Alkaline-earth derivatives of diphenylphosphine-borane

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Abstract

Treatment of β-diketiminato (BDI = $HC\{C(CH_3)Ndipp)\}_2$ where dipp = 2,6-*i*$Pr_2C_6H_3$) magnesium butyl [(BDI)MgBu] (**I**) and calcium hexamethyldisilazide $[(BDI)Ca\{N(SiMe_3)_2\}]$ (**II**) complexes with equimolar quantities of diphenylphosphine-borane, $Ph_2PH{\cdot}BH_3$, results in formation of the respective alkaline earth (Ae) phosphidoborane derivatives, $[(BDI)Mg(Ph_2PBH_3)]_2$ (**6a**) and $[(BDI)Ca(Ph_2PBH_3)]$ (**7a**). Although satisfactory single-crystals of **7a** could not be obtained, **6a** was crystallographically characterized and both compounds display similar NMR spectra. The dimeric Ae-hydride complexes, $[(BDI)AeH]_2$ (**IIIa**, Ae = Mg; **IIIb**, Ae = Ca), react with substoichiometric quantities of $Ph_2PH{\cdot}BH_3$ allowing the crystallization of dimeric Mg- and trimeric Ca phosphidoborane species, $[(BDI)Mg(H)(H_3BPPh_2)Mg(BDI)]$ (**8**), and $[\{(BDI)Ca\}_3(H)(H_3BPPh_2)_2]$ (**9**). In the absence of coordinating Lewis bases, compounds **6a**, **7a**, **8** and **9** display dynamic solution-state behaviour (in benzene and toluene), while addition of THF furnishes the monomeric adducts $[(BDI)Mg(H_3BPPh_2){\cdot}THF]$ (**6b**) and $[(BDI)Ca(H_3BPPh_2){\cdot}THF]$ (**7b**). Addition of $Ph_2PH{\cdot}BH_3$ to compound **6a** results in BH_3 transfer to eliminate Ph_2PH and generate the phosphinodiboronate complex $[(BDI)Mg\{(H_3B)_2PPh_2\}]_2$ (**10**) in preference to dehydrocoupling of the phosphidoborane and phosphine-borane reagents.

Introduction

The last two decades have witnessed widespread interest in the potential of amine-borane adducts as hydrogen storage media and precursors to materials such as polyaminoboranes and single layer hexagonal boron nitride.[1-5] Although many amine-boranes undergo thermal dehydrogenation, catalysis provides a higher degree of control and efficiency, enabling the

production of well-defined, processable materials.[1, 2, 6] Although the majority of catalysts for this purpose have been transition metal-based,[1, 7-18] several main group-catalyzed processes are known,[19-23] with alkaline-earth (Ae)-based systems providing notable examples.[24-26] The reactivity of well-defined heteroleptic β-diketiminato (BDI = $HC\{C(CH_3)Ndipp)\}_2$ where dipp = 2,6-*i*$Pr_2C_6H_3$) Ae-amidoborane complexes such as **1a** and **1b** has made a significant contribution to a mechanistic understanding of Ae-mediated catalytic amine-borane dehydrogenation (**Figure 1**). Complexes of this type are straightforward to synthesize by exposure of amine-borane to an appropriate Ae amide, alkyl, or hydride precursor.[24, 27-32] At elevated temperatures, related primary amidoborane derivatives may provide dehydrogenated species such as **2a**-**c** and **3**.[27, 28] For secondary amine-boranes, catalytic turnover is facilitated by the presence of further equivalents of amine-borane and is believed to involve isolable $[R_2NBH_2NR_2BH_3]^-$ containing intermediates (**Figure 1**, **4a**, **b**).[24, 32, 33] Subsequent protonolysis of such species potentially obviates the formation of high-energy Ae-hydride species *via* β- and/or δ-hydride elimination.[32]

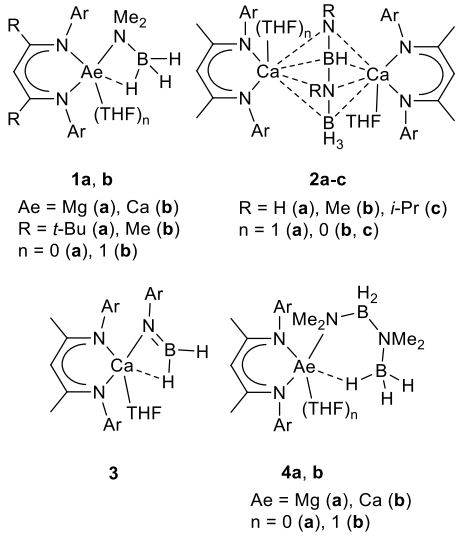


Figure 1: Representative β-diketiminato (BDI) alkaline-earth (Ae) amidoborane complexes and derivatives.[24, 27-32] Ar = 2,6-di-*iso*-propylphenyl.

In contrast, the reactivity of Ae-complexes towards phosphine-borane adducts remains unexplored and, more generally, the comparably few phosphine-borane dehydrogenation catalysts in the literature are almost entirely transition-metal based.[8, 34-43] The catalogue of known Ae-phosphidoborane complexes are limited to a series of compounds (**5a**-**c**) reported by Izod and co-workers (**Figure 2**).[44] These complexes display a variety of coordination modes, and were prepared *via* salt metathesis of anisole-substituted lithium or potassium phosphidoborane derivatives with AeI_2 (Ae = Mg, Ca, Sr).

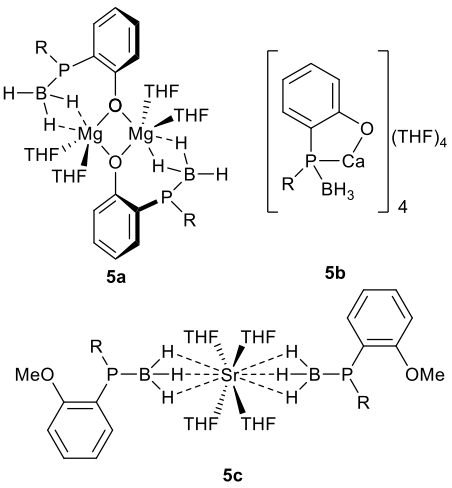


Figure 2: Mg, Ca, and Sr phosphidoboranes reported by Izod and co-workers.[44] R = $CH(SiMe_3)_2$.

In an effort to address this lacuna in Ae phosphine-borane chemistry, we undertook an investigation of the reactivity of β-diketiminato magnesium and calcium complexes towards the secondary phosphine-borane, $Ph_2PH{\cdot}BH_3$. This chemistry was undertaken to facilitate an initial assessment of the resultant phosphidoborane complexes as catalysts for the dehydrocoupling of $Ph_2PH{\cdot}BH_3$ and as part of a wider effort to develop transition metal-free routes to polyphosphinoboranes.

Synthetic procedures

Compound 6a

Preparative scale: A Schlenk flask was charged with 1.0 g **I** (2.0 mmol) and 0.4 g Ph_2PHBH_3 (2.0 mmol). The mixture was stirred and approx. 20 ml toluene was added *via* cannula, resulting in an off-white suspension. After stirring at room-temperature for 2 hours, the reaction mixture was heated to 50°C, resulting in dissolution of the precipitate and formation of a pale-yellow solution. The mixture was slowly cooled to room temperature and placed in a freezer at -30°C, resulting in the deposition of colourless crystals. Filtration and washing with fresh toluene resulted in the isolation of pure compound **6a**. Yield 0.66 g, 51%.

NMR scale: In a J. Young's NMR tube, 50 mg **I** (0.1 mmol) was dissolved in 0.6 ml d_8-toluene. 20 mg $Ph_2PH.BH_3$ (0.1 mmol) was dissolved in 0.1 ml d_8-toluene and added to the reaction mixture, providing a cloudy colourless suspension. After 24 hours, the NMR tube contained a large quantity of colourless solid and complete consumption of the starting materials was demonstrated by multinuclear NMR spectroscopy. The solid was re-dissolved by heating to 80°C, then allowed to slowly cool to room temperature to yield a crop of colourless crystals suitable for single crystal X-ray diffraction analysis. Yield 42.5 mg, 66%. A second crop of

crystals (8 mg, 12%) could be obtained by cooling the supernatant to -30°C. Compound **6a** is poorly soluble in aromatic solvents at room temperature and NMR spectra recorded at 298 K were broad and uninformative. Heating a d_8-toluene solution to 349 K within the spectrometer resulted in well-defined, sharp signals and allowed good-quality spectra to be recorded. ^{1}H NMR (400 MHz, d_8-toluene, 349 K) δ 7.12-7.03 (m, 4H, *o*-P(C_6H_5)$_3$), 7.03 – 6.93 (m, 6H, NAr), 6.93 – 6.82 (m, 6H, *m*+*p*-P(C_6H_5)$_3$), 4.95 (s, 1H, NC(CH_3)C*H*), 3.20 (hept, *J* = 6.8 Hz, 4H, (H_3C)$_2$C*H*), 1.70 (s, 6H, NC(CH_3)CH), 1.11 (m, 24H, (H_3C)$_2$CH). Boron-bound hydrogen atoms could not be detected. ^{31}P{^{1}H} NMR (162 MHz, d_8-toluene, 349 K) δ -57.09 (*br*). ^{11}B NMR (128 MHz, d_8-toluene, 349 K) δ -34.01 (qd, J_{1H} = 91.1, J_{31P} = 44.3 Hz). ^{13}C{^{1}H} NMR (101 MHz, d_8-toluene, 349 K) δ 170.89 (N*C*(CH_3)CH), 144.37 (NAr-C_{ipso}), 143.06 (NAr-C_{ortho}), 133.83 (d, J_{31P} = 12.4 Hz, *o*-P(C_6H_5)$_3$), 127.63(*m*-P(C_6H_5)$_3$), 126.27 (*p*-P(C_6H_5)$_3$), 125.71 (NAr-C_{para}), 124.49 (NAr-C_{meta}), 95.41 (NC(CH_3)*C*H), 29.00 (NC(*C*H_3)CH), 24.69 (H_3C)$_2$CH), 24.50 (H_3C)$_2$CH), 24.32 (NC(*C*H_3)CH). Analysis calculated for $C_{82}H_{108}B_2Mg_2N_4P_2$: C 76.83, H 8.49, N 4.37 %. Found: C 76.32, H 8.38, N 4.25%.

