Monomeric 16-Electron π-Diborene Complexes of Zn(II) and Cd(II)

Sunewang R. Wang,[†,‡] Merle Arrowsmith,[†,‡] Holger Braunschweig,*[,†,‡] Rian D. Dewhurst,[†,‡] Michael Dömling,[†,‡] James D. Mattock,[§] Conor Pranckevicius,[†,‡] Alfredo Vargas[§]

[†]Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[‡]Institute for Sustainable Chemistry and Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[§]Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, UK

Supporting Information Placeholder

ABSTRACT: Despite the prevalence of stable π-complexes of most d^{10} metals, such as Cu(I) and Ni(0), with ethylene and other olefins, complexation of d^{10} Zn(II) to simple olefins is too weak to form isolable complexes due to the metal ion's limited capacity for π-backdonation. By employing more strongly donating π-ligands, namely neutral diborenes with a high-lying π(B=B) orbital, monomeric 16-electron M(II)-diborene (M = Zn, Cd) π-complexes were synthesized in good yields. Metal–B_2 π-interactions in both the solid and solution state were confirmed by single-crystal X-ray analyses and their solution NMR and UV-vis absorption spectroscopy, respectively. The M(II) centers adopt a trigonal planar geometry and interact almost symmetrically with both boron atoms. The MB_2 planes significantly twist out of the MX_2 planes about the M-centroid(B–B) vector, with angles ranging from 47.0° to 85.5°, depending on the steric interactions between the diborene ligand and the MX_2 fragment.

π-Coordination of olefins to transition metals (TMs), first observed in Zeise's anionic platinum ethylene complex K[PtCl$_3$(C$_2$H$_4$)],[1] is one of the most fundamental interactions in organometallic chemistry and plays important roles in organic synthesis and catalysis.[2] Such interactions can be qualitatively interpreted by the Dewar–Chatt–Duncanson model, which connects the synergetic process of σ-donation from the ligand π-orbital to an unoccupied metal orbital and π-backbonding from a filled metal d-orbital into the π*-orbital of the olefin.[3] In the case of metals that are not able to effectively deliver π-backdonation, their olefin π-complexes are, therefore, very labile or even difficult to form. For example, only a few olefin complexes of metals lacking d-electrons available for π-backbonding have so far been characterized by X-ray crystallography, most of which were stabilized by the chelation effect.[4] It is also well known that the d^{10} zinc(II) ion does not form stable complexes with simple olefins due to its very high promotion energy (17.1 eV),[5] in stark contrast to its neighbors Cu(I) and Ni(0), and other d^{10} TMs.[6] Although weak intermolecular Zn–C π-interactions were observed in the crystal structures of a polymeric divinylzinc complex and a dimeric zinc acetylide,[7,8] there is only one structurally authenticated example of a zinc(II) ion interacting with a neutral tethered olefin so far.[9-11] Likewise, structurally authenticated monomeric complexes of Cd(II) with neutral olefins are unknown.[7d,8e,f,12]
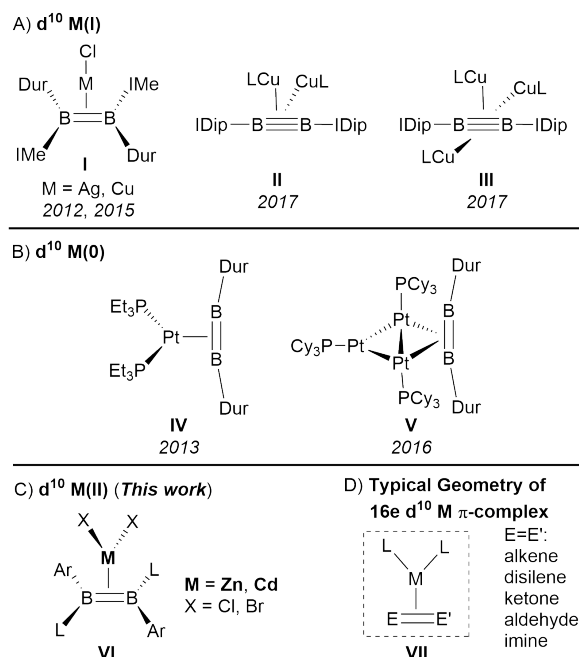

Figure 1. Coordination chemistry of neutral B–B multiple bonding ligands. Schematic of typical geometry of 16-electron d^{10} π-complexes (bottom right).

