

Published on Web 11/04/2006

Synthesis, Structural Characterization, and Spectroscopy of the Cadmium–Cadmium Bonded Molecular Species Ar'CdCdAr' (Ar' = C_6H_3 -2,6-(C_6H_3 -2,6- Pr_2^i)₂)

Zhongliang Zhu, Roland C. Fischer, James C. Fettinger, Eric Rivard, Marcin Brynda, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

Received August 22, 2006; E-mail: pppower@ucdavis.edu

Molecular compounds featuring homonuclear metal-metal bonds between group 12 elements Zn and Cd are rare.¹⁻⁸ The work of Carmona and his group, which has resulted in the isolation and characterization of the first stable Zn-Zn bonded compound,⁴ Cp*ZnZnCp* ($Cp = \eta^5-C_5Me_5$), has proven that the Zn–Zn bond can be stabilized by electronic and steric effects. At present, only two examples of compounds with stable Cd-Cd bonds are known,^{6,7} and detailed structural information exists only for the ionic species [Cd₂][AlCl₄]₂ (1).⁶ However, the molecular Cd₂Tp^{Me₂₂} (2) $(Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)$ borate) has been synthesized by treatment of CdCl2 with TlTpMe2/LiBHEt3.7 The existence of its Cd-Cd bond was established by the observation of Cd¹¹¹-Cd¹¹³ coupling in its ¹¹³Cd NMR spectrum. Calculations on simple model compounds $M_2(\eta^5-C_5H_5)_2$ (M = Zn or Cd) have suggested that molecular compounds with simple organic groups should be stable and capable of isolation, although the Cd-Cd bonding was calculated to be weaker than that in the Zn-Zn species.9 We now describe the synthesis and characterization of the molecular species Ar'CdCdAr' (3) and show that it possesses considerable thermal stability.

Compound **3** was prepared by the reduction of the aryl cadmium halide Ar'CdI (**4**).¹⁰ The use of several reducing reagents, for example, Na, Na/naphthalene, and NaH was investigated. Among them, Na and Na/naphthalene led to over-reduction and the isolation of Ar'H and Cd metal. However, the addition of 2 equiv of NaH to Ar'CdI in THF resulted in the synthesis of the title compound Ar'CdCdAr' in a low yield in accordance with the eq 1.

$$CdI_{2} + Ar'Li \xrightarrow{Et_{2}O, 25 °C} Ar'CdI \xrightarrow{2 NaH} Ar'CdCdAr'$$
(1)
(4) THF, 25 °C (3)

Although the mechanism of this reduction is still not clear, the X-ray crystal structure of 3^{11} (Figure 1) confirmed the presence of a Cd-Cd bond in the product 3. The observed Cd-Cd distance of 2.6257(5) Å in 3 is ca. 0.20 Å shorter than the sum of Pauling's single-bond metallic radii for Cd [2.82 Å].¹² This shortening is similar to that in its zinc analogue Ar'ZnZnAr' (5) [ca. 0.14 Å]^{5b} and thus is indicative of a considerable Cd-Cd bonding interaction. The Cd-Cd distance in 3 is also ca. 0.05 Å longer than the value of 2.576(1) Å found in the ionic cadmium(I) salt 1^6 and is ca. 0.02 Å longer than that of 2.605 Å predicted in the as yet unknown compound Cp*CdCdCp* (6).9 A similar elongation (ca. 0.05 Å) is found for Ar'ZnZnAr' (Zn-Zn = 2.3591(9) Å)^{5b} versus Cp*ZnZnCp* $(Zn-Zn = 2.305(3) \text{ Å}).^{4a}$ The crystal structure of **3** also showed that the two Ar' ligands are arranged in a nearly orthogonal orientation to each other which provides effective steric protection of the [-Cd-Cd-]²⁺ moiety. An almost linear arrangement is observed for the [C(ipso)-Cd-Cd-C(ipso)] unit [Cd(1A)-Cd-



Figure 1. Thermal ellipsoid (30%) drawing of **3**; H atoms are not shown. Selected bond lengths (Å) and angles (deg): Cd(1)–Cd(1A) 2.6257(5), Cd-(1)–C(1) 2.138(3); Cd(1A)–Cd(1)–C(1) 177.5(3), C(2)–C(1)–Cd(1) 116.5(6), C(6)–C(1)–Cd(1) 121.8(6).

 $(1)-C(1) = 177.5(3)^{\circ}$], which is very similar to the geometry observed in the zinc analogue 5.

