



### Diborane heterolysis and P(v) reduction by $\text{Ph}_3\text{P}=\text{O}$ coordination to magnesium†

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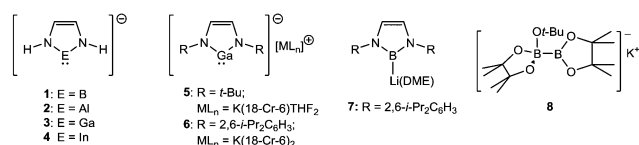
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**Reaction of a magnesium diboranate complex with triphenylphosphine oxide provides a terminal magnesium boryl, which is itself a potent reagent for the deoxygenative reduction of  $\text{Ph}_3\text{PO}$ . Computational analysis with density functional theory (DFT) indicates that B–B bond activation results from initial coordination of the P=O bond of the phosphine oxide to magnesium.**

The chemistry of nucleophilic group 13-centred anions has been an area of interest for over 20 years. The viability of singlet lithium boryl anions ( $\text{X}_2\text{B-Li}$ ; X = F, Cl, O) was posited by Schleyer in 1995,<sup>1</sup> while the electronic structures of a range of model boron, aluminium, gallium and indium imidazolate anions (1–4) were evaluated by Schoeller and co-workers a short time later.<sup>2</sup> Schmidbauer's realisation of the N-heterocyclic gallyl anion (5) in 1999, therefore, was a true landmark in group 13 element synthesis.<sup>3</sup> Although the chemistry of compound 5 was never exploited, Jones' subsequent exploration of the reactivity of the closely-related gallyl (6),<sup>4</sup> definitively established the potential of such species as gallium-centred nucleophiles and reducing agents.<sup>5–17</sup>



While related aluminium- and indium-centred anions are of a very recent origin,<sup>18–21</sup> the veracity of Schleyer's initial speculation was realised in Yamashita and Nozaki's synthesis of the lithium boryl (7) in 2006.<sup>22–25</sup> In a similar manner to Jones' gallium anions, the stability of the carbenoid B(1) centre is based on the combination of kinetic, inductive and

mesomeric stability provided by the steric demands of the bulky 2,6-di-iso-propylphenyl (Dipp) and electronegative N-donor substituents, respectively. While the nucleophilic reactivity of compound 7 has been validated toward an array of organic and inorganic electrophiles,<sup>26–33</sup> in common with many other subsequently reported boron nucleophiles,<sup>34–37</sup> its synthesis requires the synthetically inconvenient reduction of a trivalent boron precursor with a strong alkali metal reducing agent.

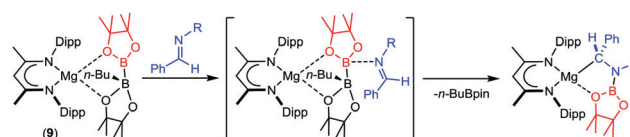
During a similar timeframe, the study of desymmetrised diborane derivatives, for example the bis(pinacolato)diborane ( $\text{B}_2\text{pin}_2$ ) derivative 8,<sup>38,39</sup> has attracted significant attention.<sup>40–44</sup>

Applied under either 'metal-free' or 'metal-catalysed' conditions, such species have been found to provide nucleophilic boron surrogates, albeit without the explicit generation of any observable boryl anion.

Our own research has focused on  $\beta$ -diketiminato (BDI) magnesium compounds such as  $[(\text{BDI})\text{Mg}\{\text{pinBB}(n\text{-Bu})\text{pin}\}]$  (9, Scheme 1).<sup>45,46</sup> The  $[\text{pinBB}(n\text{-Bu})\text{pin}]^-$  diboranate anion is analogous to that of species 8 and we have observed that compound 9 reacts similarly through elimination of  $n\text{-BuBpin}$  and as a reagent for nucleophilic B–C and B–B bond formation when treated with C- or B-centred electrophiles.<sup>47–49</sup> Although this is consistent with the generation of an intermediate boryl species, we have also observed that reaction of 9 with imines provides the N–B bonded organomagnesium compounds rather than the product of nucleophilic C-borylation (Scheme 1).<sup>50</sup> In this case, B–B cleavage does not result in a terminal magnesium boryl species but occurs through attack of the imine nitrogen at the three-coordinate boron of the diboranate anion.<sup>50</sup> In contrast, treatment of 9 with 4-dimethylaminopyridine does provide the

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Scheme 1 Reaction of compound 9 with aldimines (R = alkyl or aryl).