Recently, dibora-analogues of olefins and alkynes have shown fascinating coordination chemistry with d^{10} TMs.[13] Since 2012, two coinage metal π-complexes with doubly NHC-stabilized diborenes (**I**, Figure 1) have been synthesized and found to show bright fluorescence with exceptionally high quantum yields.[14] The extremely strong electron-donating ability of a doubly NHC-stabilized diboryne (LB≡BL) was first demonstrated by the isolation of encapsulation complexes of the naked alkali metal cations and very recently elucidated with the formation of strongly phosphorescent di- and trinuclear Cu(I) π-complexes (**II** and **III**).[15] While a mononuclear Pt^0 π-complex coordinated by an in-situ-generated base-free diborene (**IV**), featuring bond-strengthening π-backdonation, was isolated in 2013,[16] a complex containing the same diborene ligand bound across one Pt−Pt bond of the trimetallic fragment [Pt$_3$(PCy$_3$)$_3$] (**V**) was synthesized via Pt-mediated borane dehydrogenation in 2016.[17]

In view of the long-standing absence of d[10] Zn(II) and Cd(II) π-complexes with simple olefins and our curiosity about the TM-coordinating potential of neutral diborenes,[14a,18] which are boron analogues of olefins, we were interested in their coordination chemistry with Group 12 TMs. However, we kept in mind that diborene binding to metals is likely limited by their inherently strong reducing nature and the hindrance created by their bulky substituents used for kinetic stabilization. As shown in Figure 1, d[10] TM-diborene π-complexes were thereby sucessfully extended from M(0) and M(I) to M(II) ions (**VI**), and the structural details of monomeric 16-electron Zn(II) and Cd(II) π-complexes were obtained for the first time, which are reported herein. A striking structural observation in these d[10] M(II) π-complexes is that the MB$_2$ planes significantly twist out of the MX$_2$ planes about the M-centroid(B–B) vector with angles from 47.0° to 85.5°, differing from the typical coplanar arrangement as observed in known d[10] TM π-complexes (**VII**, Figure 1),[3c,16,19] suggesting the absence of significant π-backbonding.

Taking advantage of the attenuated reducing ability and reduced steric demand of 9-anthryl diborene **1a**,[18i] a green suspension of **1a** and anhydrous ZnCl$_2$ in benzene was stirred for 3 h at room temperature, which gave a yellow solution with a large amount of yellow precipitate (Table 1, entry 1).[20] The reaction solution provided near-silent ^{11}B and ^{31}P{^{1}H} NMR spectra due to the poor solubility of **2** in benzene (see below). Thus, the reaction solution was removed by filtration and the yellow precipitate was washed with benzene and then extracted with dichloromethane (DCM) to give a light yellow solution of **2**, as indicated by a ^{11}B NMR signal at δ = 27.4 ppm and a broad ^{31}P{^{1}H} NMR signal at δ = –14.0 ppm, from which analytically pure **2** was obtained as light yellow crystals in 80% yield. Similarly, complexes **3** and **4** were also obtained from the corresponding metal halides in good yields (Table 1, entries 2 and 3).

Table 1. Synthesis of π-Complexes 2–6[a]

Entry	Ar, L	MX$_2$	Product (%)[b]
1	9-anthryl, PMe$_3$ (**1a**)	ZnCl$_2$	80 (**2**)
2	9-anthryl, PMe$_3$ (**1a**)	ZnBr$_2$	73 (**3**)
3	9-anthryl, PMe$_3$ (**1a**)	CdCl$_2$	71 (**4**)
4	mesityl, PMe$_3$ (**1b**)	ZnCl$_2$	59 (**5**)
5	2-thienyl, *I*Me[c] (**1c**)	ZnCl$_2$	50 (**6**)

[a]For detailed procedures, see the Supporting Information. [b]Isolated yield. [c]*I*Me=1,3-dimethylimidazol-2-ylidene.