Compound 6b

In a J. Young's NMR tube, 20 mg **6a** (0.016 mmol) was suspended/dissolved in 0.6 ml d_8-toluene and 5.1 µl THF (0.063 mmol) was added. The tube was shaken until the mixture became a clear, colourless solution. After a few minutes, compound **6b** started to crystallise directly from the reaction mixture as large colourless needles. On standing overnight, the product was collected by filtration and the mother liquor placed in a vial in the glovebox freezer, yielding a second crop of crystals. Yield 16.6 mg, 73%. ^{1}H NMR (500 MHz, 298 K, d_8-toluene) δ 7.27-7.21 (m, 4H, *o*-P(C_6H_5), 7.21-7.16 (m, 2H, *p*-P(C_6H_5)), 7.16-7.11 (m, 4H, NAr), 6.97 (4H, *m*-P(C_6H_5)), 4.74 (s, 1H, NCC*H*), 3.50 (m, 4H, 2,5-THF), 3.13 (br, 4H, C*H*(CH_3)$_2$), 1.59 (s, 6H, NCCH_3), 1.27 (m, 4H, 3,4-THF), 1.17 (d, *J* = 6.8 Hz, 24H, CH(CH_3)$_2$), 0.64 (q, ^1J(^{11}B) = 78 Hz, 3H, BH_3). ^{31}P{^{1}H} NMR (202 MHz, 298 K, d_8-toluene) δ -53.3 (q, ^1J(^{11}B) = 46.8 Hz). ^{11}B NMR (160 MHz, 298 K, d_8-toluene) δ -34.77 (dq, *J* = 79.0, 47.3 Hz). ^{13}C NMR (126 MHz, 298 K, d_8-toluene) δ 169.39 (N*C*CH_3), 145.33 (d, $J(^{31}P)$ = 16.7 Hz, *i*-P(C_6H_5)), 144.76 (1-NAr), 142.77 (2,6-NAr), 133.74 (d, $J(^{31}P)$ = 16.7 Hz, *o*-P(C_6H_5)), 127.86 (*m*-P(C_6H_5)), 125.74 (d, $J(^{31}P)$ = 11.0 Hz, *p*-P(C_6H_5)), 124.64 (4-NAr), 124.15 (3,5-NAr), 94.84 (NC*C*H), 69.40 (2,5-THF), 28.29 (br, *C*HCH$_3$), 25.50 (3,4-THF), 25.08 (*C*HCH$_3$), 24.58 (CH*C*H$_3$), 24.25 (NC*C*H$_3$). Analysis calculated for $C_{45}H_{62}BMgN_2OP$: C 75.80, H 8.76, N 3.93. Found: C 75.38, H 8.59, N 4.20.

Compound 7a

In the glove box, 200 mg **II** (0.324 mmol) was added to a Schlenk flask and dissolved in 5 ml toluene with stirring. $Ph_2PH.BH_3$ (65 mg, 0.324 mmol) was dissolved in 1 ml of toluene in a

vial, then added to the Schlenk flask. The reaction was removed from the glove box and stirred at room temperature for 16 hours before volatiles were removed under vacuum. The resulting pale-yellow solid was washed with three portions of hexane, then vacuum dried to yield compound **7a** in near analytical purity. Yield 52 mg, 24%. Despite repeated attempts to crystallise compound **7a** from various solvent systems, we were unable to obtain satisfactory single crystals. Although the NMR spectra were broad and uninformative at 298 K (probably due to monomer/dimer equilibration), analysis by multinuclear NMR spectroscopy at 320 K was unambiguous. Furthermore, addition of two molar equivalents of THF to a C_6D_6 solution of **7a** lead to the quantitative formation of the THF adduct **7b**. ^{1}H NMR (400 MHz, d_8-toluene, 320.6 K) δ 7.28 (br, 4H, *o*-P(C_6H_5)$_3$), 7.08-7.02 (m, 6H, NAr), 6.95-6.85 (m, 6H, *m*+*p*-P(C_6H_5)$_3$), 5.03 (s, 1H, NC(CH_3)C*H*), 3.10 (br m, 4H, (H_3C)$_2$C*H*), 1.74 (s, 6H, NC(C*H*$_3$)CH), 0.99 (br m, 24H, (*H*$_3$C)$_2$CH). Boron-bound hydrogen atoms could not be detected. ^{13}C{^{1}H} NMR (101 MHz, d_8-toluene, 320.6 K) δ 166.57 (N*C*(CH_3)CH), 145.80 (NAr-C_{ipso}), 142.08 (NAr-C_{ortho}), 134.22 (d, $^{2}J_{13P}$ = 12.7 Hz, *o*-P(*C*$_6$H$_5$)$_3$), 128.51 (*m*-P(*C*$_6$H$_5$)$_3$), 127.46 (*p*-P(*C*$_6$H$_5$)$_3$), 125.02 (NAr-C_{para}), 124.08 (NAr-C_{meta}), 93.24 (NC(CH_3)*C*H), 28.76 (H_3C)$_2$*C*H), 25.45 (*H*$_3$*C*)$_2$CH), 24.77 (NC(*C*H$_3$)CH), 24.42 (H$_3$*C*)$_2$CH). ^{11}B NMR (128 MHz, d_8-toluene, 320.6 K) δ -30.16 (br m). ^{31}P{^{1}H} NMR (162 MHz, d_8-toluene, 320.6 K) δ -44.96 (br). Although the reluctance of compound **7a** to crystallise prevented us from obtaining the compound in sufficient purity for satisfactory elemental microanalysis, the results are nevertheless shown here for completeness. Analysis calculated for $C_{41}H_{54}BCaN_2P$: C 74.98, H 8.29, N 4.27%. Found: C 73.13, H 8.30, N 4.12%.

Compound 7b

Preparative scale: In the glove box, a Schlenk flask was charged with 200 mg **II.THF** (0.29 mmol) and 58 mg $Ph_2PH.BH_3$ (0.29 mmol). Toluene (approx. 5 ml) was added *via* cannula on the Schlenk line. The reaction was stirred at room temperature for 60 minutes, before being concentrated to two-thirds volume and placed in a freezer at -20°C, yielding colourless crystals of compound **7b**. The product was isolated by filtration, washed with hexane, dried under vacuum. Colourless block-like crystals suitable for X-ray diffraction analysis were obtained by cooling a saturated toluene solution to -30°C. Yield 66 mg, 31%.

NMR scale: A d_8-toluene solution (0.3 ml) of **IIIb.THF$_2$** (20 mg, 0.019 mmol) was added to a J. Young's NMR tube containing a d_8-toluene solution (0.3 ml) of $Ph_2PH.BH_3$ (7.5 mg, 0.038 mmol). The reaction mixture bubbled immediately and was concentrated to approx. 0.2 ml under vacuum after 24 hours at room temperature. Colourless crystals were obtained by cooling the concentrated reaction mixture to -30°C. Yield 5.2 mg, 38%. ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.28 – 7.22 (m, 4H, *o*-P(C_6H_5)$_2$), 7.22 – 7.17 (m, 6H, 3,4,5-NAr), 7.06 – 6.93

(m, 6H, *m*+*p*-P(C_6H_5)$_2$), 4.83 (s, 1H, NC(CH_3)C*H*), 3.68 (t, *J* = 6.2 Hz, 4H, 2,5-THF), 3.23 (hept, *J* = 6.8 Hz, 4H, C*H*(CH_3)), 1.69 (s, 6H, NC(C*H*$_3$)CH), 1.4-1.0 (br, B*H*$_3$), 1.22 (t, *J* = 7.0 Hz, 28H, CH(C*H*$_3$) + 3,4-THF). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) δ 166.35 (N*C*(CH_3)CH), 145.63 (*1*-NAr), 142.03 (2,6-NAr), 133.96 (*o*-P(C_6H_5)$_2$), 133.85 (*o*-P(C_6H_5)$_2$), 128.17 (*m*-P(C_6H_5)$_2$), 127.97 (*p*-P(C_6H_5)$_2$), 126.91 (*i*-P(C_6H_5)$_2$), 125.08 (4-NAr), 124.21 (3,5-NAr), 94.04 (NC(CH_3)*C*H), 69.85 (2,5-THF), 28.59 (*C*H(CH_3)), 25.28 (CH(*C*H_3), 25.22 (3,4-THF), 24.66 (CH(*C*H_3), 24.49 (NC(*C*H_3)CH). Boron-bound hydrogen atoms could not be detected. ^{11}B NMR (160 MHz, C_6D_6, 298 K) δ -27.10. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K) δ -38.06 (br). Analysis calculated for $C_{45}H_{62}BCaN_2OP$: C 74.16, H 8.57, N 3.84%. Found: C 73.62, H 8.47, N 3.97%.