Mg–B bonded species, [(BDI)Mg(Bpin)DMAP] (**10**),<sup>45,46</sup> raising questions about the generality of such an ‘outer sphere’ process. In this contribution, we extend our study to the reaction of compound **9** with triphenylphosphine oxide and address the mechanism of the resultant B–B heterolysis.

An equimolar equivalent of Ph<sub>3</sub>P=O was added at room temperature to a d<sub>8</sub>-toluene solution of compound **9**. Immediate analysis by NMR spectroscopy demonstrated the generation of a single new β-diketiminato derivative (**11**), which was most clearly characterised by the emergence of a BDI methine resonance at δ 4.91 ppm and a signal at δ 35.2 ppm in the respective <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra. Although resonances associated with the displacement of neutral *n*-BuBpin were also observed in both the <sup>1</sup>H and <sup>11</sup>B NMR spectra, it was clear from continued monitoring that compound **11** itself was subject to a further onward transformation. This was most readily apparent in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum where a second new species (**12**) was manifested from the development of a resonance at δ 36.4 ppm. The emergence of compound **12** was accompanied by the simultaneous appearance of a further <sup>31</sup>P{<sup>1</sup>H} resonance with an identical intensity at δ –5.3 ppm, which was readily assigned to triphenylphosphine.<sup>51</sup> Although monitoring of these changes to the <sup>31</sup>P{<sup>1</sup>H} NMR spectra over 24 hours confirmed the selective conversion of **11** to compound **12** and Ph<sub>3</sub>P, inspection of the corresponding <sup>1</sup>H NMR data also demonstrated that this process was accompanied by the re-formation of half of the initial compound **9**.

The origin of these observations (Scheme 2), was resolved by single crystal X-ray diffraction analysis of both compounds, **11** and **12**. Although samples of **12** were readily obtained by fractional crystallisation from a saturated toluene solution of the ultimate reaction mixture, the onward reactivity of **11** made the isolation of an analytically pure sample more problematic. Nevertheless, termination of a further reaction after only one hour provided colourless single crystals, which formed during removal of the reaction solvent under reduced pressure. The resultant solid state structures are illustrated in Fig. 1.

Compound **11** was identified as a four-coordinate terminal magnesium boryl derivative. A molecule of Ph<sub>3</sub>PO fulfils a similar role to the unidentate DMAP ligand in **10**,<sup>45,46</sup> while the three remaining magnesium-to-ligand contacts are similarly provided by the nitrogen atoms of the BDI ligand and a single terminal Bpin unit. The Mg1–B1 distance [2.327(7) Å] observed in compound **11** is effectively identical to that determined for [(BDI)Mg(Bpin)DMAP] (**10**) [2.324(2) Å] and the further DMAP-coordinated species, [(BDI)Mg(Bhex)DMAP] [2.319(3) Å], which was synthesised by analogous Mg-centred heterolysis of

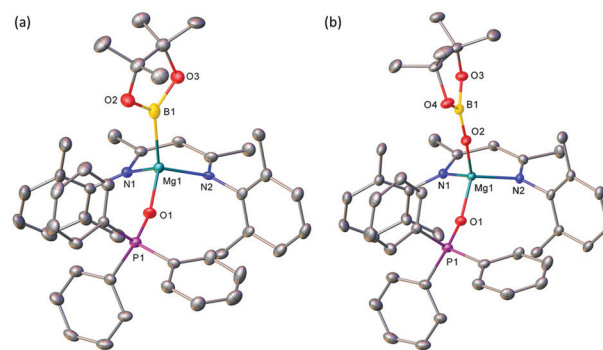
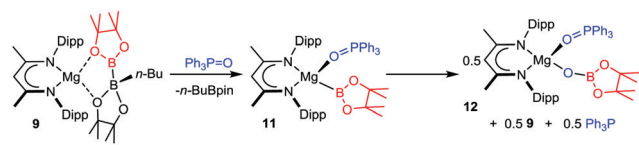