With a spin of $1/_2$ and a natural abundance of 12.22%, 113Cd has a receptivity relative to ¹³C of 7.6 and is widely employed as a useful method to characterize cadmium compounds.¹³ A solution ¹¹³Cd NMR spectrum of aryl cadmium halide 4 displayed only one signal at 210.91 ppm, which lies between the 328.80 ppm signal observed for the bis(aryl)cadmium species Cd(C₆H₅)₂ (1.0 M) and the 55.13 ppm for CdI₂ (1.0 M).¹⁴ In contrast, **3** displayed a signal at 540.28 ppm with two symmetrically disposed satellite resonances in the correct intensity ratio for coupling to a bound ¹¹¹Cd nucleus $(I = \frac{1}{2}, 12.81\%)$ (see Figure 2). The ¹¹³Cd NMR spectrum thus ruled out the possibility of an Ar'CdH¹⁵ species since the aryl cadmium hydride would yield a 1:1 doublet or 1:2:1 triplet pattern [for monomeric or doubly hydrogen bridged structures, respectively] instead of the satellite pattern observed in the spectrum of 3. The large ¹¹¹Cd-¹¹³Cd coupling constant of 8650 Hz is well outside the reported range of Cd-H couplings: for example, ¹J(¹¹³Cd-¹H) = 2520 Hz in Tp^{Bu'}CdH (Tp^{Bu'} = hydrotris(3-*tert*-butylpyrazolyl)borate),^{7 2} $J(^{113}Cd^{-1}H)$ of ca. 50 Hz,^{14,16} and $^{3}J(^{113}Cd^{-1}H)$ of ca. 60 Hz in dialkyl cadmium compounds.14,16 The satellite signals in 3 are thus assigned to ¹¹¹Cd-¹¹³Cd coupling. The intensity of these two satellite signals was in reasonable agreement with the theoretical value of ca. 1:7 based on the isotopic ratio. However, the ¹¹¹Cd-¹¹³Cd coupling constant is less than half the previous reported value of 20 650 Hz for 2.7

Spin-restricted DFT calculations were performed on Ar'CdCdAr' (3) at B3LYP/6-31 g* level using a simplified model where the isopropyls were replaced by hydrogen atoms and the coordinates



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



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

were extracted from the X-ray structure.17 The calculations showed that the HOMO corresponded to a σ -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 $5p_x$ and $5p_y$ 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.⁴ 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 Cd₂Tp^{Me₂}.

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 ¹¹³Cd 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.

Acknowledgment. We thank the National Science Foundation for financial support. R.C.F. thanks the Max Kade foundation for a postdoctoral fellowship. E.R. thanks NSERC of Canada for a postdoctoral fellowship.

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.