Encouraged by the successful complexation of **1a** with Zn(II) and Cd(II) dihalides, other diborenes bearing different aryls and bases were then examined to investigate the scope of this synthetic approach (Table 1, entries 4 and 5).[20] The mesityl diborene **1b**[18f] reacted with ZnCl$_2$ overnight at room temperautre to give a colorless solution, from which **5** was isolated as white solids in 59% yield. Unidentified green solids formed on the surface of the unreacted ZnCl$_2$ powders, which may result from redox reactions as a result of the slight steric and electronic changes from **1a** to **1b**.[18f,i] The 2-thienyl diborene **1c** has a more open space surrounding the π(B=B) orbital, which in previous work allowed direct B=B hydroboration,[18c,21] and was found to react with ZnCl$_2$ overnight at room temperature to give orange complex **6** in 50% yield and – somewhat expectedly – a significant amount of gray Zn(0) powder. Furthermore, B$_2$Dur$_2$(*I*Me)$_2$, the diborene used in the previ-

ously-reported synthesis of coinage metal complexes (**I**, Figure 1),[14] was also attempted. Instead of complexation with ZnCl$_2$, redox reactions occurred and no pure compounds were identified, possibly due to its more bulky substituents than those of **1c**.

The molecular structures of **2**–**4**, and **6** were confirmed by X-ray crystallographic analyses (Figure 2).[20] Similar to the coinage metal diborene complexes,[14] the B1–B2 bond lengths in **2**–**4** are slightly enlongated with respect to the diborene ligand **1a** (cf. 1.524(6) Å),[18i] and the planarity of the diborene ligands is effectively retained, as indicated by the sums of the bond angles around the boron atoms. In general, the Zn(II) and Cd(II) centers interact symmetrically with both boron atoms,[22] however, cadmium complex **4** crystallizes with two molecules in the unit cell, one in which the Cd atom symmetrically bridges the B=B bond, the other where the Cd atom slightly unsymmetrically bridges the B=B bond. The metal centers adopt a trigonal planar geometry with the third position occupied by the center of the B=B bond, as seen clearly from the sums of the bond angles around the metal centers (360° for **2**–**4** and 359.5° for **6**, respectively). The MB$_2$ planes significantly twist out of the MX$_2$ planes about the M-centroid(B–B) vector, with angles ranging from 47.0° to 85.5°, these angles correlating inversely with the M-centroid(B–B) distance (Table 2). In other words, a shorter M–centroid(B–B) distance roughly correlates with a greater angle between the MB$_2$ and MX$_2$ planes, which demonstrates the dependence of this torsion angle on the steric interactions between the diborene ligand and the metal fragment. In contrast with the typical coplanar arrangement observed in known 16-electron d[10] TM π-complexes with considerable π-backbonding (**VII**, Figure 1),[3c,19] the orientational flexibility of the B=B moieties suggests the absence of significant π-backbonding in these 16-electron Zn(II) and Cd(II) π-complexes. The approximately orthogonal arrangement in **6** should be fundamentally different from that of the platinum complex **IV** in Figure 1, which is directed by bond-strengthening π-backdonation to an empty π(B=B) bonding orbital.[16] Although zinc atoms are much smaller than platinum atoms, the Zn(II)-centroid(B–B) distance in **6** is in fact longer than the Pt(0)-centroid(B–B) distance in **IV** (2.154 vs. 1.928 Å), indicating a much weaker M-B$_2$ interaction in **6** than in **IV**.
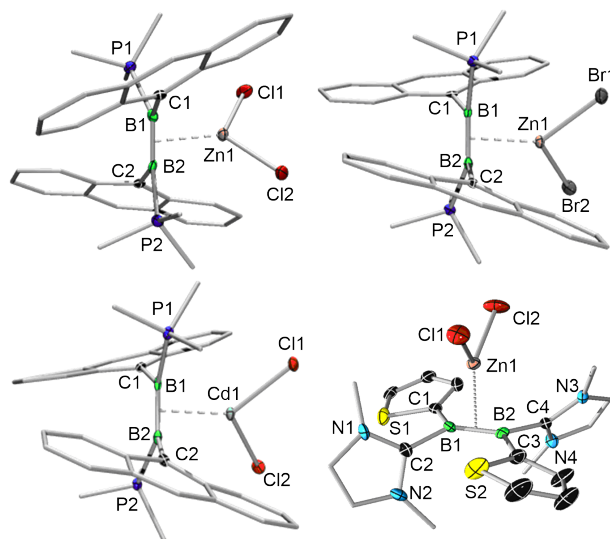

