

Intramolecularly coordinated organocadmium iodides



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ABSTRACT

The synthesis of the compounds $[L^1Cd(\mu-I)]_2$ (**1**), $L^2Cd(\mu-I)_2 \cdot Li(THF)_2$ (**2**), and $[L^3 \cdot CdI_2]$ (**3**) with $L^1 = \{2,6-(Me_2NCH_2)_2C_6H_3\}^-$, $L^2 = \{2,6-[(CH_3)C=N(C_6H_3-2',6'-iPr_2)]_2C_6H_3\}^-$ and $L^3 = \{2-[(CH_3)C=N(C_6H_3-2,6-iPr_2)]-6-(CH_3O)C_5H_3N\}$ is reported. The compounds were characterized by elemental analyses, 1H and ^{13}C NMR spectroscopy, and single crystal X-ray diffraction analyses

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1. Introduction

Synthesis of organoderivatives RMMR (R is organic or related substituent) of the group 12 elements (Zn, Cd, and Hg) having M–M bond has proven to be a considerable synthetic challenge. The molecular M(I) compounds of formula RMMR were thought to exist only as short-lived transient species [1]. In 1999, Apeloig and co-workers reported the first stable, molecular, σ -bonded mercury(I) compound in the form of the silyl derivative $Hg_2[Si(SiMe_2SiMe_3)_2]_2$ [2]. In 2004, the landmark compound, $Zn_2Cp_2^*$ ($Cp^* = C_5Me_5$) featuring a Zn–Zn bond was reported by Carmona and co-workers [3]. Subsequent work led to the preparation and characterization of $Zn_2[HC(CMeNAr)_2]_2$ ($Ar = 2,6-iPr_2C_6H_3$) [4] and Zn_2Ar_2 ($Ar = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$) [5]. Later on, the first structurally characterized stable molecular species containing a Cd–Cd bond was reported [6]. In 2007, Power and co-workers reported on the synthesis of the homologous M–M bonded compounds $ArMMAr$ (M is Zn, Cd, or Hg) that were stabilized by sterical bulky ligand $\{2,6-(C_6H_3-2,6-iPr_2)_2C_6H_3\}^-$ [2]. As the synthesis of the organoderivatives RMMR is usually accompanied with the reduction of the parent arylmetal halides $ArMX$ ($X = Cl, Br$ or I), the synthesis of the latter precursors is thus very important step.

The field of main group element demonstrated that application of Y,C,Y-chelating build-in ligands can be an alternative pathway to sterical demanding ligands for the stabilization of the metal–metal

bonds, where the metal atoms are in the formal oxidation state +I [7].

However, the literature search showed that the applying of N,C- or N,C,N-chelating ligands in the chemistry of Zn or Cd provided homoleptic intramolecularly N-stabilized organozinc, or cadmium compounds of the general formula MR_2 ($M = Zn, Cd$; $R = \{2-(CH_2NEt_2)C_6H_4\}^-$, $\{2,6-(CH_2NMe_2)_2C_6H_3\}^-$, $\{2,6-(CH_2NEt_2)_2C_6H_3\}^-$, $\{2,6-[CH=N(2',6'-iPr_2C_6H_3)]_2C_6H_3\}^-$, $\{(CH_2)_3NMe\}^-$, or $\{(CH_2)_3NC_5H_{10}\}^-$) [8]. Similarly, the group of Beck and Schmidt used C,N-chelating ligand $\{[(2,6-iPr_2C_6H_3)N=CH]C_6H_3(OCH_2O)\}^-$ for the synthesis of homoleptic organozinc compound $Zn\{[(2,6-iPr_2C_6H_3)N=CH]C_6H_3(OCH_2O)\}_2$, regardless of the stoichiometry used [9]. Finally, Liu and co-workers reported on the synthesis of $\{2,6-[CH=N(2',6'-iPr_2C_6H_3)]_2C_6H_3\}ZnEt$ by the use of N,C,N-chelating ligand [10]. These examples demonstrate, that the monoanionic N,C,N-chelating ligands were not able to stabilize the parent organozinc, or cadmium halides $ArMX$ ($X = Cl, Br$ or I).

This forces us to apply two different N,C,N-chelating ligands $\{2,6-(CH_2NMe_2)_2C_6H_3\}^-$ (hereafter, assigned as L^1) and $\{2,6-[(CH_3)C=N(C_6H_3-2',6'-iPr_2)]_2C_6H_3\}^-$ (hereafter, assigned as L^2) to stabilize heteroleptic N → Cd coordinated organocadmium iodides $[L^1Cd(\mu-I)]_2$ (**1**), $L^2Cd(\mu-I)_2 \cdot Li(THF)_2$ (**2**). We have also applied neutral N,N-chelating ligand $\{2-[(CH_3)C=N(C_6H_3-2,6-iPr_2)]-6-(CH_3O)C_5H_3N\}$ (hereafter, assigned as L^3) for the synthesis of complex $[L^3 \cdot CdI_2]$ (**3**), where monomeric CdI_2 fragment is coordinated by two N → Cd interactions. The synthesis of **3** allowed us to compare the strength of both N → Cd interactions found in organocadmium iodides **1** and **2** with those found in N-coordinated CdI_2 in **3**. It is worth noticing, that the reaction of DIMPY ligand, as a close

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neutral *N,N,N*-analogue of L^2 , with CdI_2 did not provide any complex (DIMPY = {2,6-[(CH₃)C=N(C₆H₃-2,6-^{*i*}Pr₂)]}C₅H₃N, see [Supporting Information](#)).