Compound 8

In a J. Young's NMR tube, 20 mg **IIIa** (0.023 mmol) was dissolved in 0.5 ml d_8-toluene. A solution containing 4.6 mg $PH_2PH.BH_3$ (0.023 mmol) in 0.1 ml d_8-toluene was added. The tube was shaken, with immediate and vigorous bubbling. The reaction was left to stand at room temperature for 24 hours, before being decanted into a vial and placed in a freezer at -30°C, yielding a crop of colourless crystals suitable for single-crystal X-ray diffraction analysis. Yield: 16 mg, 64%. Although crystals of **8** were isolated in an analytically pure form, when re-dissolved in d_8-toluene, the ^1H NMR spectrum was complex and accompanied by the appearance of an additional, unidentified minor species containing resonances corresponding to BDI and Ph_2P environments. Addition of a small quantity of d_8-THF, however, produced a well-defined spectrum containing the THF-adducts **IIIa.THF$_2$**[8] and [LMg(H_3BPPh_2).THF] (**6b**), allowing the constituent parts of compound **8** to be unambiguously identified. ^1H NMR (500 MHz, d_8-toluene, 298 K) δ 7.95 (t, *J* = 7.9 Hz, 1H, *o*-(C_6H_5)P)*, 7.30-6.80 (m, *N*Ar), 6.89 (m, 4H, *o*-(C_6H_5)P), 6.73 (t, *J* = 8.8 Hz, 2H, *p*-(C_6H_5)P), 6.70-6.65 (m, 1H, *m*-(C_6H_5)P)*, 6.65-6.58 (m, 4H, *m*-(C_6H_5)P), 6.56-6.44 (br, 2H), 4.83 (s, 2H, NCC*H*), 4.78 (s, 0H, NCC*H*)*, 3.46 (br, 4H (H_3C)$_2$C*H*), 3.40 (s, 1H, Mg*H*), 3.34-3.17 (m, br, 4H, (H_3C)$_2$C*H*), 3.04 (hept, *J* = 7.0 Hz, 1H, (H_3C)$_2$C*H*)*, 2.67 (br, 2H, (H_3C)$_2$C*H*), 1.60-1.50 (m, br, 18H), 1.50-1.41 (m, br, 15H (NC(C*H*$_3$)CH + (H_3C)$_2$CH), 1.38 (br, 12H, (H_3C)$_2$CH), 1.28-1.10 (m, br, 23H, (H_3C)$_2$CH), 1.09 (d, *J* = 6.9 Hz, 6H, (H_3C)$_2$CH)*, 1.01 (br, 9H, (H_3C)$_2$CH), 0.85 (d, *J* = 6.7 Hz, 3H)*, 0.49 (br, m, 5H), -0.35 (br, 1H), -0.71 (br, 2H). Boron-bound hydrides could not be unambiguously detected. $^{13}C\{^1H\}$ NMR (126 MHz, d_8-toluene, 298 K) δ 169.14 (N*C*(CH_3)CH), 148.04 (1-*N*Ar)*, 146.92 (1-*N*Ar), 143.74 (2,6-*N*Ar), 142.07 (2,6-*N*Ar)*, 138.97 (*i*-(C_6H_5)P), 135.34 (d, *J*(^{31}P-^{13}C) = 11.1 Hz, *o*-(C_6H_5)P), 133.96 (*o*-(C_6H_5)P)*, 132.75 (d, *J*(^{31}P-^{13}C) = 9.9 Hz, *p*-(C_6H_5)P), 127.52 (3,5-*N*Ar), 127.46 (3,5-*N*Ar), 127.20 (d, *J*(^{31}P-^{13}C) = 8.1 Hz, *m*-(C_6H_5)P), 125.85 (*m*-(C_6H_5)P)*, 123.98 (4-*N*Ar), 123.51 (4-*N*Ar), 95.28 (NC(CH_3)*C*H), 28.26 ((H_3C)$_2$CH), 24.83 ((H_3C)$_2$CH), 24.67 ((H_3C)$_2$CH), 24.51 ((H_3C)$_2$CH), 24.07 (NC(*C*H_3)CH). $^{31}P\{^1H\}$ NMR (202 MHz, d_8-toluene, 298 K) δ -42.8*, -46.80. ^{11}B NMR (160 MHz, d_8-toluene, 298 K) δ -31.21. * = unidentified minor

product formed upon dissolution of crystals. Analysis calculated for $C_{70}H_{96}BMg_2N_4P$: C 77.56, H 8.93, N 5.17 %. Found: C 77.50, H 8.80, N 4.79 %.

Compound 9

A solution of **IIIb** (20 mg, 0.0218 mmol) in 0.3 ml C_6D_6 was added to a J. Young's NMR tube containing 4.3 mg $Ph_2PH.BH_3$ (0.0218 mmol) in 0.2 ml C_6D_6. On mixing, the reaction mixture bubbled. After 30 minutes at room temperature, solvent was removed under vacuum and the resulting solid dissolved in toluene. Cooling the toluene solution to -30 °C yielded colourless crystalline blocks suitable for single-crystal X-ray diffraction analysis. Yield 5.0 mg, 19%. Although crystals of **9** were isolated in an analytically pure form, when re-dissolved in d_8-toluene, the ^{1}H NMR spectrum was complex and appeared to be composed of more than one species, accompanied by the appearance of an additional minor species. Recording spectra at multiple temperatures between 210 and 348 K revealed a dynamic and temperature-dependant system, but unambiguous assignment of solution-state species was precluded. Addition of d_8-THF to the same d_8-toluene solution provided a well-defined NMR spectrum containing two BDI-containing species, which were identified as **7b** and **IIIb.THF$_2$**,[7] as well as minor quantities of the homoleptic complex $[(BDI)_2Ca]$[9] resulting from ligand redistribution during variable-temperature NMR investigations**.** ^{1}H NMR (500 MHz, d_8-toluene, 298 K) δ 7.70 (t, *J* = 7.9 Hz, 4H, *o*-(C_6H_5)P), 7.50-7.11 (br, 8H, *o*-(C_6H_5)P), 7.09-7.03 (m, 13H, *p*-(C_6H_5)P + NAr), 7.01-6.98 (m, 12H, NAr + (C_6H_5)P), 6.97-6.85 (m, 10H, *m*-(C_6H_5)P), 5.04 (s, br, 1H, (NCC*H*)), 4.86 (s, 2H, (NCC*H*)), 4.52 (s, 0.5H, (Ca*H*)), 4.50 (s, 0.5H, (Ca*H*)), 3.50-3.30 (m, br, 9H, (C*H*(CH_3)$_2$)) 2.97 (hept, *J* = 6.4 Hz, 9H, (C*H*(CH_3)$_2$)), 1.74 (s, 11H, (NCC*H*$_3$)), 1.65 (s, 13H, (NCC*H*$_3$)), 1.22-1.16 (m, 14H, (CH(C*H*$_3$)$_2$)), 1.14 (d, *J* = 6.8 Hz, 9H, (CH(C*H*$_3$)$_2$)), 1.14 (d, *J* = 6.8 Hz, 28H, (CH(C*H*$_3$)$_2$)), 0.99 (d, *J* = 6.8 Hz, 24H, (CH(C*H*$_3$)$_2$)). Hydrogen atoms attached to boron could not be detected by ^{1}H NMR spectroscopy. ^{13}C{^{1}H} NMR (126 MHz, d_8-toluene, 298 K) δ 166.41 (N*C*(CH_3)CH), 166.08 (N*C*(CH_3)CH), 161.39 (N*C*(CH_3)CH), 145.08 (*i*-NAr), 142.69 (*o*-NAr), 141.74 (*o*-NAr), 139.05 (d, *J* = 10.2 Hz, *i*-(*C*$_6$H$_5$)P), 137.76 (toluene), 136.29 (*o*-NAr), 134.19 (*o*-(*C*$_6$H$_5$)P), 134.07 (*o*-(*C*$_6$H$_5$)P), 133.98 (*o*-(*C*$_6$H$_5$)P), 128.45 (*m*-NAr), 128.22 (*p*-(*C*$_6$H$_5$)P), 126.97 (*m*-(*C*$_6$H$_5$)P), 124.07 (*p*-NAr), 124.01 (*m*-(*C*$_6$H$_5$)P), 123.48 (4-*N*Ar), 123.26 (4-*N*Ar), 91.99 (NC*C*H), 28.69 (*C*H(CH_3)$_2$), 28.63 (*C*H(CH_3)$_2$), 28.57 (*C*H(CH_3)$_2$), 28.36 (*C*H(CH_3)$_2$), 25.39 (CH(*C*H$_3$)$_2$), 24.80 (CH(*C*H$_3$)$_2$), 24.72 (CH(*C*H$_3$)$_2$), 24.47 (CH(*C*H$_3$)$_2$), 24.15 (NC*C*H$_3$), 23.92 (NC*C*H$_3$), 23.70 (CH(*C*H$_3$)$_2$), 23.35 (CH(*C*H$_3$)$_2$), 23.08 (CH(*C*H$_3$)$_2$).^{31}P{^{1}H} NMR (202 MHz, d_8-toluene, 298 K) δ -45.50. ^{11}B NMR (160 MHz, d_8-toluene, 298 K) δ -30.54. Analysis calculated for $C_{111}H_{150}B_2Ca_3N_6P_2$: C 75.23, H 8.53, N 4.74%. Found: C 75.39, H 8.51, N 4.63%.