Figure 2. Molecular structures of **2** (top left), **3** (top right), **4** (bottom left), and **6** (bottom right). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, solvent molecules (benzene in **2** and DCM in **4** and **6**), and the symmetrical molecule of **4** in the unit cell are omitted for clarity. Selected bond lengths [Å] and angles [°]. Complex **2**: B1–B2 1.617(6), Zn1–B1 2.308(3), Zn1–Cl1 2.2483(7),; Cl1–Zn1–Cl2 112.73(4), B1–Zn1–

B2 41.01(15), $\Sigma\angle_{B1}$ 358.7. Complex **3**: B1–B2 1.607(7), Zn1–B1 2.357(5), Zn1–B2 2.342(5), Zn1–Br1 2.3926(8), Zn1–Br2 2.4141(8),; Br1–Zn1–Br2 107.53(3), B1–Zn1–B2 40.01(17), $\Sigma\angle_{B1}$ 358.6, $\Sigma\angle_{B2}$ 358.0. Complex **4**: B1–B2 1.624(8), Cd1–B1 2.513(5), Cd1–B2 2.443(5), Cd1–Cl1 2.4415(12), Cd1–Cl2 2.4653(12),; Cl1–Cd1–Cl2 104.95(4), B1–Cd1–B2 38.22(18), $\Sigma\angle_{B1}$ 358.9, $\Sigma\angle_{B2}$ 358.6. Complex **6**: B1–B2 1.615(8), Zn1–B1 2.307(6), Zn1–B2 2.293(6), Zn1–Cl1 2.2474(15), Zn1–Cl2 2.2287(15),; Cl1–Zn1–Cl2 106.12(6), B1–Zn1–B2 41.1(2), $\Sigma\angle_{B1}$ 359.1, $\Sigma\angle_{B2}$ 359.3.

Table 2. M–Centroid(B–B) Distance and Dihedral Angles between MB_2 and MX_2 Planes in 2–4 and 6

	2	**3**	**4**	**6**
d (Å)	2.162	2.208	2.338,[a] 2.341[b]	2.154
Δ (°)	70.5	62.6	47.0,[a] 56.2[b]	85.5

[a]Molecule in which the Cd(II) center interacts symmetrically with boron atoms. [b]Molecule in which the Cd(II) center interacts unsymmetrically with boron atoms.

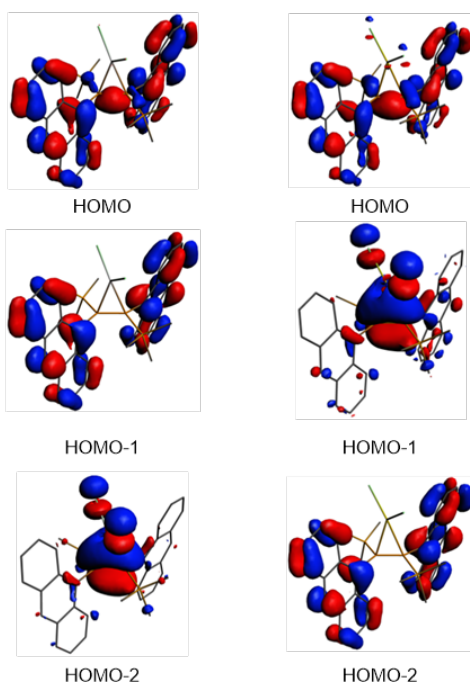| HOMO | HOMO |
| HOMO-1 | HOMO-1 |
| HOMO-2 | HOMO-2 |

Figure 3. Selected frontier molecular orbitals of **2** (left) and **4** (right).

