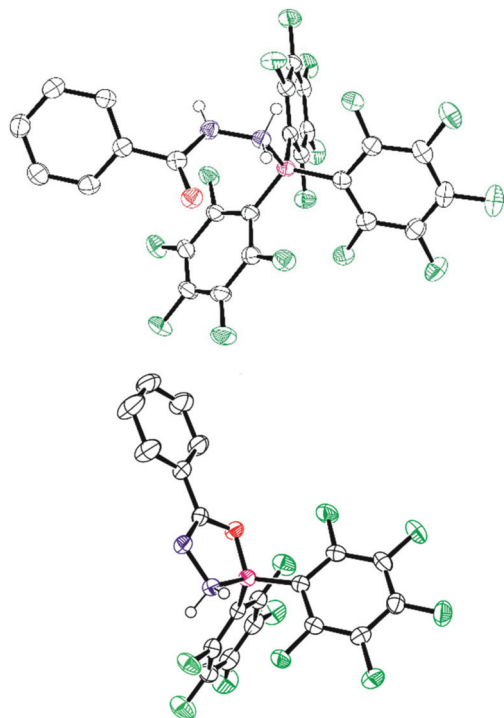


Fig. 4 Solid-state structures of **6b** (top) and **7** (bottom). C: black, N: blue, O: red, B: pink, F: green. Thermal ellipsoids drawn at 50% probability. Non-essential H atoms omitted for clarity.

lengths of 1.621(2) Å and 1.608(3) Å are slightly shorter than that in the adduct **6a–b** (1.635(3) Å and 1.643(2) Å respectively) presumably due to the formation of a 5-membered intramolecular chelate. Conversely, the N–N bond in **7** is slightly longer at 1.468(2) Å and 1.464(3) Å compared to 1.429(3) Å and 1.426(2) Å in **6a–b**.

Preliminary computational studies (DFT B3LYP-D3/6-31G(d,p)) to probe these elimination reactions (Scheme 3) focused on the model compound $\text{MeCONHNH}_2 \rightarrow \text{BPh}_3$. Calculations revealed 1,4-elimination of C_6H_6 (implementing the NH_2 proton) appears to be the thermodynamically favoured process and forms acyclic MeCON(H)N(H)BPh_2 , whereas 1,5-elimination (using the amide-NH) is a near energetically neutral process leading to formation of a 3-membered BN_2 heterocycle as the initial elimination product (see ESI†).

Conclusions

In conclusion we have prepared a series of hydrazone and hydrazide adducts of Lewis acidic boranes to investigate the interactions of Lewis acidic boranes with nitrogen containing compounds which may be of interest to those working in the area of metal-free dinitrogen activation and conversion. Initially adducts are formed which upon heating lead to loss of $\text{Ar}^{\text{F}}\text{H}$ to generate novel covalent N–N–B systems including the chain compound **5** and heterocyclic compound **7**. Of particular interest is the reaction to generate the bisborane hydrazine

dimer **4** from a hydrazone metathesis reaction. Subsequent studies to explore the independent synthesis and reactivity of **4** in hydrogen release are ongoing within our group.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

T. A. G. thanks the EPSRC Cardiff/Bristol/Bath CDT in Catalysis for funding (EP/L016443/1). A. D. and R. L. M. would like to acknowledge the EPSRC for an Early Career Fellowship for funding (EP/R026912/1). J. M. R. thanks NSERC for financial support.

Notes and references

- Y. Nishibayashi, *Nitrogen Fixation*, Springer, New York, 2017; K. C. MacLeod and P. L. Holland, *Nat. Chem.*, 2013, **5**, 559; P. L. Holland, *Dalton Trans.*, 2010, **39**, 5415.
- A. J. Ruddy, D. M. C. Ould, P. D. Newman and R. L. Melen, *Dalton Trans.*, 2018, **47**, 10377.
- (a) R. C. Neu, C. Jiang and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 726; (b) C. Schneider, J. H. W. LaFortune, R. L. Melen and D. W. Stephan, *Dalton Trans.*, 2018, **47**, 12742.
- J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 5952.
- A. Simonneau, R. Turrel, L. Vendier and M. Etienne, *Angew. Chem., Int. Ed.*, 2017, **56**, 12268.
- K. C. Janda, L. S. Bernstein, J. M. Steed, S. E. Novick and W. Klemperer, *J. Am. Chem. Soc.*, 1978, **100**, 8074.
- M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels and H. Braunschweig, *Science*, 2018, **359**, 896. Also see: C. Hering-Junghans, *Angew. Chem., Int. Ed.*, 2018, **57**, 6738; 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.
- C. Tang, Q. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. Song, S. Grimme and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2017, **56**, 16588. Also see: R. L. Melen, *Angew. Chem., Int. Ed.*, 2018, **57**, 880.
- Y. Katsuma, L. Wu, Z. Lin, S. Akiyama and M. Yamashita, *Angew. Chem., Int. Ed.*, 2019, **58**, 317.
- J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. – Eur. J.*, 2017, **23**, 10997; Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381; J. L. Carden, L. J. Gierlich, D. F. Wass, D. L. Browne and R. L. Melen, *Chem. Commun.*, 2019, **55**, 318.
- M. Santi, D. M. C. Ould, J. Wenz, Y. Soltani, R. L. Melen and T. Wirth, *Angew. Chem., Int. Ed.*, 2019, **58**, 7861.
- Bond Energies, *Encyclopedia of Inorganic Chemistry*, 2006; DOI: 10.1002/0470862106.id098.



- 13 J. Lasri, N. E. Eltayeb and A. I. Ismail, *J. Mol. Struct.*, 2016, **1121**, 35.
- 14 J. Safari and S. Gandomi-Ravandia, *RSC Adv.*, 2014, **4**, 46224.
- 15 R. Bertani, M. Biasiolo, K. Darini, R. A. Michelin, M. Mozzon, F. Visentin and L. Zanotto, *J. Organomet. Chem.*, 2002, **642**, 32.
- 16 M. L. Trudell, N. Fukada and J. M. Cook, *J. Org. Chem.*, 1987, **52**, 4293.
- 17 J. J. Kiernicki, M. Zeller and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 18194.
- 18 Y. Yu, W. W. Brennessel and P. L. Holland, *Organometallics*, 2007, **26**, 3217; Y. Lee, N. P. Mankad and J. C. Peters, *Nat. Chem.*, 2010, **2**, 558; C. T. Saouma, C. C. Lu and J. C. Peters, *Inorg. Chem.*, 2012, **51**, 10043; K. Umehara, S. Kuwata and T. Ikariya, *J. Am. Chem. Soc.*, 2013, **135**, 6754; Y. Li, Y. Li, B. Wang, Y. Luo, D. Yang, P. Tong, J. Zhao, L. Luo, Y. Zhou, S. Chen, F. Cheng and J. Qu, *Nat. Chem.*, 2013, **5**, 320.
- 19 T. Hügler, M. F. Kühnel and D. Lentz, *J. Am. Chem. Soc.*, 2009, **131**, 7444.
- 20 C.-H. Chen and F. P. Gabbaï, *Chem. Sci.*, 2018, **9**, 6210.
- 21 S. Mebs, S. Grabowsky, D. Förster, R. Kickbusch, M. Hartl, L. L. Daemen, W. Morgenroth, P. Luger, B. Paulus and D. Lentz, *J. Phys. Chem. A*, 2010, **114**, 10185.
- 22 S. Pylypko, E. Petit, P. G. Yot, F. Salles, M. Cretin, P. Miele and U. B. Demirci, *Inorg. Chem.*, 2015, **54**, 4574.