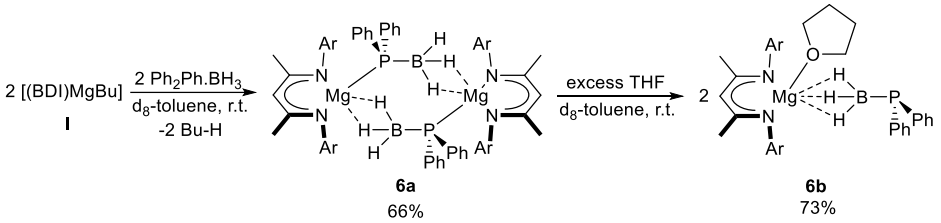
Compound 10

A 0.3 ml C_6D_6 solution containing 8 mg $Ph_2PH.BH_3$ (0.04 mmol) was added to a J. Young's NMR tube containing 20 mg **I** (0.04 mmol). A colourless solid rapidly precipitated from the reaction mixture. After 3 hours, a further 8 mg Ph_2PHBH_3 (0.04 mmol) was added as a solution in 0.1 ml C_6D_6 and the reaction mixture was heated to 60°C for 16 h, resulting in a colourless solution. The solution was concentrated and a colourless solid was deposited. The mother liquor was decanted and the solid washed twice with hexane then vacuum dried to obtain **10**. Yield 20 mg, 76%. Single crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated toluene solution from 80°C to room temperature. ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 7.29-7.21 (m, 4H, *o*-$(C_6H_5)_2$P), 7.11 (s, 6H, NAr-*H*), 6.87 (m, 6H, *m*+*p*-C_6H_5), 4.96 (s, 1H, NC(CH_3)C*H*), 3.38 (hept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.74 (s, 6H, NC(C*H*$_3$)CH), 1.33 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.16 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$). The hydrogen atoms attached to boron could not be detected by ^{1}H NMR spectroscopy. ^{31}P{^{1}H} NMR (122 MHz, C_6D_6, 298 K) δ -24.83 (br). ^{11}B NMR (96 MHz, C_6D_6, 298 K) δ -34.28 (br). ^{13}C{^{1}H} NMR (76 MHz, C_6D_6, 298 K) δ 169.79 (N*C*(CH_3)CH), 144.10 (NAr-C_{ipso}), 143.14 (NAr-C_{ortho}), 132.83 (d, $^2J_{31P}$ = 9.0 Hz, *o*-$(C_6H_5)_2$P), 130.47 (d, $^1J_{31P}$ = 54.0 Hz, *i*-$(C_6H_5)_2$P), 129.86 (d, $^4J_{31P}$ = 2.5 Hz, *p*-$(C_6H_5)_2$P), 128.60 (d, $^3J_{31P}$ = 10.1 Hz, *m*-$(C_6H_5)_2$P), 125.91 (NAr-C_{para}), 124.35 (NAr-C_{meta}), 95.19 (NC(CH_3)*C*H), 28.69 (*C*H$(CH_3)_2$), 25.25 (NC(*C*H$_3$)CH), 24.57 (CH(*C*H$_3)_2$), 24.54 (CH(*C*H$_3)_2$). Elemental analysis calculated for $C_{41}H_{57}B_2MgN_2P$: C 75.20, H 8.77, N 4.28%. Found: C 74.87, H 8.60, N 4.12%.

Results and discussion

An equimolar reaction between the alkyl magnesium complex [(BDI)MgBu] (**I**) and $Ph_2PH{\cdot}BH_3$ in d_8-toluene resulted in the formation of a cloudy colorless suspension (Scheme 1). Although analysis of the reaction mixture by ^{1}H NMR spectroscopy evidenced complete conversion of the characteristic upfield α-CH_2 butyl resonance of **I** to butane within minutes, the spectrum was largely uninformative. Broad resonances centered at δ –34 and –60 ppm in the respective ^{11}B and ^{31}P NMR spectra were indicative of the formation of new species. The initially formed precipitate redissolved on heating to 80 °C and single crystals were obtained by slow cooling of the solution to room temperature. X-ray diffraction analysis provided structural confirmation of the dimeric β-diketiminato magnesium phosphidoborane complex, **6a**. Although the broad room temperature NMR spectra most likely originate from the establishment of a monomer-dimer equilibrium, detailed investigations of any fluxionality were precluded by poor solubility at low temperatures. Consistent with this hypothesis, however, warming a d_8-toluene solution of **6a** to 349 K provided sharp and well-defined spectra. Under these conditions, the ^{1}H NMR

spectrum presented a single BDI environment with a γ-C*H* resonance located at δ 4.95 ppm. A single resonance was observed in the ^{11}B NMR spectrum, consisting of a quartet of doublets ($^{1}J_{1H}$ = 91.1 Hz, $^{2}J_{31P}$ = 44.3 Hz) at δ –34.0 ppm, while the ^{31}P{^{1}H} NMR spectrum comprised one broad resonance centered at δ –57.1 ppm.



Scheme 1: Synthesis of compounds **6a** and **6b**. Yields shown refer to isolated products of analytical purity. Ar = 2,6-di-*iso*propylphenyl.

Compound **6a** crystallizes in the *P*2$_1$/*n* space group, with four disordered molecules of toluene and one molecule of **6a** per asymmetric unit. A satisfactory convergence was obtained after treatment with a solvent mask and the complex consists of two {(BDI)Mg} units, each bound to a diphenylphosphidoborate anion *via* P1-Mg1/P2-Mg2 bonds. Crystallographically characterized examples of magnesium-phosphorus bonds are relatively rare, especially when the phosphorus atom is a constituent of a non-chelating ligand. The Mg-P bond lengths of **6a** (2.7001(10) Å, 2.6931(10) Å) are significantly longer than that of the related magnesium phosphide complex [(BDI)Mg(PPh$_2$)·THF] (Mg-P = 2.531 Å).[45] All other reported terminal magnesium-phosphide complexes also display relatively short Mg-P distances and involve the primary phosphide anion [HPPh]$^-$ (Mg-P = 2.550-2.593 Å)[46, 47] or the bulky secondary phosphide [P(SiMe$_3$)$_2$]$^-$ (Mg-P = 2.450-2.502 Å).[48-50] This effect can be rationalized by the presence of a BH$_3$ group, which denudes the Lewis basicity of the already soft phosphorus donor towards magnesium. Although the structure is non-centrosymmetric, the dimer is propagated through two agostic-type B-H-Mg interactions per boron. The magnesium centers project from the mean planes defined by the N-C-C-C-N atoms of the BDI ligands by 0.910(3) and 0.905(3) Å for Mg1 and Mg2, respectively, whilst the phosphorus-bound phenyl substituents are constrained by the flanking dipp substituents, distorting the tetrahedral geometry of phosphorus (C30-P1-Mg1 = 125.55(9) Å *cf.* C30-P1-B1 = 103.88(14) Å). The P-B bonds lengths (*ca.* 1.94 Å) are typical of diphenylphosphidoborate anions (1.89-1.98 Å). Although B-H-M agostic-type interactions are commonly found in phosphidoborane complexes,[16, 38, 51, 52] they are often absent from those derived from later transition metals.[53-58] With the exception of the potassium species, [(18-crown-6)K][Ph$_2$PBH$_3$],[59] and the tin complex, [Me$_3$Sn(Ph$_3$PBH$_3$)],[60] crystallographically characterized examples of diphenylphosphidoborate complexes are exclusively transition-metal based. Although directly analogous dimeric complexes of this type are absent from the literature, and most crystallographically

characterized examples of β-diketiminato magnesium and calcium amidoborane complexes also display monomeric structures in the solid state, compound **6a** is structurally reminiscent of the dimeric amidoborane complexes, $[(BDI)Ae(i\text{PrNHBH}_3)]_2$ (Ae = Mg, Ca)[31, 61] and $[(BDI)Mg(H_2NBH_2)]_2$.[62]

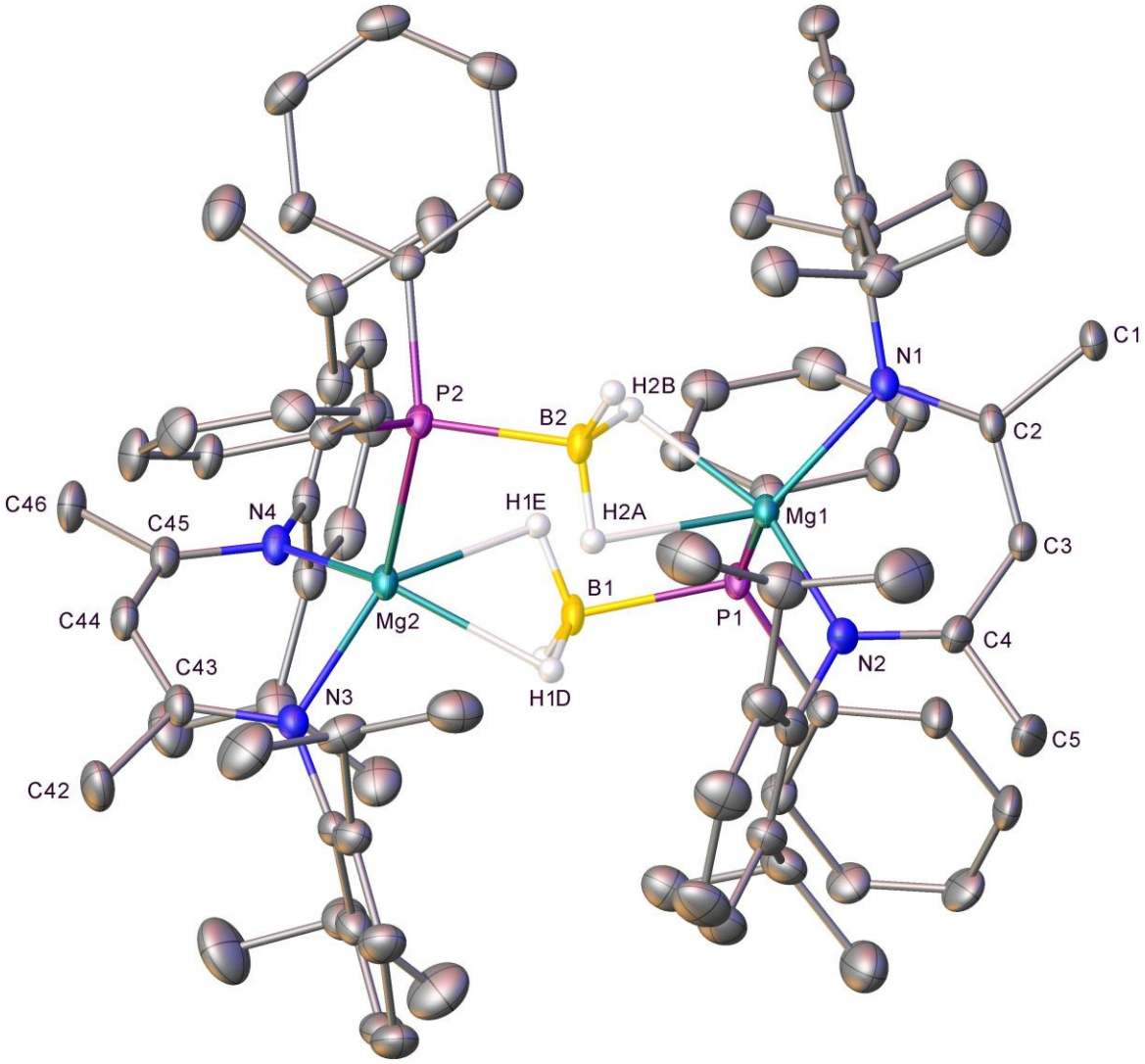


Figure 3: X-ray crystal structure of compound **6a**. Disordered solvent molecules and hydrogen atoms, except for those bound to boron, are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): P1-Mg1 2.7001(10), P1-C30 1.841(3), P1-C36 1.833(3), P1-B1 1.944(3), P2-Mg2 2.6931(10), P2-C71 1.848(3), P2-C77 1.836(3), P2-B2 1.939(3), Mg1-N1 2.046(2), Mg1-N2 2.056(3), Mg2-N3 2.057(2), Mg2-N4 2.047(2), C30-P1-Mg1 125.55(9), C30-P1-B1 103.88(14), C36-P1-Mg1 114.78(10), C36-P1-C30 97.62(12), C36-P1-B1 110.15(13), B1-P1-Mg1 104.10(10), C71-P2-Mg2 124.79(9), C71-P2-B2 103.86(13), C77-P2-Mg2 115.57(9), C77-P2-C71 98.33(12), C77-P2-B2 109.74(13), B2-P2-Mg2 103.70(9), N1-Mg1-P1 117.89(7), N1-Mg1-N2 96.38(10), N2-Mg1-P1 112.39(8), N3-Mg2-P2 112.10(7), N4-Mg2-P2 119.06(7), N4-Mg2-N3 96.12(10).