The calculated HOMO levels of both **2** and **4** (Figure 3) are almost exclusively based on the diborene ligand and do not involve the metal centers. Although a distinct ligand-to-metal σ-donation can be observed (HOMO-2 for **2** and HOMO-1 for **4**), no occupied orbital could be found to contain a π-backdonation interaction akin to those in conventional π-olefin complexes.[3c] Energy decomposition analysis on **2** and **4** indicates that the covalent contribution to the M-B_2 interaction in **2** and **4** (42% and 40% of the total attractive interactions energy, respectively)[20] is significantly higher than in our previously-calculated diborene and diboryne complexes of Cu and Ag (covalent energy component is 29–33% of the total attractive interaction energy).[14b,15c] While the M-B_2 covalent bonding in these Group 12 complexes is relatively strong, this stems almost exclusively from the B_2→M σ-donation (given the very high-energy HOMOs of the constituent diborene molecules) with negligible π-backdonation. This is supported by

the charge deformation density maps (Figure S8) and the electron localization maps along the MB_2 plane (Figure S9) for **2** and **4**, which show strong electron flow from the B_2 unit to the metal centers, and electron density accumulation near the B_2 edge of the MB_2 plane, respectively. The presence of strong σ-donation with negligible π-backdonation also explains the observed orientational flexibility of the ligand atop the metal center in the complexes **2–4** and **6**.

While **2–4** and **6** are sparingly soluble in benzene at room temperature, **5** shows greater solubility in this solvent. Interestingly, **2** dissociates slowly in THF to release free **1a** as indicated by NMR spectroscopic analysis and the color change of the solution from yellow to green.[20] On the other hand, **6** is slightly soluble and stable in THF at room temperature, consistent with the stronger donating ability of **1c** relative to **1a**. Fortunately, **2–4** are soluble and stable in DCM at room temperature, albeit the solution of **6** in DCM decomposes slowly at room temperature. Thus, complexes **2–4** in CD_2Cl_2, **5** in C_6D_6, and **6** in d_8-THF were fully characterized by ^1H, ^{11}B, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy.[20]

In order to make comparisons with NMR spectral data of **1a** in C_6D_6, ^1H, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra of **2** were also acquired in C_6D_6.[20] The extremely dilute benzene solution of **2** showed a weak ^{11}B NMR signal at δ = 26.5 ppm and a broad $^{31}P\{^1H\}$ NMR signal at δ = –14.6 ppm, both somewhat downfield shifted in comparison with those of **1a** (δ_B = 22.0 and δ_P = –21.3 ppm in C_6D_6, respectively),[18i] consistent with a decrease of electron density around the B and P atoms upon complexation to Zn(II). Along with this change in the ^{11}B and $^{31}P\{^1H\}$ NMR spectra, ^1H NMR signals from the anthryl hydrogens were desymmetrized into nine sets (from the original five). Such desymmetrization of symmetric aryl and *I*Me's hydrogens was also observed in the ^1H NMR spectra of **2–4** and **6** in CD_2Cl_2 due to the groups' free rotation being hampered by complexation. The methyl proton signals of the PMe_3 donors were also deshielded with a shift from 0.29 ppm to 0.49 ppm.[18i] Similar spectroscopic changes were also observed between **5** and **1b** in C_6D_6. The complexation of **2** in benzene was also supported by its solution UV–vis absorption spectrum, with the disappearance of the intramolecular charge-transfer absorption band that was observed for **1a**.[18i]

These results, including the first structural authentication of monomeric complexes of Zn(II) and Cd(II) with π-olefin analogues, clearly demonstrate that zinc-diborene π-interactions are stable in non-donating solvents (and even THF in the case of **6**), and that they are significantly stronger than zinc-olefin π-interactions in general.[9-11] DFT calculations suggest that this strong M-B_2 bonding interaction is partly a result of enhanced covalent interactions (presumably the B_2→M σ-donation), which contributes more heavily to the ligand binding energy than in related B–B multiple bond π-complexes with Group 11 metals.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website:

Experimental and spectroscopic data, and DFT results (PDF)
Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*h.braunschweig@uni-wuerzburg.de

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

REFERENCES

(1) Seyferth, D. *Organometallics* **2001**, *20*, 2–6.

(2) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books: Sausalito, 2010.