Fig. 1 ORTEP representations (30% probability ellipsoids) of the Mg1-containing molecules of (a) compound **11** and (b) compound **12**. Hydrogen atoms and iso-propyl methyl groups are removed for clarity. Selected bond lengths (Å) and angles (°): (**11**) B1–Mg1 2.327(7), B1–O2 1.430(8), B1–O3 1.458(8), Mg1–N1 2.076(4), Mg1–N2 2.076(4), Mg1–O1 1.954(4), P1–O1 1.490(3), N1–Mg1–B1 117.1(2), N1–Mg1–N2 91.48(17), N2–Mg1–B1 115.6(2), O1–Mg1–B1 114.8(2), O1–Mg1–N1 107.71(18), O1–Mg1–N2 107.64(17); (**12**) B1–O2 1.302(3), B1–O3 1.400(3), B1–O4 1.405(3), Mg1–N1 2.0529(19), Mg1–N2 2.0538(19), Mg1–O1 1.9256(17), Mg1–O2 1.8697(17), O1–P1 1.4989(16), O2–B1–O3 125.4(2), O2–B1–O4 125.2(2), O3–B1–O4 109.4(2), N1–Mg1–N2 92.81(8), O1–Mg1–N1 108.41(8), O1–Mg1–N2 111.31(8), O2–Mg1–N1 119.93(8), O2–Mg1–N2 117.11(8), O2–Mg1–O1 106.69(8).

4,4,4',6,6'-hexamethyl-2,2'-bi(1,3,2-dioxaborinane) (B<sub>2</sub>hex<sub>2</sub>).<sup>46</sup> These measurements also lie within the range seen for three reported magnesium derivatives synthesised by reactions of compound **7** with MgBr<sub>2</sub> [2.281(6)–2.377(4) Å].<sup>26</sup>

While three of the coordination sites of compound **12** are again occupied by the bidentate BDI ligand and a molecule of Ph<sub>3</sub>PO, the fourth is provided by a terminal pinacoloboryloxide unit. The structure of compound **12** [Mg1–O1 1.9256(17), Mg2–O5 1.9188(17) Å] is, thus, reminiscent of two previously described magnesium diphenylboryloxide complexes, [(BDI)Mg(OBPh<sub>2</sub>)(*n*-BuBpin)] [Mg–O 1.8492(16) Å] and [(BDI)Mg(OBPh<sub>2</sub>)DMAP] [Mg–O 1.856(3) Å].<sup>48</sup> These latter compounds were synthesised by the respective reactions of compounds **9** and **10** with diphenylborinic anhydride as the source of the {OBPh<sub>2</sub>} ligand. In contrast, the boryloxide ligand of **12** arises from formal insertion of an oxygen atom into the Mg–B bond of compound **11**. Although compound **11** clearly holds the potential for direct oxygenation through the ingress of atmospheric oxygen, this possibility may be discounted by the overall stoichiometry and notable selectivity of the reaction (Scheme 2).

Although the selective deoxygenation of small molecule oxygenates including CO<sub>2</sub> by copper and rhodium pinacoloboryl species has been described,<sup>52–54</sup> and the catalytic and stoichiometric reduction of secondary and tertiary phosphine oxides to phosphines has significant precedent,<sup>55</sup> the current transformation appears to be unique. The reaction stoichiometry displayed in Scheme 2 implies the establishment of an equilibrium between Ph<sub>3</sub>PO and the displaced molecule of *n*-BuBpin such that the generation of every molecule of compound **12** requires two molecules of phosphine oxide. On this basis, a further reaction was performed in a 2:1 stoichiometry between Ph<sub>3</sub>PO and compound **9**. Although the initial formation of the boryl derivative (**11**) was again clearly evident by <sup>31</sup>P{<sup>1</sup>H} NMR



Scheme 2 Synthesis of compounds **11** and **12** from the stoichiometric reaction of compound **9** and Ph<sub>3</sub>PO and the reductive deoxygenation of Ph<sub>3</sub>PO.