References

- (1) Parkin, G. Science 2004, 305, 1117-1118
- (2) Corbett, J. D.; Burkhard, W. J.; Druding, L. F. J. Am. Chem. Soc. 1961, 83 76-80
- (3) Taylor, M. J. Metal to Metal Bonded States of the Main Group Elements, Academic: London, 1975; Chapter 2. (a) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**,
- 305, 1136-1138. (b) del Río, D.; Galindo, A.; Resa, I.; Carmona, E. Angew. Chem., Int. Ed. 2005, 44, 1244-1247.
- Angew. Chem., Int. Ed. 2005, 44, 1244 (1247).
 Other examples of Zn–Zn bonded compounds can be found in (a) Wang,
 Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.;
 Schleyer, P. v. R.; Schaefer, H. F., III; Robinson, G. H. J. Am. Chem.
 Soc. 2005, 127, 11944–11945. (b) Zhu, Z.; Wright, R. J.; Olmstead, M. (5)M.; Rivard, E.; Brynda, M.; Power, P. P. Angew. Chem., Int. Ed. 2006, 45. 5807-5810.
- (a) Faggiani, R.; Gillespie, R. J.; Vekris, J. E. J. Chem. Soc., Chem. (a) Faggiani, K., Ginespie, K. J., Vekis, J. E. J. Chem. Soc., Chem. Commun. **1986**, 517–518. (b) Staffel, T.; Meyer, G. Z. Anorg. Allg. Chem. **1987**, 548, 45–54.
- (7) Reger, D. L.; Mason, S. S.; Rheingold, A. L. J. Am. Chem. Soc. 1993, 115, 10406-10407.
- (8) Zn-Zn and Cd-Cd bonded molecular species have been detected Spectrs and Cd Cd Fonded inforcural spectrs have been detected, spectrs copically in frozen matrices at low temperature. Greene, T. M.; Brown, W.; Andrews, L.; Downs, A. J.; Chertihin, G. V.; Runeberg, N.; Pyykkö, P. J. Phys. Chem. 1995, 99, 7925–7943.
 (a) Xie, Z.-Z.; Fang, W.-H. Chem. Phys. Lett. 2005, 404, 212–216. (b) Kang, H. S. J. Phys. Chem. A 2005, 109, 4342–4351.
- (10) All manipulations were carried out under anaerobic and anhydrous conditions. 4: Ar'Li^{10a} (1.11 g, 2.73 mmol) and CdI₂ (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 (Li)). 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. Yieldi 1.17 g, 67.2%; mp 287 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.07 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.6Hz), 1.24 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.9Hz), 2.99 (sept, 4H, CH(CH₃)₂, ³J_{HH} = 7.2Hz), 7.13-7.31 (m, 9H, m-C₆H₃, p-C₆H₃, m-Dipp, and p-Dipp). ¹³C {¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ 24.5 (CH(CH₃)₂, 25.2 (CH(CH₃)₂), 30.6 (CH(CH₃)₂), 123.7 (m-Dipp), 126.7 (p-C₆H₃), 127.8 (p-Dipp), 128.9 (m-C₆H₃), 144.2 (*i*-Dipp), 146.6 (o-C₆H₃), 148.2 (o-Dipp), 162.3 (*i*-C₆H₃). ¹¹³Cd {¹H} NMR^b(C₆D₆, 133.1 MHz, 25 °C): δ 210.91. **3**: The iodic derivative **4** (1.00 g, 1.57 mmol) and NaH (0.075 g, 3.14 mmol) were combined with THF (50 mL) by hexane (50 mL). The slurry was allowed to settle, and the mother 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. ¹H NMR decomposition of **3** to a gel-like grey solid was seen at 182 °C. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.05 (d, 12H, CH(CH₃)₂, ${}^{3}J_{HH} = 7.2Hz)$, 1.12 (d, 12H, CH(CH₃)₂, ${}^{3}J_{HH} = 6.6Hz)$, 2.95 (sept, 4H, CH(CH₃)₂, ${}^{3}J_{HH} = 6.9Hz)$, 7.10–7.27 (m, 9H, m-C₆H₃, p-C₆H₃, m-Dipp, and p-Dipp). ¹³C {¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ 24.3 (CH(CH₃)₂), 24.9 (CH-(CH₃)₂), 30.4 (CH(CH₃)₂), 122.9 (m-Dipp), 125.8 (p-C₆H₃), 127.1 (p-Dipp), 128.6 (m-C₆H₃), 144.0 (*i*-Dipp), 147.0 (o-C₆H₃), 147.2 (o-Dipp), 176.5 (*i*-C₆H₃). ¹¹³Cd {¹H} NMR^b (C₆D₆, 133.1 MHz, 25 °C): δ 540.28 (${}^{1}J_{CdCd}$ = 8650Hz). (a) Schiemenz, B.; Power, P. P. Angew. Chem., Int. Ed. 1996, 35. 2150–2152. (b) Chemical shifts are reported in ppm with respect to 35, 2150-2152. (b) Chemical shifts are reported in ppm with respect to crystallographic data for **3** at 223 K with Mo Kα radiation ($\lambda = 0.71073$
- (11)Å). **3**: monoclinic, space group C2/*m*, a = 15.2430(9), b = 17.3351(11), c = 15.0018(9) Å, $\beta = 120.5340(10)^\circ$, Z = 2, R1 = 0.0363 for 2872 (*I*) $2\sigma(I)$) data, wR2 (all data) = 0.1018.

- Cardin, A. D.; Ellis, P. D.; Odom, J. D.; Howard, J. W., Jr. J. Am. Chem. Soc. 1975, 97, 1672-1679.
- (15) Full details of the preparation and structure of the aryl cadmium hydride intermediate species Ar'CdH will form part of a full account of our work on Cd–Cd bonded compounds.
 (16) Turner, C. J.; White, R. F. M. J. Magn. Reson. 1977, 26, 1–5.
- (17) The single point (SP) calculations were performed using Gaussian 03 software: Frisch, M. J.; et al. Gaussian 03, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003 (see Supporting Information for full reference). The representations of Kohn–Sham orbitals were generated using MOLEKEL package: Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. MOLEKEL, version 4.3; Swiss Center for Scientific Computing: Manno, Switzerland, 2000-2002.

JA066108H