(3) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71–C79. (b) Chatt, J. L.; Duncanson, A. *J. Chem. Soc.* **1953**, 2939–2947. (c) Frenking, G.; Frohlich, N. *Chem. Rev.* **2000**, *100*, 717–774.

(4) (a) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2454–2455. (b) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867–5868. (c) Evans, W. J.; Perotti, J. M.; Brady, J. C.; Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5204–5212. (d) Schumann, H.; Schutte, S.; Kroth, H.-J.; Lentz, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 6208–6211. (e) Berg, D. J.; Barclay, T.; Fei, X. *J. Organomet. Chem.* **2010**, *695*, 2703–2712. (f) Roşca, S.-C.; Caytan, E.; Dorcet, V.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Organometallics* **2017**, *36*, 1269–1277.

(5) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2ed.; VCH Publishers Inc.: New York, 1992.

(6) (a) Wang, X.-S.; Zhao, H.; Li, Y.-H.; Xiong, R.-G.; You, X.-Z. *Top. Catal.* **2005**, *35*, 43–61. (b) Hartly, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 6.

(7) (a) Wooten, A.; Carroll, P. J.; Maestri, A. G.; Walsh, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 4624–4631. (b) Wilson, E. E.; Oliver, A. G.; Hughes, R. P.; Ashfeld, B. L. *Organometallics* **2011**, *30*, 5214–5221. For Group 12 M(II)-complexes π-tweezered by a titanium bis(acetylide): (c) Lang, H.; Mansilla, N.; Rheinwald, G. *Organometallics* **2001**, *20*, 1592–1596. (d) Dietrich, S.; Mansilla, N.; Hildebrandt, A.; Wetzold, N.; Rheinwald, G.; Rüffer, T.; Lang, H. *J. Organomet. Chem.* **2011**, *696*, 2491–2498.

(8) Cyclopentadienyl zinc complexes are relatively more stable as a result of Coulombic interaction. For selected examples: (a) Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Organomet. Chem.* **1978**, *146*, C29–C36. (b) Budzelaar, P. H. M.; Boersma, J.; Kerk, G. J. M. V. D.; Spek, A. L.; Duisenberg, A. J. M. *J. Organomet. Chem.* **1985**, *281*, 123–130. (c) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136–1138. (d) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 693–703. For cadmium, see: (e) Barr, D.; Edwards, A. J.; Raithby, P. R.; Rennie, M.-A.; Verhorevoort, K. L.; Wright, D. S. *J. Organomet. Chem.* **1995**, *493*, 175–179. (f) Bentz, D.; Wolmershäuser, G.; Sitzmann, H. *Organometallics* **2006**, *25*, 3175–3178.

(9) Lichtenberg, C.; Engel, J.; Spaniol, T. P.; Englert, U.; Raabe, G.; Okuda, J. *J. Am. Chem. Soc.* **2012**, *134*, 9805–9811.

(10) For a Zn(II) η^2-toluene complex: Guerrero, A.; Martin, E.; Hughes, D. L.; Kaltsoyannis, N.; Bochmann, M. *Organometallics* **2006**, *25*, 3311–3313.

(11) Weak π-interactions between Zn(II) and the tethered alkynes have been observed: Bukhaltsev, E.; Goldberg, I.; Cohen, R.; Vigalok, A. *Organometallics* **2007**, *26*, 4015–4020.

(12) For a complex containing (supported) arene-cadmium π-coordination: Stępień, M.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2002**, *124*, 3838–3839.

(13) (a) Braunschweig, H.; Dewhurst, R. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3574–3583. (b) Arrowsmith, M.; Braunschweig, H.; Stennett, T. E. *Angew. Chem., Int. Ed.* **2017**, *56*, 96–115.

(14) (a) Bissinger, P.; Braunschweig, H.; Damme, A.; Kupfer, T.; Vargas, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 9931–9934. (b) Bissinger, P.; Steffen, A.; Vargas, A.; Dewhurst, R. D.; Damme, A.; Braunschweig, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 4362–4366.

