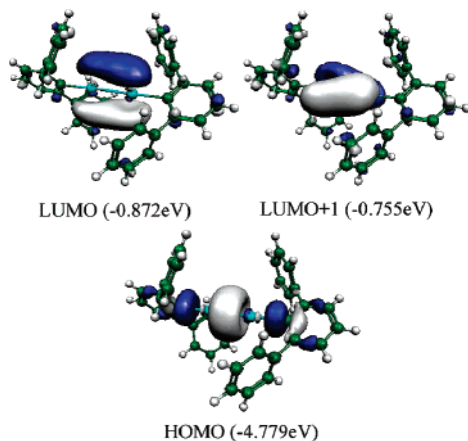


**Figure 2.**  $^{113}\text{Cd}$  NMR spectrum of **3**. Signals marked with (\*) indicate the  $^{111}\text{Cd}$ – $^{113}\text{Cd}$  coupling ( $^1J_{\text{CdCd}} = 8650$  Hz).



**Figure 3.** Representation of the frontier molecular orbitals of **3** from DFT calculations.

were extracted from the X-ray structure.<sup>17</sup> The calculations showed that the HOMO corresponded to a  $\sigma$ -bond between the cadmium atoms, which is composed mainly of 5p and 5s orbital character in a ratio of about 5:3 (see Figure 3). The Cd–C bonds are derived from in phase and out of phase orbital combinations HOMO-14 and HOMO-3, which also have minor Cd–Cd bonding character (see Figure S1, Supporting Information). The LUMO and LUMO + 1 combinations are almost degenerate and are formed mainly from the cadmium 5p<sub>x</sub> and 5p<sub>y</sub> orbitals. The metal–metal bonding in **3** is thus similar to that in Ar'ZnZnAr'. This is in contrast to Cp\*ZnZnCp\* where the Zn–Zn bond is of mainly 4s character.<sup>4</sup> It seems likely that the influence of the different ligands on the metal–metal bonding may likewise account for the large differences in the Cd–Cd coupling constant between **3** and Cd<sub>2</sub>Tp<sup>Me</sup><sub>2</sub>.

We have described the synthesis and first structural characterization of a molecular compound containing a Cd–Cd bond. The existence of the metal–metal bond was confirmed by  $^{113}\text{Cd}$  NMR spectroscopic studies. Similar to the Zn–Zn bonded compound Ar'ZnZnAr', DFT calculations showed that Ar'CdCdAr' (**3**) had significant p-character in the Cd–Cd bonding orbital. Work to elucidate the details of the mechanism of the reduction of **4**, the isolation of the putative aryl cadmium hydride intermediate Ar'CdH, and the synthesis and reactivity of **3** and other Cd–Cd bonded compounds are in hand.

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**Supporting Information Available:** Computation studies and X-ray data for **2** (CIF) as well as the full citation for ref 17. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) All manipulations were carried out under anaerobic and anhydrous conditions. **4**: Ar'Li<sup>10a</sup> (1.11 g, 2.73 mmol) and CdI<sub>2</sub> (1.00 g, 2.73 mmol) were combined with diethyl ether (50 mL) and stirred for 2 d. The solvent was then removed under a dynamic vacuum, and the residue was extracted by hexane (50 mL). The slurry was allowed to settle, and the mother liquor was separated from the precipitate (LiI). The hexane was removed, and the pale yellow residue was extracted again with hexane (50 mL). Filtration and removal of the hexane yielded **4** as a white powder. Yield: 1.17 g, 67.2%; mp 287 °C.  $^1\text{H}$  NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.07 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 6.6$  Hz), 1.24 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 6.9$  Hz), 2.99 (sept, 4H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 7.2$  Hz), 7.13–7.31 (m, 9H, *m*-C<sub>6</sub>H<sub>3</sub>, *p*-C<sub>6</sub>H<sub>3</sub>, *m*-Dipp, and *p*-Dipp).  $^{13}\text{C}$  { $^1\text{H}$ } NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C):  $\delta$  24.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.7 (*m*-Dipp), 126.7 (*p*-C<sub>6</sub>H<sub>3</sub>), 127.8 (*p*-Dipp), 128.9 (*m*-C<sub>6</sub>H<sub>3</sub>), 144.2 (*i*-Dipp), 146.6 (*o*-C<sub>6</sub>H<sub>3</sub>), 148.2 (*o*-Dipp), 162.3 (*i*-C<sub>6</sub>H<sub>3</sub>).  $^{113}\text{Cd}$  { $^1\text{H}$ } NMR<sup>b</sup> (C<sub>6</sub>D<sub>6</sub>, 133.1 MHz, 25 °C):  $\delta$  210.91. **3**: The iodide derivative **4** (1.00 g, 1.57 mmol) and NaH (0.075 g, 3.14 mmol) were combined with THF (50 mL) and stirred for 3 d. The solvent was then removed under a dynamic vacuum, and the residue was extracted with benzene (50 mL). The slurry was allowed to settle, and the mother liquor was decanted from the precipitate (NaI and excess NaH). The volume was concentrated to ca. 10 mL, and storage over 2 d in a refrigerator (ca. 8 °C) afforded colorless X-ray quality crystals of **3**. Yield: 0.22 g, 27.6% (based on **4**); decomposition of **3** to a gel-like grey solid was seen at 182 °C.  $^1\text{H}$  NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.05 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 7.2$  Hz), 1.12 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 6.6$  Hz), 2.95 (sept, 4H, CH(CH<sub>3</sub>)<sub>2</sub>),  $^3J_{\text{HH}} = 6.9$  Hz), 7.10–7.27 (m, 9H, *m*-C<sub>6</sub>H<sub>3</sub>, *p*-C<sub>6</sub>H<sub>3</sub>, *m*-Dipp, and *p*-Dipp).  $^{13}\text{C}$  { $^1\text{H}$ } NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 25 °C):  $\delta$  24.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 122.9 (*m*-Dipp), 125.8 (*p*-C<sub>6</sub>H<sub>3</sub>), 127.1 (*p*-Dipp), 128.6 (*m*-C<sub>6</sub>H<sub>3</sub>), 144.0 (*i*-Dipp), 147.0 (*o*-C<sub>6</sub>H<sub>3</sub>), 147.2 (*o*-Dipp), 176.5 (*i*-C<sub>6</sub>H<sub>3</sub>).  $^{113}\text{Cd}$  { $^1\text{H}$ } NMR<sup>b</sup> (C<sub>6</sub>D<sub>6</sub>, 133.1 MHz, 25 °C):  $\delta$  540.28 ( $^1J_{\text{CdCd}} = 8650$  Hz). (a) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed.* **1996**, *35*, 2150–2152. (b) Chemical shifts are reported in ppm with respect to external 0.01 M Cd(ClO<sub>4</sub>)<sub>2</sub>.
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