Addition of tetrahydrofuran (THF) to a d_8-toluene suspension/solution of compound **6a** provided a colorless solution (Scheme 1), from which deposited single crystals of the monomeric THF adduct **6b**. The solid-state structure of **6b** was deduced by X-ray diffraction analysis to comprise a *pseudo* four-coordinate magnesium center chelated by a BDI ligand, one molecule of coordinated THF and one diphenylphosphidoborate anion. The latter anion is bound to magnesium through three bridging B-H-Mg interactions (**Figure 4**) such that the non-bonded apex of the pyramidal phosphorus atom is oriented away from the N1-bound dipp substituent, resulting in a non-linear Mg-B-P geometry (Mg1-B1-P1 = 164.69(10) Å, N1-Mg1-B1 = 125.85(7) Å, N2-Mg1-B1 = 117.70(6) Å). The P-B bond length is similar to that of compound **6a**, whilst the Mg-N and Mg-O bond lengths are unremarkable. The ^{1}H NMR spectrum of **6b** is sharp and well-defined at 298 K, with the γ-C*H* proton resonating at δ 4.74 ppm. The THF-bound protons resonate at δ 3.14 and 1.27 ppm, suggesting that the adduct remains intact in solution (*cf.* δ 3.54 and 1.43 ppm for free THF in d_8-toluene).[63] The ^{11}B and ^{31}P{^{1}H} NMR spectra of compound **6b** are closely comparable to those of **6a**.

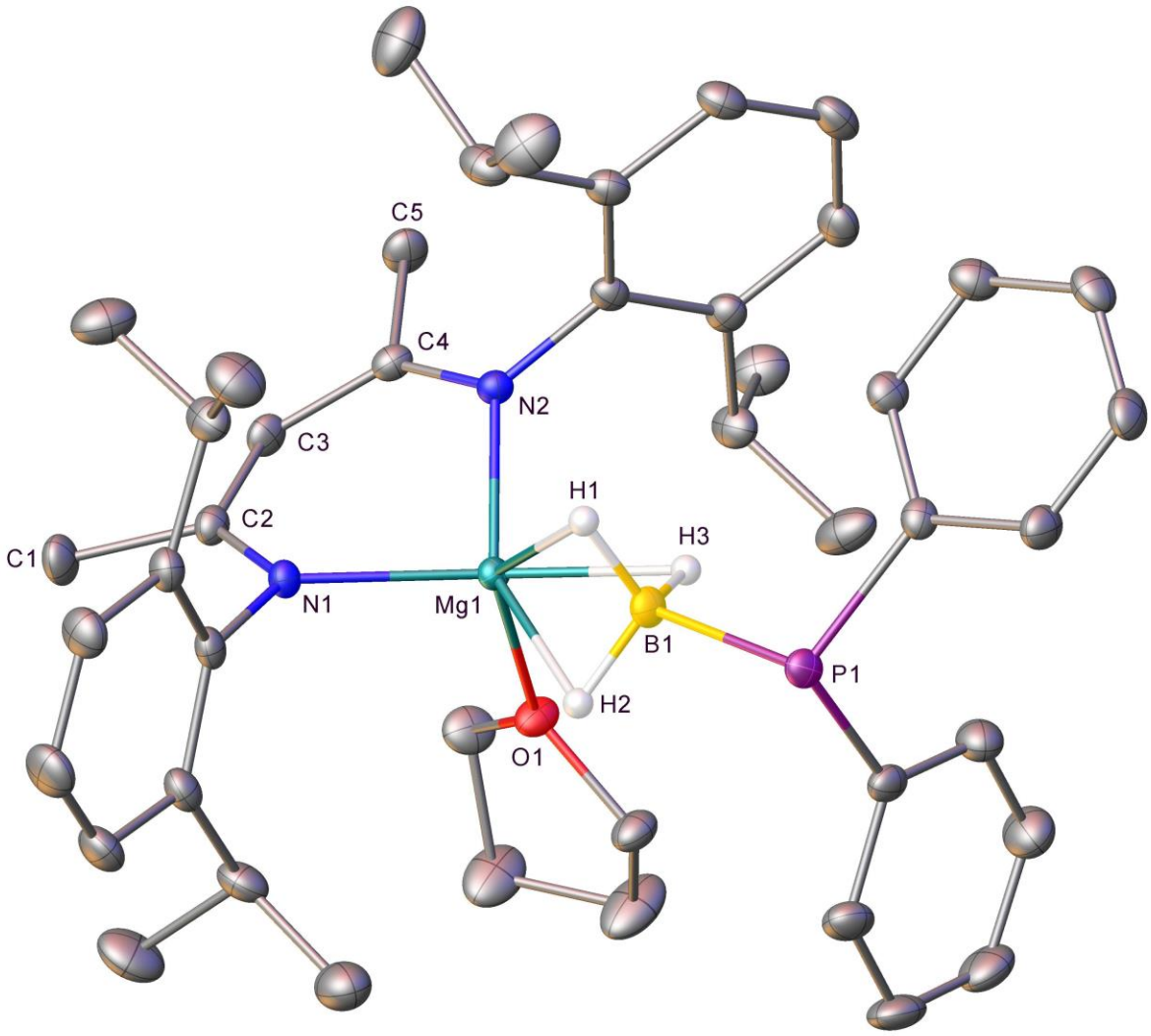
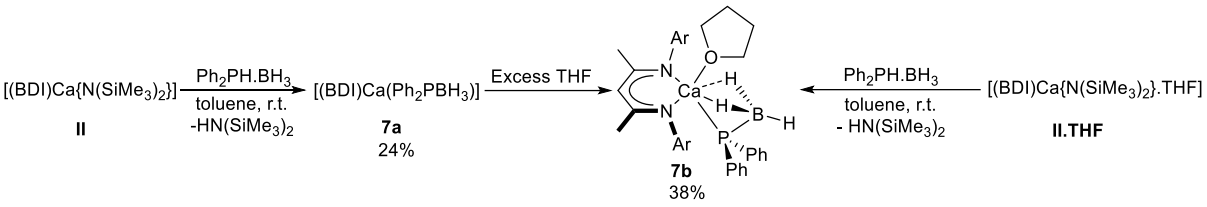


Figure 4: X-ray crystal structure of compound **6b**. Thermal ellipsoids are shown at the 30% probability level, with solvent plus hydrogen atoms omitted for clarity, except those bound to boron. Only the major component of the disordered THF ligand is shown. Selected bond lengths (Å) and angles (°): P1-C34 1.8433(18), P1-C40 1.8370(18), P1-B1 1.9466(18), Mg1-O1 2.0244(12), Mg1-N1 2.0394(14), Mg1-N2 2.0409(14), C34-P1-B1 99.21(8), C40-P1-C34 102.24(8), C40-P1-B1 103.58*8), O1-Mg1-N1 104.85(6), O1-Mg1-N2 106.27(5), N1-Mg1-N2 94.35(6).

In contrast to the reaction with compound **I**, analogous treatment of [(BDI)Ca{N(SiMe$_3$)$_2$}] (**II**) with an equimolar quantity of $Ph_2PH{\cdot}BH_3$ in toluene (Scheme 2) provided a clear and homogeneous solution. While single crystals of compound **7a** suitable for X-ray diffraction analysis could not be obtained, NMR spectra recorded in d_8-toluene after removal of the reaction solvent were consistent with its formulation as a β-diketiminato calcium phosphidoborane **7a**. While **7a** is most likely dimeric by analogy to the structure adopted by compound **6a**, its ^{1}H NMR spectrum in d_8-toluene was broad and uninformative at room temperature. Warming of the solution to 320 K, however, provided well-defined resonances indicative of a single BDI environment with the γ-C*H* proton resonating at δ 5.03 ppm. The ^{11}B and ^{31}P{^{1}H} spectra of **7a** were broad at all temperatures but comprised resonances that

experienced downfield shifts, at δ –30.2 and –45.0 ppm, respectively, relative to the comparable data provided by its magnesium congener **6a**.



Scheme 2: Synthesis of compounds **7a** and **7b**. Yields shown refer to isolated products of analytical purity, Ar = 2,6-di-*iso*propylphenyl.

The proposed identity of compound **7a** was further substantiated by addition of THF to a C_6D_6 solution, which resulted in formation of the monomeric THF-adduct, **7b**. Compound **7b** could also be prepared directly from the THF-solvated calcium amide [(BDI)Ca{N(SiMe$_3$)$_2$}·THF] (**II.THF**), and was isolated as single crystals suitable for X-ray diffraction analysis from a saturated toluene solution at −30 °C. Compound **7b** (**Figure 5**) crystallizes in the triclinic space group *P-1*, with the calcium center adopting a heavily distorted *pseudo*-trigonal bipyramidal geometry, wherein N1, N2, and B1 provide the equatorial plane about Ca1 (O1-Ca1-X = 91.70(4)° – 100.03(3)° where X = N or B) and P1 and a molecule of THF reside in significantly perturbed axial positions (O1-Ca1-P1 130.28(2)º). In contrast to the magnesium analogue **6b**, the larger calcium cation maintains a close contact with the phosphorus center such that, despite the unusual geometry at phosphorus (Ca1-P1-B1 = 65.54(4) Å), the Ca-P distance (2.8962(4) Å) is similar to those of Izod's calcium phosphidoborane **5b** (2.878 Å) and borane-free calcium diphenylphosphinate complexes (2.872-3.038 Å).[64-68] Whereas the P1-B1 bond length (1.9689(15) Å) is slightly elongated in comparison to those of compounds **6a** and **6b**, the C-P-B and C-P-C angles are close to the ideal tetrahedral angle of 109.5°, suggesting that the negative charge of the phosphidoborane anion resides in a largely phosphorus-centered sp^3-like orbital.

