

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

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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 $\pi(\text{B}=\text{B})$ orbital, monomeric 16-electron M(II)-diborene (M = Zn, Cd) π -complexes were synthesized in good yields. Metal–B₂ 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 MB₂ planes significantly twist out of the MX₂ 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 MX₂ fragment.

π -Coordination of olefins to transition metals (TMs), first observed in Zeise's anionic platinum ethylene complex $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$,¹ is one of the most fundamental interactions in organometallic chemistry and plays an important role 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}

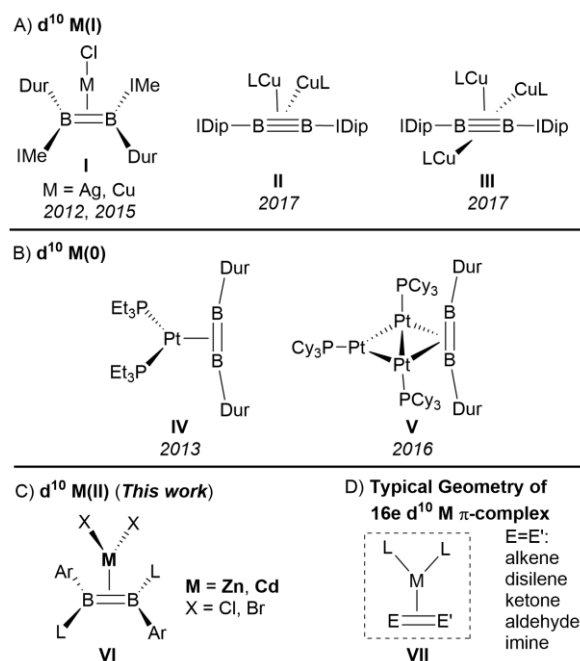


Figure 1. Coordination chemistry of neutral B–B multiple bonding ligands. Schematic of typical geometry of 16-electron d^{10} π -complexes (bottom right).

Recently, dibora-analogues of olefins and alkynes, discovered by Robinson in 2007 and our group in 2012, respectively,¹³ have shown fascinating coordination chemistry with d^{10} TMs. Since 2012, two highly fluorescent coinage metal π -complexes with doubly NHC-stabilized diborenes (**I**, Figure 1) have been synthesized.¹⁴ The extremely strong electron-donating ability of a doubly NHC-stabilized diboryne ($\text{LB}\equiv\text{BL}$) was demonstrated by encapsulation complexes of naked alkali metal cations and strongly phosphorescent di- and trinuclear Cu(I) π -complexes (**II** and **III**).¹⁵ While a mononuclear Pt⁰ π -complex coordinated by an in-situ-generated base-free diborene (**IV**) was isolated in 2013,¹⁶ a complex containing the same diborene ligand bound across one Pt–Pt bond of the trimetallic fragment $[\text{Pt}_3(\text{PCy}_3)_3]$ (**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,^{13a,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, d¹⁰ TM-diborene π -complexes were thereby successfully 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 d¹⁰ M(II) π -complexes is that the MB₂ planes significantly twist out of the MX₂ 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 d¹⁰ 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**,^{18h} a green suspension of **1a** and anhydrous ZnCl₂ 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 ¹¹B and ³¹P{¹H} NMR spectra due to the poor solubility of **2** in benzene. 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 ¹¹B NMR signal at 27.4 ppm and a broad ³¹P{¹H} NMR signal at –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 2–6

Entry	Ar, L	MX ₂	Product (%) ^a
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, /Me ^b (1c)	ZnCl ₂	50 (6)

^aIsolated yield. ^b/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 (Table 1, entries 4 and 5).²⁰ The mesityl diborene **1b**^{18c} reacted with ZnCl₂ overnight to give a colorless solution, from which **5** was isolated as a white solid in 59% yield. 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,^{18b,21} and was found to react with ZnCl₂ overnight to give orange complex **6** in 50% yield and – somewhat expectedly – a significant amount of gray Zn(0) powder. The use of B₂Dur₂(/Me)₂, the diborene used in the previously-reported synthesis of coinage metal π -complexes (**I**, Figure 1),¹⁴ was however unsuccessful.