(15) (a) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420–1422. (b) Bertermann, R.; Braunschweig, H.; Constantinidis, P.; Dellermann, T.; Dewhurst, R. D.; Ewing, W. C.; Fischer, I.; Kramer, T.; Mies, J.; Phukan, A. K.; Vargas, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 13090–13094. (c) Braunschweig, H.; Dellermann, T.; Dewhurst, R. D.; Hupp, B.; Kramer, T.; Mattock, J. D.; Mies, J.; Phukan, A. K.; Steffen, A.; Vargas, A. *J. Am. Chem. Soc.* **2017**, *139*, 4887–4893.

(16) Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Vargas, A. *Nat. Chem.* **2013**, *5*, 115–121.

(17) Arnold, N.; Braunschweig, H.; Dewhurst, R. D.; Ewing, W. C. *J. Am. Chem. Soc.* **2016**, *138*, 76–79.

(18) For synthesis of neutral diborenes: (a) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413. (b) Wang, Y.; Quillian, B.; Wei, P.; Xie, Y.; Wannere, C. S.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299. (c) Braunschweig, H.; Dewhurst, R. D.; Hörl, C.; Phukan, A. K.; Pinzner, F.; Ullrich, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 3241–3244. (d) Bissinger, P.; Braunschweig, H.; Damme, A.; Kupfer, T.; Krummenacher, I.; Vargas, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 5689–5693. (e) Bissinger, P.; Braunschweig, H.; Damme, A.; Hörl, C.; Kupfer, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 359–362. (f) Bissinger, P.; Braunschweig, H.; Celik, M. A.; Claes, C.; Dewhurst, R. D.; Endres, S.; Kelch, H.; Kramer, T.; Krummenacher, I.; Schneider, C. *Chem. Commun.* **2015**, *51*, 15917–15920. (g) Braunschweig, H.; Krummenacher, I.; Lichtenberg, C.; Mattock, J. D.; Schäfer, M.; Schmidt, U.; Schneider, C.; Steffenhagen, T.; Ullrich, S.; Vargas, A. *Angew. Chem., Int. Ed.* **2017**, *56*, 889–892. (h) Lu, W.; Li, Y.; Ganguly, R.; Kinjo, R. *J. Am. Chem. Soc.* **2017**, *139*, 5047–5050. (i) Wang, S. R.; Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Dellermann, T.; Dewhurst, R. D.; Kelch, H.; Krummenacher, I.; Mattock, J. D.; Müssig, J. H.; Thiess, T.; Vargas, A.; Zhang, J. *Angew. Chem., Int. Ed.* **2017**, *56*, DOI: 10.1002/anie.201704063.

(19) For selected recent solid-state structures: (a) Brunkan, N. M.; Brestensky, D. M.; Jones, W. D. *J. Am. Chem Soc.* **2004**, *126*, 3627–3641. (b) Iwamoto, T.; Sekiguchi, Y.; Yoshida, N.; Kabuto, C.; Kira, M. *Dalton Trans.* **2006**, 177–182. (c) Matas, I.; Cámpora, J.; Palma, P.; Álvarez, E. *Organometallics* **2009**, *28*, 6515–6523. (d) Oguadinma, P. O.; Schaper, F. *Organometallics* **2009**, *28*, 6721–6731. (e) Qiu, Z.; Deng, L.; Chan, H.-S.; Xie, Z. *Organometallics* **2010**, *29*, 4541–4547. (f) Kruckenberg, A.; Wadepohl, H.; Gade, L. H. *Organometallics*, **2013**, *32*, 5153–5170.

(20) Experimental, spectroscopic, crystallographic, and computational details are given in the Supporting Information.

(21) Braunschweig, H.; Hörl, C. *Chem. Commun.* **2014**, *50*, 10983–10985.

(22) The Zn–B distances in complexes **2**, **3**, and **6** (2.293(6)–2.357(5) Å) are significantly longer than those found in the borylzinc reagents derived from Nozaki and Yamashita's boryl anion (2.052(3)–2.088(3) Å): (a) Kajiwara, T.; Terabayashi, T.; Yamashita, M.; Nozaki, K. *Angew. Chem. Int., Ed.* **2008**, *47*, 6606–6610. (b) Campos, J.; Aldridge, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 14159–14163.

Table of Contents artwork:

M = Zn(II) and Cd(II)

Δ : 47.0° to 85.5°

High yields
General scope