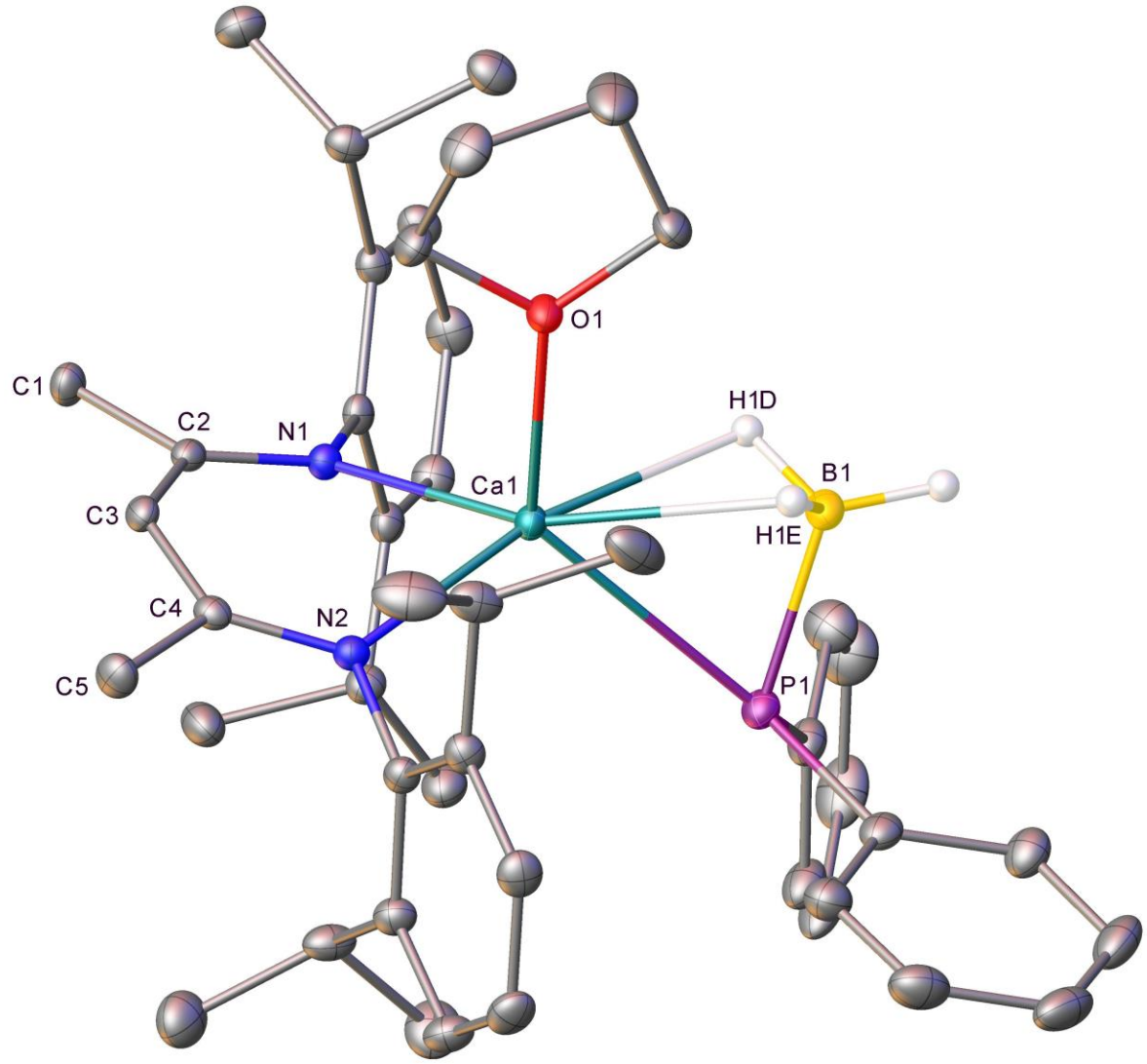
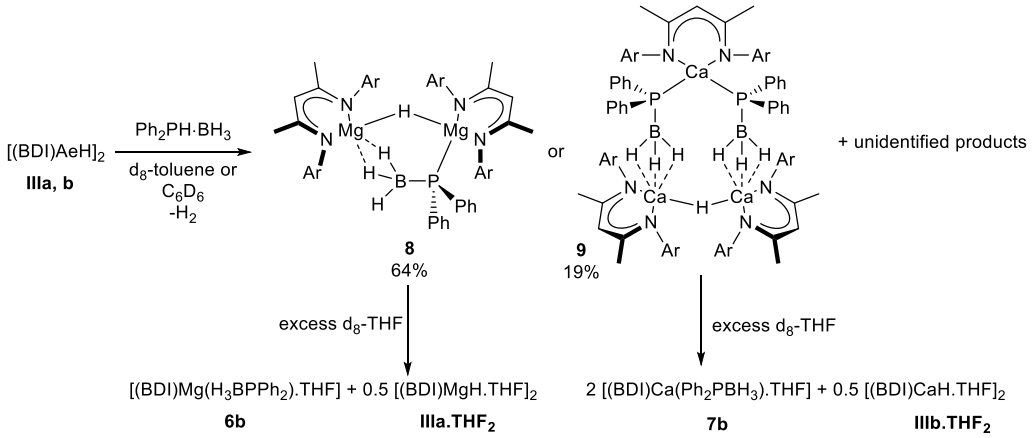


Figure 5: X-ray crystal structure of compound **7b**. Thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity, except for those bound to boron. Only the major component of the disordered THF ligand is shown. Selected bond lengths (Å) and angles (°): Ca1-P1 2.8962(4), Ca1-O1 2.3238(9), Ca1-N1 2.3432(10), Ca1-N2 2.3361(10), Ca1-B1 2.7463(15), P1-C34 1.8269(14), P1-C40 1.8235(14), P1-B1 1.9689(15), O1-Ca1-P1 130.28(2), O1-Ca1-N1 99.30(3), O1-Ca1-N2 100.03(3), O1-Ca1-B1 91.70(4), N1-Ca1-P1 121.86(3), N1-Ca1-B1 131.63(4), N2-Ca1-P1 112.58(3), N2-Ca1-N1 80.10(3), N2-Ca1-B1 143.99(4), B1-Ca1-P1 40.74(3), C34-P1-Ca1 127.88(4), C34-P1-B1 105.31(6), C40-P1-Ca1 127.29(5), C40-P1-C34 104.66(6), C40-P1-B1 108.07(7), B1-P1-Ca1 65.54(4), P1-B1-Ca1 73.72(5).

Although compounds **6a**, **7a,** and **7b** could also be prepared from 2:1 reactions of $Ph_2PH{\cdot}BH_3$ with the dimeric BDI-Ae hydride complexes, $[(BDI)AeH{\cdot}(THF)_n]_2$ (Ae = Mg (**IIIa**), n = 0; Ae = Ca, n = 0 (**IIIb**) or 1 (**IIIb.THF$_2$**)), equimolar reactions of **IIIa** and **IIIb** with the phosphine borane provided solutions displaying complex but sharp ^{1}H NMR spectra. Recrystallization of the crude products from toluene at −30 °C (Mg) or slow evaporation at room temperature (Ca) resulted in single crystals of the respective β-diketiminato magnesium and calcium-hydrido-

phosphidoborate complexes, **8** and **9**, whose structures were resolved by X-ray diffraction analysis (Scheme 3, Figures 6 and 7).



Scheme 3: Reactions of BDI-Ae hydride complexes with $Ph_2PH{\cdot}BH_3$. Yields shown refer to isolated products of analytical purity. Ar = 2,6-di-*iso*propylphenyl.

The molecular structure of compound **8** consists of two {(BDI)Mg} units linked by a μ_2-bridging hydride ligand and a diphenylphosphidoborate anion. The latter substituent interacts with the magnesium centers in a similar manner to **6a** through a Mg1-P1 bond and two agostic-type B-H-Mg2 interactions. The Mg1-P1 (2.7241(6) Å) and P1-B1 (1.9610(19) Å) bonds are slightly longer than those of compound **6a** (Mg-P = 2.7001(10), 2.6931(10) Å, P-B = 1.944(3), 1.939(3) Å), albeit the Mg-N bond lengths are similar in both compounds. Re-dissolving crystals of compound **8** in d_8-toluene produced a complex ^{1}H NMR spectrum, which contained an unidentified minor species with resonances assigned to β-diketiminate and Ph_2P environments. The $^{31}P\{^1H\}$ NMR spectrum comprised a major resonance at δ −46.5 ppm and a minor species at δ −42.8 ppm which, by ^{31}P-^{1}H HMBC NMR spectroscopy, was found to correspond to the minor species in the ^{1}H NMR spectrum. Although the origin of these observations could not be unambiguously resolved, it seems likely that compound **8** exists in equilibrium with other species in solution, presumably *via* monomerization. In support of this hypothesis, addition of a few drops of d_8-THF to the same d_8-toluene solution resulted in a well-defined ^{1}H NMR spectrum comprising two BDI-containing species, which were identified as compound **6b** and $[(BDI)MgH{\cdot}THF]_2$ (**IIIa.THF$_2$**).[30]