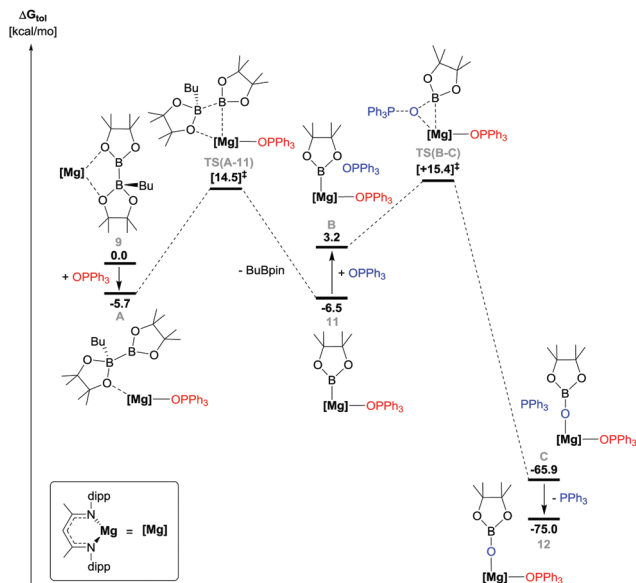


Fig. 2 DFT (BP86-D3BJ(BS2,toluene)//BP86(BS1)) calculated free energy (kcal mol<sup>-1</sup>) profile for the reaction of Ph<sub>3</sub>PO with compound **9** (in toluene), relative to **9** and the free substrates.

spectroscopy ( $\delta$  35.2 ppm), this signal was observed with a resonance of equal intensity associated with the unreacted equivalent of Ph<sub>3</sub>PO ( $\delta$  24.1 ppm). Continued monitoring of this reaction over 24 hours again evidenced the production of Ph<sub>3</sub>P, which occurred simultaneously with the complete transformation of **9** to compound **12**. The dynamic nature of the magnesium-to-Ph<sub>3</sub>PO and magnesium-to-DMAP interactions was also underscored by a further reaction performed between equimolar quantities of [(BDI)Mg(Bpin)DMAP] (**10**) and Ph<sub>3</sub>PO, which provided a mixture of compounds **10–12** alongside free DMAP and Ph<sub>3</sub>PO (Fig. S9–S11, ESI<sup>†</sup>).

The origins of the B–B and P=O bond breaking processes were investigated by DFT (BP86 optimised, see ESI<sup>†</sup> for full methodology details). Initial calculations assessed the potential for spontaneous cleavage of the B–B bond of compound **9** in the absence of any external reagent. Although the generation of a putative three-coordinate boryl species, [(BDI)MgBpin] (shown as species **E** in Fig. S12, ESI<sup>†</sup>) was found to be endergonic by 12.9 kcal mol<sup>-1</sup>, the facility of *n*-BuBpin elimination was emphasised by the location of a transition state, [TS(**9-D**)], describing a barrier toward B–B bond breaking of only 19.4 kcal mol<sup>-1</sup>. Incorporation of Ph<sub>3</sub>PO into the reaction profile led us to address three scenarios invoking the attack of the phosphine oxide either at the Mg centre or the three-coordinate boron of the [pinBB(*n*-Bu)pin]<sup>-</sup> anion. While the latter of these possibilities yielded a credible transition state, [TS(**G-H**)], the barrier associated with this ‘outer sphere’ process was 23.2 kcal mol<sup>-1</sup> and led to the direct reduction and deoxygenation of the phosphine oxide reagent circumventing the production of compound **11** (Fig. S13, ESI<sup>†</sup>). Addition of Ph<sub>3</sub>PO to species **E**, however, indicated that the formation of compound **11** is mildly exergonic ( $\Delta G = -3.6$  kcal mol<sup>-1</sup>, Fig. S12, ESI<sup>†</sup>). Although this process enables the construction of a plausible

profile for the subsequent conversion of compound **11** to **12** (*vide infra*), further assessment indicated the existence of the more kinetically-accessible pathway shown in Fig. 2.

Coordination of Ph<sub>3</sub>PO to the Mg centre of compound **9** necessitates the formation of an adduct species (**A**) and the decoordination of the trigonal pinB component of the [pinBB(*n*-Bu)pin]<sup>-</sup> anion. Although entropically-disfavoured, this process is exergonic ( $\Delta G = -5.7$  kcal mol<sup>-1</sup>) and is facilitated by the low steric demands of the P=O donor. Consistent with the spontaneous generation of **11** at room temperature, this process induces the rupture of the B–B bond *via* transition state TS(**A-11**), which is located 14.5 kcal mol<sup>-1</sup> above compound **9**.

