

## Syntheses of the First Molecular Complexes Containing a Cadmium–Cadmium Bond and a Cadmium–Hydrogen Bond

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We have recently been exploring the coordination chemistry of the post transition metals using the flexible poly(pyrazolyl)-borate family of ligands.<sup>1</sup> The chemistry of cadmium is particularly interesting because both the <sup>111</sup>Cd and the <sup>113</sup>Cd isotopes are spin 1/2 nuclei with good relative sensitivities for NMR observation. Reported here is the synthesis of the first molecular complex containing a Cd–Cd bond and the measurement of its Cd–Cd coupling constant. In addition, we report the first molecular metal–hydride complex of cadmium and the synthesis and structure of a cadmium borohydride complex.

The reaction of CdCl<sub>2</sub> with 2 equiv of KBH<sub>4</sub> in diethyl ether at –78 °C followed by 1 equiv of Ti[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>] (pz = pyrazolyl ring) produces [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]CdBH<sub>4</sub> (eq 1).<sup>2</sup>

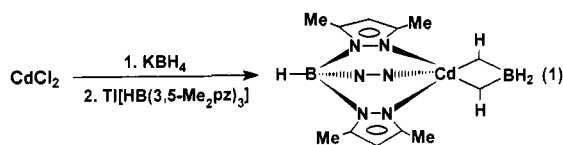
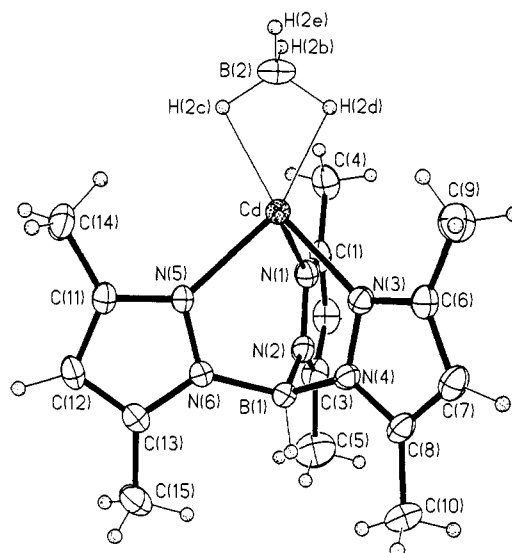


Figure 1 shows an ORTEP drawing of [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]CdBH<sub>4</sub>.<sup>3</sup> The complex is monomeric in the solid phase with a normally bonded η<sup>3</sup>-[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sup>–</sup> ligand. The BH<sub>4</sub><sup>–</sup> ligand shows only η<sup>2</sup>-coordination to cadmium. Given that three [RB(pz)<sub>3</sub>]<sub>2</sub>-Cd (R = H, pz = 3,5-Me<sub>2</sub>pz; R = pz = pz and 3-Me<sub>2</sub>pz) complexes have been characterized crystallographically and shown to be six coordinate,<sup>4</sup> η<sup>3</sup>-BH<sub>4</sub> coordination was expected. The asymmetry

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(2) To a solution of CdCl<sub>2</sub> (1 equiv) in Et<sub>2</sub>O at –78 °C was added KBH<sub>4</sub> (2 equiv), and the solution was stirred cold for 0.25 h. Ti[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>] (0.9 equiv) was added, and the resulting black solution was warmed to room temperature (2 h) and stirred for 3 h. The solvent was removed under vacuum, the solid was extracted with benzene and filtered, and the benzene was removed under vacuum, leaving a white solid. This solid was reextracted with toluene and filtered, and the solvent was removed, leaving a white solid (44% yield), mp 168–172 °C dec. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.76 (3 H, s, 4-H pz), 2.36, 2.27 (9 H each, s each, 3,5-Me pz); 0.85 (4 H, q, J = 86 Hz, BH<sub>4</sub>). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>): δ –9.54 (br, B pz); –52.96 (quintet, J = 87.2, BH<sub>4</sub>). <sup>113</sup>Cd NMR (CDCl<sub>3</sub>): δ 393.9. IR spectrum (ν(BH), Nujol): 2523 (HB pz); 2426, 2384, 2037 (BH<sub>4</sub>). Mass spectrum (clusters have appropriate isotope patterns): m/z 424 (M<sup>+</sup>); 411 (M<sup>+</sup> – BH<sub>2</sub>). Accurate mass spectrum (m/z) for M<sup>+</sup> – BH<sub>4</sub>: calcd for C<sub>15</sub>H<sub>22</sub>N<sub>6</sub><sup>111</sup>B<sup>1029</sup>Cd 407.1029, found 407.1040.