The molecular structures of **2–4** and **6** were confirmed by X-ray crystallographic analyses (Figure 2).²⁰ Like the coinage metal diborene complexes,¹⁴ the B1–B2 bond lengths in **2–4** are slightly elongated with respect to the diborene ligand **1a** (cf. 1.524(6)

Å),^{18h} and the planarity of the diborene ligands is effectively retained. 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, in which the Cd atom symmetrically or 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 MB₂ planes significantly twist out of the MX₂ planes around the M-centroid(B–B) vector, with angles ranging from 47.0° to 85.5° (Table 2). These angles correlate inversely with the M-centroid(B–B) distance, demonstrating the dependence of this torsion angle on the steric interactions between the diborene ligand and the metal fragment. In contrast to the typical coplanar arrangement observed in 16-electron d¹⁰ 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 the current π -complexes. The approximately orthogonal arrangement in **6** should be fundamentally different from that of the platinum complex **IV** (Figure 1), which is directed by bond-strengthening π -backdonation to an empty π (B=B) bonding orbital.¹⁶ Although Zn atoms are much smaller than Pt 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–B₂ interaction in **6** than in **IV**.

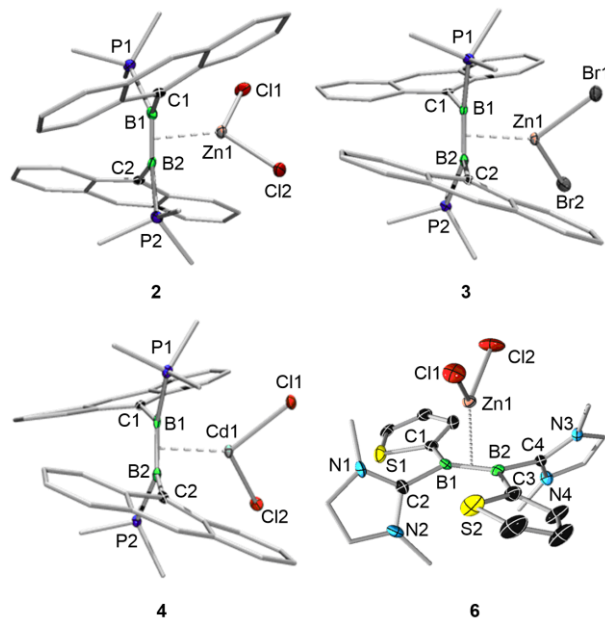


Figure 2. Molecular structures of **2**, **3**, **4**, and **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, solvent molecules (benzene in **2** and DCM in **4** and **6**), and the symmetrical molecule of **4** in the unit cell are omitted for clarity. Selected bond lengths [Å] and angles [°]. **2**: B1–B2 1.617(6), Zn1–B1 2.308(3); $\Sigma \angle_{B1}$ 358.7. **3**: B1–B2 1.607(7), Zn1–B1 2.357(5), Zn1–B2 2.342(5); $\Sigma \angle_{B1}$ 358.6, $\Sigma \angle_{B2}$ 358.0. **4**: B1–B2 1.624(8), Cd1–B1 2.513(5), Cd1–B2 2.443(5); $\Sigma \angle_{B1}$ 358.9, $\Sigma \angle_{B2}$ 358.6. **6**: B1–B2 1.615(8), Zn1–B1 2.307(6), Zn1–B2 2.293(6); $\Sigma \angle_{B1}$ 359.1, $\Sigma \angle_{B2}$ 359.3.