The subsequent transformation of **11** to compound **12** is significantly exergonic ( $\Delta G = -68.5$  kcal mol<sup>-1</sup>) and involves the traversal of a barrier, [TS(**B-C**)], of only 12.2 kcal mol<sup>-1</sup>. Formal P(v) reduction is facilitated *via* the assembly of a three-centre Mg–O–B interaction at this transition state *en route* to species **C**, which ensues with simultaneous P–O bond cleavage and the generation of the requisite Mg–O and O–B bonds.<sup>56</sup>

In conclusion, treatment of compound **9** with Ph<sub>3</sub>PO provides a magnesium boryl derivative by inner sphere coordination of the P=O bond to magnesium. This deduction, therefore, contrasts with the outer sphere attack at boron implicated in reactions of **9** with more sterically encumbered imine reagents (Scheme 1).<sup>50</sup> In both cases, however, B–B bond cleavage is facile, indicating that the mode of [pinBB(*n*-Bu)pin]<sup>-</sup> heterolysis is subtly dependent on the degree of kinetic discrimination provided by the co-reagent. We are, thus, continuing to examine the implications of these observations for a wider range of substrates and element centres.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- M. Wagner, N. Hommes, H. Noth and P. V. Schleyer, *Inorg. Chem.*, 1995, **34**, 607–614.
- A. Sundermann, M. Reiher and W. W. Schoeller, *Eur. J. Inorg. Chem.*, 1998, 305–310.
- E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9758–9759.
- R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844–3850.
- R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.*, 2003, **42**, 2660–2663.
- R. J. Baker, C. Jones and J. A. Platts, *J. Am. Chem. Soc.*, 2003, **125**, 10534–10535.
- R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Organometallics*, 2004, **23**, 4811–4813.
- R. J. Baker, C. Jones and M. Kloth, *Dalton Trans.*, 2005, 2106–2110.
- S. Aldridge, R. J. Baker, N. D. Coombs, C. Jones, R. P. Rose, A. Rossin and D. J. Willock, *Dalton Trans.*, 2006, 3313–3320.