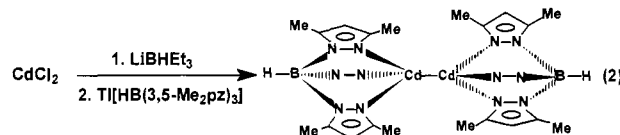
(3) Crystal data: C<sub>15</sub>H<sub>26</sub>N<sub>6</sub>B<sub>2</sub>Cd, colorless, triclinic, P1, a = 7.827(3), b = 11.148(3), and c = 11.639(3) Å, α = 76.44(3)°, β = 85.22(3)°, γ = 82.83(3)°, V = 978.2(7) Å<sup>3</sup>, Z = 2, D<sub>x</sub> = 1.441 g cm<sup>–3</sup>, T = 239 K. Of 4589 reflections collected (Siemens P4, Mo Kα, 2θ<sub>max</sub> = 55°), 4388 were independent and 3761 were observed (5σ<sub>F</sub>). The five hydrogen atoms bonded to B(1) and B(2) were found and refined; the remainder were idealized. All non-hydrogen atoms were refined with anisotropic thermal parameters. At convergence, R(F) = 3.36, R(wF) = 4.53.



**Figure 1.** ORTEP drawing of [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]CdBH<sub>4</sub>. Bond lengths and bond angles: Cd–N(1) 2.289(3), Cd–N(3) 2.246(3), Cd–N(5) 2.231(3), and Cd···B(2) 2.423(5) Å; N(1)–Cd–N(3) 84.0(1), N(1)–Cd–N(5) 86.5(1), N(3)–Cd–N(5) 86.9(1), B(2)···Cd–N(1) 114.1(1), B(2)···Cd–N(3) 135.6(1), and B(2)···Cd–N(5) 132.1(2)°.

in the BH<sub>4</sub><sup>–</sup> bonding is also demonstrated by the B···Cd···B angle of 165.4(4)°. The η<sup>2</sup>-coordination is confirmed by the typical η<sup>2</sup>-pattern of ν(B–H) bands in the IR spectrum in both the solution and solid phases of the complex.<sup>5a</sup> Solutions containing cadmium halides and BH<sub>4</sub><sup>–</sup> have been studied previously by NMR methods, and η<sup>2</sup>-coordination of the BH<sub>4</sub><sup>–</sup> ligands was observed.<sup>5b</sup>

An interesting feature of the mass spectrum of [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]CdBH<sub>4</sub> is the appearance of a cluster of peaks corresponding to {[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]Cd}<sub>2</sub>. This dimeric complex can be synthesized in the reaction of CdCl<sub>2</sub> and LiBHET<sub>3</sub> followed by Ti[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>] (eq 2).<sup>6</sup> The <sup>1</sup>H NMR spectrum of the



dimer is normal for complexes of the [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sup>–</sup> ligand, with no other resonances present. It has not yet proven possible to grow crystals suitable for a crystallographic study, but definitive evidence that the complex contains a Cd–Cd bond comes from <sup>113</sup>Cd NMR. The two spin 1/2 isotopes of cadmium allow the determination of the Cd–Cd coupling constant in this symmetrical molecule. The spectrum consists of a large central resonance that shows satellites due to the <sup>111</sup>Cd isotope with appropriate relative intensities. The <sup>111</sup>Cd–<sup>113</sup>Cd coupling constant is extremely large, 20 646 Hz, clearly indicating a strong bond between the cadmium atoms. The lack of observed coupling due to bridging hydrogen atoms and resonances in the <sup>1</sup>H NMR spectrum attributable to hydride ligands rules out a formulation of the complex as {[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>](μ-H)Cd}<sub>2</sub>.