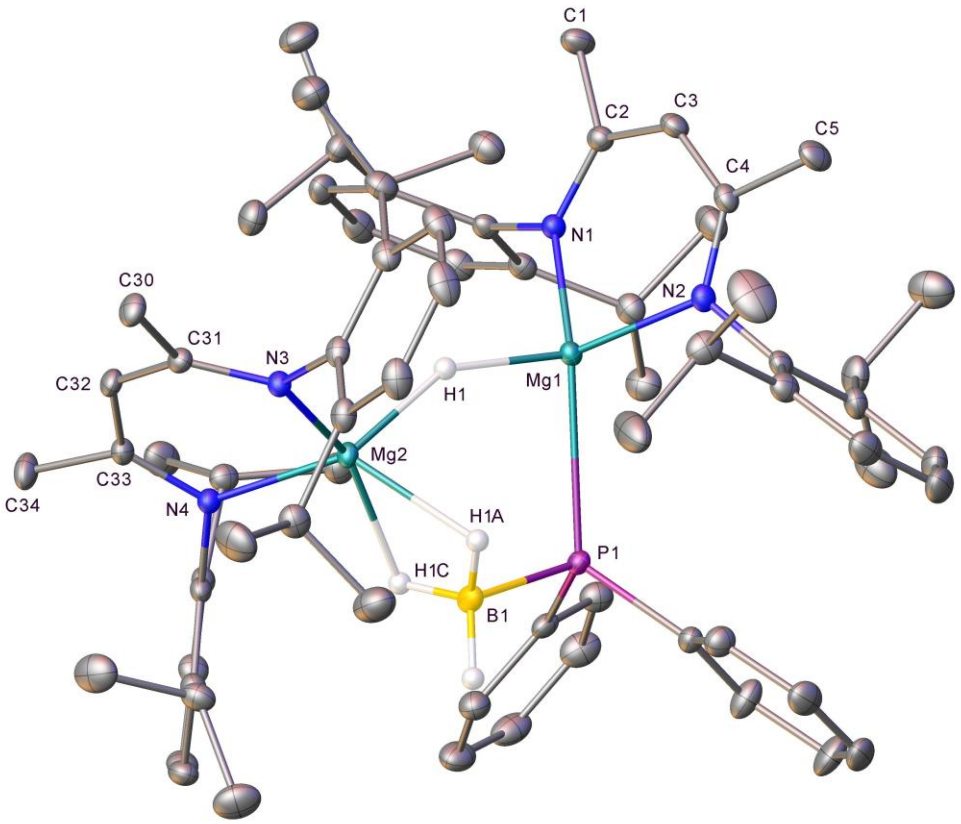


Figure 6: X-ray crystal structure of compound **8**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, except for those bound to boron and magnesium, are omitted for clarity. Solvent molecules are not shown. Selected bond lengths (Å) and angles (°): P1-Mg1 2.7241(6), P1-C59 1.8337(17), P1-C65 1.8406(16), P1-B1 1.9610(19), Mg1-N1 2.0814(14), Mg1-N2 2.0614(14), Mg2-N3 2.0543(13), Mg2-N4 2.0572(14), C59-P1-Mg1 118.37(5), C59-P1-C65 100.23(7), C59-P1-B1 106.22(8),C65-P1-Mg1 124.34(6), C65-P1-B1 105.29(8), B1-P1-Mg1 100.71(6), N1-Mg1-P1 140.40(4), N2-Mg1-P1 109.74(4), N2-Mg1-N1 93.48(6), N3-Mg2-N4 92.64(5).

The three unique {(BDI)Ca} units of compound **9** assemble as a trinuclear cyclic structure propagated by one hydride and two diphenylphosphidoborate anions. The hydride ligand bridges Ca2 and Ca3 in a μ_2 fashion, whilst the latter ligands are each bound to Ca1 *via* a phosphorus and to Ca2 and Ca3 by three agostic-type B-H-Ca interactions. The P1-B1-Ca2 and P2-B2-Ca3 angles are close to linearity (174.51(51), 176.32(14)°) and the resultant –{Ca-P-BH_3-Ca-H-Ca-H_3B-P}– macrocycle adopts a twisted geometry with a *pseudo*-C_2 rotational axis about Ca1/H1. The Ca2-N and Ca3-N bonds (2.333(2)-2.3690(19) Å) are slightly longer than Ca1-N (2.3069(18), 2.3124(18) Å). In contrast to Ca2 and Ca3, which are again almost co-planar with their respective BDI ligand backbones, Ca1 projects some 1.476(2) Å out of the mean plane defined by the N1/N2-containing BDI ligand due to the proximity of the phosphorus-bound phenyl groups. The geometry at both phosphorus atoms is close to tetrahedral, whilst the P-B bond lengths (1.946(3), 1.945(3) Å) are slightly shorter and the Ca-P bonds (2.9811(7), 3.0307(7) Å) are significantly longer than those of compounds **7** and **8**.

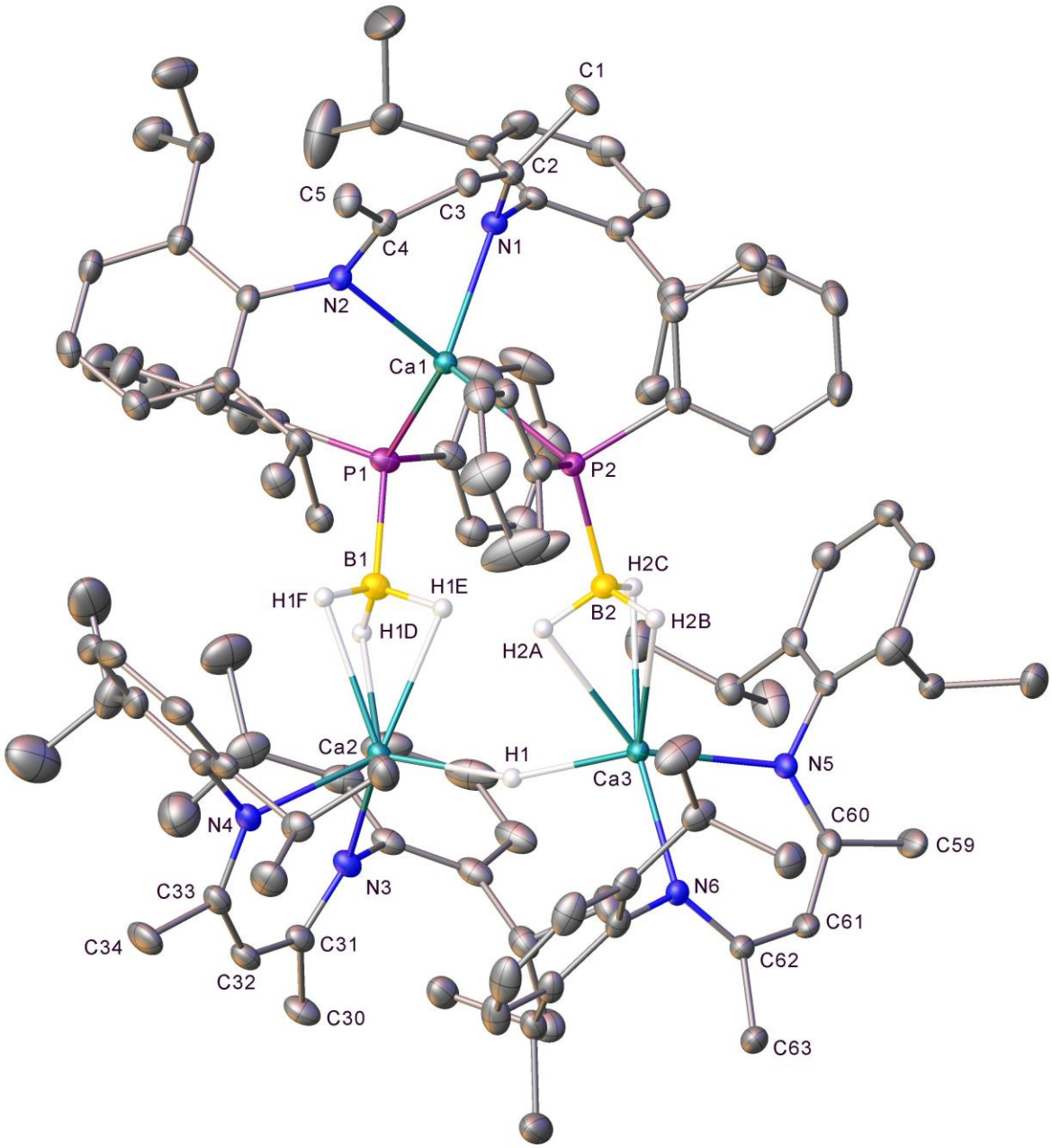
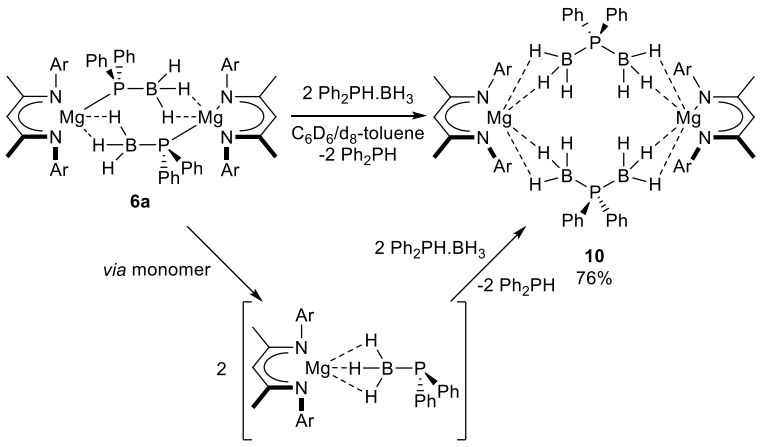


Figure 7: X-ray crystal structure of compound **9**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, except for those bound to boron and calcium, are omitted for clarity. Solvent molecules are also omitted. Selected bond lengths (Å) and angles (°): Ca1-P1 2.9811(7), Ca1-P2 3.0307(7), Ca1-N1 2.3069(18), Ca1-N2 2.3124(18), Ca2-N3 2.333(2), Ca2-N4 2.3498(19), Ca2-B1 2.602(3), Ca3-N5 2.3550(18), Ca3-N6 2.3690(19), Ca3-B2 2.634(3), P1-C89 1.835(3), P1-C95 1.840(3), P1-B1 1.946(3), P2-C101 1.839(2), P2-C107 1.842(3), P2-B2 1.945(3), P1-Ca1-P2 115.80(2), N1-Ca1-P1 107.16(5), N1-Ca1-P2 115.23(5), N1-Ca1-N2 82.40(6), N2-Ca1-P1 117.83(5), N2-Ca1-P2 113.70(5), N3-Ca2-N4 79.52(7), N3-Ca2-B1 118.83(8), N4-Ca2-B1 117.63(8), N5-Ca3-N6 79.67(6), N5-Ca3-B2 111.59(7), N6-Ca3-B2 139.47(8), C89-P1-Ca1 120.90(8), C89-P1-C95 103.03(12), C89-P1-B1 107.01(12), C95-P1-Ca1 110.49(8), C95-P1-B1 108.29(11), B1-P1-Ca1 106.59(9), C101-P2-Ca1 109.04(8), C101-P2-C107 100.63(11), C101-P2-B2 107.33(11), C107-P2-Ca1 114.51(8), C107-P2-B2 106.48(12), B2-P2-Ca1 117.35(9), P1-B1-Ca2 174.51(15), P2-B2-Ca3 176.32(14).