- 10 C. Jones, D. P. Mills, J. A. Platts and R. P. Rose, *Inorg. Chem.*, 2006, **45**, 3146–3148.
- 11 C. Jones, R. P. Rose and A. Stasch, *Dalton Trans.*, 2007, 2997–2999.
- 12 S. P. Green, C. Jones, K. A. Lippert, D. P. Mills and A. Stasch, *Inorg. Chem.*, 2006, **45**, 7242–7251.
- 13 P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones and D. P. Mills, *J. Am. Chem. Soc.*, 2007, **129**, 5360–5361.
- 14 C. Jones, D. P. Mills, R. P. Rose and A. Stasch, *Dalton Trans.*, 2008, 4395–4408.
- 15 C. Jones, D. P. Mills, R. P. Rose, A. Stasch and W. D. Woodul, *J. Organomet. Chem.*, 2010, **695**, 2410–2417.
- 16 S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones and W. D. Woodul, *Angew. Chem., Int. Ed.*, 2009, **48**, 1077–1080.
- 17 O. Bonello, C. Jones, A. Stasch and W. D. Woodul, *Organometallics*, 2010, **29**, 4914–4922.
- 18 J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Nature*, 2018, **557**, 92–95.
- 19 J. Hicks, A. Mansikkamaki, P. Vasko, J. M. Goicoechea and S. Aldridge, *Nat. Chem.*, 2019, **11**, 237–241.
- 20 R. J. Schwamm, M. D. Anker, M. Lein, M. P. Coles and C. M. Fitchett, *Angew. Chem., Int. Ed.*, 2018, **57**, 5885–5887.
- 21 R. J. Schwamm, M. D. Anker, M. Lein and M. P. Coles, *Angew. Chem., Int. Ed.*, 2019, **58**, 1489–1493.
- 22 Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113–115.
- 23 Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069–16079.
- 24 M. Yamashita and K. Nozaki, *J. Synth. Org. Chem., Jap.*, 2010, **68**, 359–369.
- 25 M. Yamashita and K. Nozaki, in *Synthesis and Application of Organoboron Compounds*, ed. E. Fernandez and A. Whiting, 2015, vol. 49, pp. 1–37.
- 26 M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570–9571.
- 27 Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2007, **46**, 6710–6713.
- 28 T. Terabayashi, T. Kajiura, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14162–14163.
- 29 T. Arnold, H. Braunschweig, W. C. Ewing, T. Kramer, J. Mies and J. K. Schuster, *Chem. Commun.*, 2015, **51**, 737–740.
- 30 A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500–6503.
- 31 A. V. Protchenko, D. Dange, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2014, **136**, 10902–10905.
- 32 A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjkumar, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Nat. Chem.*, 2014, **6**, 315–319.
- 33 D. Dange, A. Davey, J. A. B. Abdalla, S. Aldridge and C. Jones, *Chem. Commun.*, 2015, **51**, 7128–7131.
- 34 B. L. Wang, Y. X. Li, R. Ganguly, H. Hirao and R. Kinjo, *Nat. Commun.*, 2016, **7**, 11871.
- 35 W. Lu, H. T. Hu, Y. X. Li, R. Ganguly and R. Kinjo, *J. Am. Chem. Soc.*, 2016, **138**, 6650–6661.
- 36 H. Braunschweig, C. W. Chiu, K. Radacki and T. Kupfer, *Angew. Chem., Int. Ed.*, 2010, **49**, 2041–2044.
- 37 R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking and G. Bertrand, *Science*, 2011, **333**, 610–613.
- 38 S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Y. Mo, D. Qiu, M. S. Cheung, L. Dang, J. B. Wang, U. Radius, Z. Y. Lin, C. Kleeberg and T. B. Marder, *Chem. – Eur. J.*, 2015, **21**, 7082–7098.
- 39 M. Eck, S. Wrtemberger-Pietsch, A. Eichhorn, J. H. J. Berthel, R. Bertermann, U. S. D. Paul, H. Schneider, A. Friedrich, C. Kleeberg, U. Radius and T. B. Marder, *Dalton Trans.*, 2017, **46**, 3661–3680.
- 40 H. Gulyas, A. Bonet, C. Pubill-Ulldemolins, C. Sole, J. Cid and E. Fernandez, *Pure Appl. Chem.*, 2012, **84**, 2219–2231.
- 41 J. Cid, H. Gulyas, J. J. Carbo and E. Fernandez, *Chem. Soc. Rev.*, 2012, **41**, 3558–3570.
- 42 R. D. Dewhurst, E. C. Neeve, H. Braunschweig and T. B. Marder, *Chem. Commun.*, 2015, **51**, 9594–9607.
- 43 E. C. Neeve, S. J. Geier, I. A. I. Mkhaliid, S. A. Westcott and T. B. Marder, *Chem. Rev.*, 2016, **116**, 9091–9161.
- 44 T. Kaese, T. Trageser, H. Budy, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. Sci.*, 2018, **9**, 3881–3891.
- 45 A. F. Pécharman, A. L. Colebatch, M. S. Hill, C. L. McMullin, M. F. Mahon and C. Weetman, *Nat. Commun.*, 2017, **8**, 15022.
- 46 A. F. Pécharman, M. S. Hill and M. F. Mahon, *Dalton Trans.*, 2018, **47**, 7300–7305.
- 47 A. F. Pécharman, M. S. Hill, C. L. McMullin and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2017, **56**, 16363–16366.
- 48 A. F. Pécharman, M. S. Hill and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2018, **57**, 10688–10691.
- 49 A. F. Pécharman, M. S. Hill, C. L. McMullin and M. F. Mahon, *Organometallics*, 2018, **37**, 4457–4464.
- 50 A. F. Pécharman, M. S. Hill, G. McMullon, C. L. McMullin and M. F. Mahon, *Chem. Sci.*, 2019, DOI: 10.1039/C9SC02087J.
- 51 A. D. Hunter, T. R. Williams, B. M. Zarzyczny, H. W. Bottesch, S. A. Dolan, K. A. McDowell, D. N. Thomas and C. H. Mahler, *Organometallics*, 2016, **35**, 2701–2706.
- 52 D. S. Laitar, P. Muller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196–17197.
- 53 S. I. Kallane, T. Braun, B. Braun and S. Mebs, *Dalton Trans.*, 2014, **43**, 6786–6801.
- 54 S. I. Kallane, T. Braun, M. Telteuskoi, B. Braun, R. Herrmann and R. Laubenstein, *Chem. Commun.*, 2015, **51**, 14613–14616.
- 55 D. Herault, D. H. Nguyen, D. Nuel and G. Buono, *Chem. Soc. Rev.*, 2015, **44**, 2508–2528.
- 56 The reaction stoichiometry shown in Scheme 2 is, thus, explicable as the barrier associated with the reformation of **9** from **11** (21.0 kcal mol<sup>-1</sup>) is competitive with the onward transformation of **11** to compound **12** (21.9 kcal mol<sup>-1</sup>).