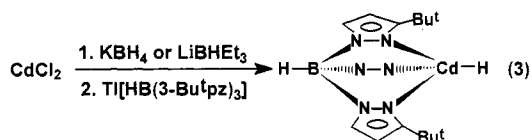
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(6) This compound was prepared in method analogous to that used for the borohydride compound with use of Li(BHET<sub>3</sub>) in ca. 40% yield. A ca. 5% impurity of [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sub>2</sub>Cd<sup>4</sup> also forms that cannot be separated. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.73 (6 H, s, 4-H pz); 2.35, 2.24 (18 H each, s each, 3,5-Me pz). <sup>113</sup>Cd NMR (C<sub>6</sub>D<sub>6</sub>): δ 298.6 (J<sub>113Cd-111Cd</sub> = 20 646 Hz). Accurate mass spectrum (m/z) for M<sup>+</sup>: calcd for C<sub>30</sub>H<sub>44</sub>N<sub>12</sub><sup>111</sup>B<sub>2</sub><sup>110</sup>Cd<sub>2</sub> 814.2058, found 814.2085.

To our knowledge this is the first report of a molecular complex with a Cd–Cd bond and the first reported  $^{111}\text{Cd}$ – $^{113}\text{Cd}$  coupling constant. The ion  $\text{Cd}_2^{2+}$  has been observed crystallographically in  $\text{Cd}_2(\text{AlCl}_4)_2$ .<sup>7</sup> In contrast to cadmium, Hg–Hg bonds are known to be present in many compounds, including  $\{[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{Hg}\}_2$ .<sup>8</sup>

The reaction of  $\text{CdCl}_2$  with either  $\text{KBH}_4$  or  $\text{LiBHEt}_3$  followed by  $\text{Ti}[\text{HB}(3\text{-Bu}^t\text{pz})_3]$  leads to the formation of  $[\text{HB}(3\text{-Bu}^t\text{pz})_3]\text{-CdH}$ ,<sup>9</sup> the first reported molecular hydride complex of cadmium (eq 3). This complex shows resonances in the  $^1\text{H}$  NMR spectrum



for the  $[\text{HB}(3\text{-Bu}^t\text{pz})_3]^-$  ligand and a resonance at  $\delta$  6.30 assigned to the hydride ligand. Both  $^{111}\text{Cd}$  ( $J = 2411$  Hz) and  $^{113}\text{Cd}$  ( $J = 2522$  Hz) satellites are observed about this  $\delta$  6.30 resonance. The  $^{113}\text{Cd}$  spectrum is a doublet with a  $^{113}\text{Cd}$ –H coupling constant of 2527 Hz. This resonance collapses to a singlet when the

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(9) This compound was prepared in a method analogous to that used for the borohydride compound in 48% yield; mp 117–121 °C dec.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.64, 5.94 (3 H each, br each, 4,5-H pz); 6.30 (1 H, s,  $J_{^{113}\text{CdH}} = 2522$  Hz,  $J_{^{111}\text{CdH}} = 2411$  Hz, CdH); 1.08 (27 H, s, 3-Bu<sup>t</sup>pz).  $^{113}\text{Cd}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  348.2 (d,  $J_{\text{CdH}} = 2527$  Hz). Accurate mass spectrum ( $m/z$ ) for  $\text{M}^+ - \text{H}$ : calcd for  $\text{C}_{21}\text{H}_{34}\text{N}_6^{111}\text{B}^{110}\text{Cd}$  491.1968, found 491.1958.

spectrum is run with proton decoupling. In contrast to the  $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$  ligand, the bulky  $[\text{HB}(3\text{-Bu}^t\text{pz})_3]^-$  ligand destabilizes a possible  $\text{BH}_4^-$  complex but stabilizes the hydride, preventing the formation of the dimer. Parkin has previously reported the analogous hydrides of zinc and beryllium.<sup>10</sup>

The new syntheses reported here demonstrate how subtle changes in reaction conditions and changes in the steric bulk of the poly(pyrazolyl)borate ligands can influence reaction products. Attempts to prepare hydride derivatives of cadmium using  $\text{BH}_4^-$  and the  $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$  ligand yield a borohydride complex. Switching the preparation to  $\text{BHEt}_3^-$  yields  $\{[\text{HB}(3,5\text{-Me}_2\text{pz})_3]\text{-Cd}\}_2$ . Use of either hydride reagent and the bulky  $[\text{HB}(3\text{-Bu}^t\text{pz})_3]^-$  ligand yields the stable hydride  $[\text{HB}(3\text{-Bu}^t\text{pz})_3]\text{CdH}$ . Preliminary results indicate that the synthetic methodology reported in this paper for the syntheses of borohydride complexes and complexes with metal–metal bonds can be extended to zinc.

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**Supplementary Material Available:** Tables of complete data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and positional parameters of H atoms (7 pages); listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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