Table 2. M–Centroid(B–B) Distance and Dihedral Angles between MB₂ and MX₂ Planes in 2–4 and 6

	2	3	4	6
<i>d</i> (Å)	2.162(1)	2.208(1)	2.339(1), ^a	2.154(1)

			2.341(5) ^b	
Δ (°)	70.5(2)	62.6(3)	47.0(2), ^a	85.5(2)
			56.2(2) ^b	

^aMolecule in which the Cd(II) center interacts symmetrically with boron atoms. ^bMolecule in which the Cd(II) center interacts unsymmetrically with boron atoms.

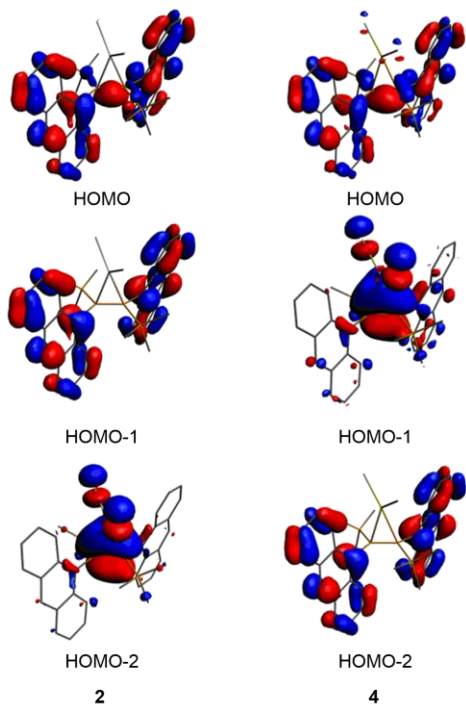


Figure 3. Selected frontier molecular orbitals of **2** and **4**.

Although a distinct ligand-to-metal σ -donation can be observed (HOMO-2 for **2** and HOMO-1 for **4**, Figure 3), 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-B₂ 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-B₂ covalent bonding in these Group 12 complexes is relatively strong, this stems almost exclusively from the B₂→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 MB₂ plane (Figure S9) for **2** and **4**, which show strong electron flow from the B₂ unit to the metal centers, and electron density accumulation near the B₂ edge of the MB₂ 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 **2–4** and **6**.

While **2–4** and **6** are sparingly soluble in benzene at room temperature, **5** shows greater solubility in this solvent. Although **2** dissociates slowly in THF to release free **1a** as indicated by NMR spectroscopic analysis and the characteristic green color,²⁰ **6** is slightly soluble and stable in THF, consistent with the stronger donating ability of **1c** relative to **1a**. Fortunately, **2–4** are soluble and stable in DCM, albeit the solution of **6** in DCM decomposes slowly at room temperature. Thus, **2–4** in CD₂Cl₂, **5** in C₆D₆, and **6** in *d*₈-THF were fully characterized by NMR spectroscopy.²⁰

To make comparisons with NMR spectral data of **1a** in C₆D₆, ¹H, ¹¹B, and ³¹P{¹H} NMR spectra of **2** were also acquired in C₆D₆.²⁰ The extremely dilute benzene solution of **2** showed a weak ¹¹B NMR signal at 26.5 ppm and a broad ³¹P{¹H} NMR signal at –14.6 ppm, both somewhat downfield shifted in comparison with those of **1a** ($\delta_B = 22.0$ and $\delta_P = -21.3$ ppm in C₆D₆, respectively),^{18h} consistent with a decrease of electron density around the B and P atoms upon complexation to Zn(II). While the methyl proton signal of the PMe₃ donors was deshielded with a shift from 0.29 ppm to 0.49 ppm,^{18h} ¹H NMR signals from the anthryl hydrogens were desymmetrized into nine sets due to the groups' free rotation being hampered by complexation. Similar spectroscopic changes were also observed between **5** and **1b** in C₆D₆. 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 observed for **1a**.^{18h}

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 solution, unlike those of olefins.^{9–11}

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)

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Notes

The authors declare no competing financial interests.

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