Having established the viability of β-diketiminato-Ae phosphidoborane formation, we turned our attention to the potential of these systems to effect catalytic phosphine-borane dehydrogenation. By analogy to earlier observations of alkaline earth amidoborane complexes,[24, 32, 33] it was surmised that the addition of further equivalents of phosphine-borane may facilitate β- or δ-hydride elimination and the generation of $[Ph_2PBH_2Ph_2PBH_3]^-$ derivatives and/or oligophosphine-borane formation. To this end, addition of two equivalents of $Ph_2PH{\cdot}BH_3$ to a d_8-toluene solution/suspension of the dimeric magnesium complex **6a** (**Scheme 4**) resulted in the formation of a clear, colorless solution. Although the quantitative generation of a single BDI-containing product (**10**) was diagnosed by the appearance of a new γ-C*H* resonance at δ 4.96 ppm in the resultant ^{1}H NMR spectrum, the emergence of this signal was concomitant with a further doublet of equal intensity centered at δ 5.20 ppm ($^1J_{31P}$ = 216 Hz). An assignment of this latter feature to the stoichiometric production of diphenylphoshine was substantiated by the presence of a sharp doublet of quintets (δ –40.7 ppm), which collapsed to a singlet in the $^{31}P\{^1H\}$ spectrum, in the corresponding ^{31}P NMR experiment. These spectra also displayed a broad resonance at δ −24.8 ppm, which was ascribed to the phosphorus environment of compound **10**. Single crystals of **10** suitable for X-ray diffraction analysis were obtained by cooling a hot saturated toluene solution to room temperature. The resultant experiment revealed **10** as a dimeric β-diketiminato magnesium phosphinodiboronate complex (**Figure 8**). This observation of BH_3 transfer rather than hydride elimination or intermolecular dehydrocoupling is tentatively attributed to both the lability of the Mg-P bond and the stronger binding of the Lewis acidic borane to the anionic phosphidoborate anion in preference to the charge neutral Ph_2PH donor.



Scheme 4: Synthesis of compound **10** *via* postulated monomerization of **6a** and BH_3 transfer. Yield shown refers to isolated crystalline product of analytical purity. Ar = 2,6-di-*iso*-propylphenyl.

Although several examples of alkali metal-phosphinodiboronate derivatives and related *f*-block complexes have been reported,[69-75] the majority contain alkyl-substituted phosphorus centers.

Compound **10** is, to the best of our knowledge, only the second crystallographically characterized example of the $[(H_3B)_2PPh_2]^-$ anion with the only direct precedent provided by Wagner and co-workers' report of [(18-crown-6)K{$(H_3B)_2PPh_2$}] (**11**).[76] Compound **10** crystallizes in the triclinic space group *P-1* and contains two crystallographically independent dimer halves (molecules *A* and *B*) and two regions of disordered toluene per unit cell. Although each dimer is propagated through agostic-type Mg-H_3B interactions, there are subtle differences in the binding mode of the $[(H_3B)_2PPh_2]^-$ anions. In molecule *B*, the anion bridges asymmetrically with a near linear Mg1-B1-P1 angle (171.76(12)°) resulting in three Mg-H-B interactions, and a bent Mg1'-B2-P1 geometry (136.69(9)°) provided by two Mg-H-B interactions. Molecule *A* contains a more symmetrically disposed anion, which engages with both magnesium centers *via* two Mg-H-B interactions per boron center. Despite these differences, the anion itself is structurally similar in both molecules. A slight increase in the B-P-B and C-P-C angles and decrease in P-B bond lengths are observed in comparison to the potassium salt, **11**. In the asymmetrically bound phosphinodiboronate anion of molecule *B*, the B1-P1 bond is slightly elongated relative to P1-B2. The Mg-N and P-C bond lengths, however, fall within the typical range and the phosphorus centers again adopt a slightly distorted tetrahedral geometry.

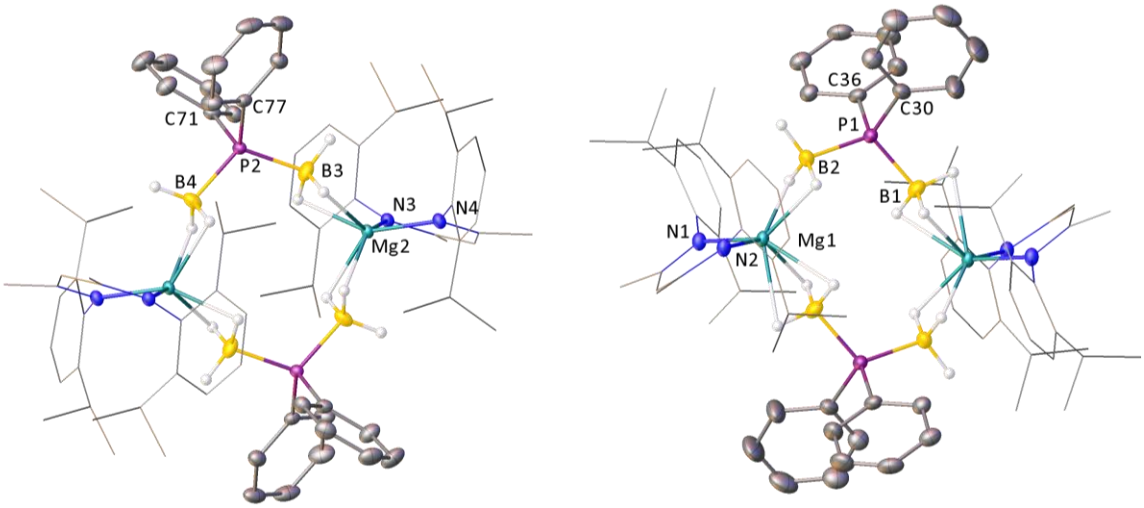


Figure 8: X-ray crystal structure of compound **10**, showing both crystallographically independent centrosymmetric dimers (left: molecule *A*, right: molecule *B*). Thermal ellipsoids are shown at the 30% probability level. For clarity, the BDI-ligands are shown in wireframe view and hydrogen atoms are omitted except for those bound to boron. Solvent molecules (toluene) present within in the crystal lattice are not shown. Selected bond lengths (Å) and angles (°) for molecule *A*: P2-C71 1.8142(14), P2-C77 1.8191(13), P2-B3 1.9152(17), P2-B4 1.9197(16), Mg2-N3 2.0493(11), Mg2-N4 2.0401(12), B4-Mg2[2] 2.3973(16), C71-P2-C77 103.68(6), C71-P2-B3 108.24(7), C71-P2-B4 108.46(7), C77-P2-B3 110.83(7), C77-P2-B4 109.70(7), B3-P2-B4 115.25(8), N4-Mg2-N3 95.12(5), P2-B4-Mg2[2] 153.63(10). Selected bond lengths (Å) and angles (°) for molecule *B*: P1-C30 1.8197(16), P1-C36 1.8195(16), P1-B1 1.9121(17), P1-B2 1.9221(17), Mg1-N1 2.0435(12), Mg1-N2 2.0402(12), Mg1-B2[1] 2.4204(18), C30-P1-B1 110.63(8), C30-P1-B2 110.24(8), C36-P1-C30 102.31(7), C36-P1-B1 108.61(8), C36-P1-B2 108.70(8), B1-P1-B2

115.50(8), N1-Mg1-B2[1] 110.15(6), N2-Mg1-N1 95.12(5), N2-Mg1-B2[1] 116.03(6), P1-B2-Mg1[1] 136.69(9). Symmetry operations used: [1]1-x,-1-y,-z; [2]2-x,1-y,1-z.

Conclusions

In summary, a series of heteroleptic alkaline-earth phosphidoborane complexes have been synthesized through deprotonation of diphenylphosphine-borane by readily accessible β-diketiminato Ae alkyl, amide, and hydride complexes. Although the resultant compounds appear labile in solution, addition of THF results in the formation of monomeric adducts **6b** (Mg) and **7b** (Ca), in which agostic-type Ae-H_3B interactions dominate over Ae-P bonds. Substoichiometric quantities of diphenylphosphine-borane react with the dimeric Ae-hydride species **IIIa** and **IIIb** to provide the μ_2-hydride bridged dimeric magnesium and trimeric calcium complexes, **8** and **9**. Attempts to effect subsequent dehydrogenation by addition of further equivalents of $Ph_2PH{\cdot}BH_3$ were thwarted by BH_3 transfer to provide the dimeric phosphinodiborate species **10**. Further work will focus on circumventing these difficulties as part of a wider effort to develop transition-metal free catalytic routes to polyphosphinoboranes.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. CCDC 1975971-1975976 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Notes

The authors declare no competing financial interest.

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For Table of Contents:

Alkaline-earth derivatives of diphenylphosphine-borane

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