The compounds **1–3** were characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy, and single crystal X-ray diffractions analyses.

2. Result and discussion

2.1. Synthesis of compounds **1–3**

The treatment of L^1Li with one molar equivalent of CdI_2 yielded the $N \rightarrow Cd$ coordinated dimeric organocadmium iodide [$L^1Cd(\mu-I)$]₂ (**1**). In contrast, the reaction of L^2Li with CdI_2 provided monomeric $N \rightarrow Cd$ coordinated compound L^2CdI , that co-crystallizes with LiI to yield $L^2Cd(\mu-I)_2 \cdot Li(THF)_2$ (**2**) (see [Scheme 1](#)).

After the synthesis of $N \rightarrow Cd$ coordinated organocadmium iodides **1** and **2**, we have focused on the stabilization of $N \rightarrow Cd$ coordinated monomeric CdI_2 fragment. Thus the reaction of CdI_2 with the neutral *N,N*-chelating ligand L^3 provided the parent complex [$L^3 \cdot CdI_2$] (**3**), containing $N \rightarrow Cd$ coordinated CdI_2 fragment ([Scheme 2](#)).

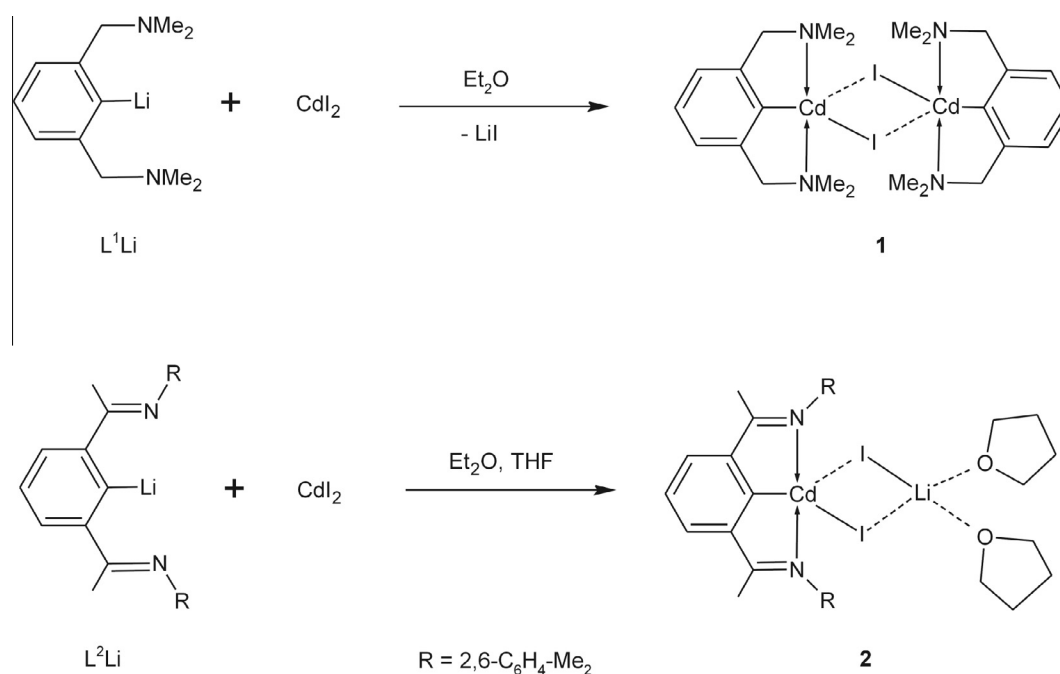
2.2. Molecular structures of **1–3**

Crystals suitable for single crystals X-ray diffraction analysis of **1** and **2**·C₇H₈ were obtained from saturated hexane (**1**) or toluene (**2**) solutions at 4 °C or –20 °C, respectively. The molecular structures of **1** and **2**·C₇H₈ are shown in [Figs. 1 and 2](#), respectively, and selected bond lengths and angles are given in [Table 1](#). The crystallographic data are given in [Table 2](#).

The molecular structure of **1** reveals the presence of centrosymmetric dimer [$L^1Cd(\mu-I)$]₂ with iodine atoms in bridging positions. The iodine atom I1a of the L^1CdI fragment coordinates cadmium atom Cd1 of the second molecule with I1a–Cd1 bond distance of 2.9288(5) Å, that is longer than the sum of the covalent radii of cadmium and iodine ($\Sigma_{cov}(Cd,I) = 2.67$ Å) [11], but shorter than the sum of the van der Waals radii ($\Sigma_{vdw}(Cd,I) = 3.56$ Å) [12] of the

corresponding atoms indicating a weak electrostatic $I \rightarrow Cd$ interaction. In addition, the Cd1 atom is coordinated by two $N \rightarrow Cd$ interactions with distances 2.6441(3) (Cd1–N1) and 2.684(3) Å (Cd1–N2), by one carbon atom (Cd1–C1 2.136(4) Å) and one iodine atom (Cd1–I1 2.7870(4) Å). As the result, compound **1** contains a five-coordinated distorted square pyramidally configured Cd1 atom with square base plane defined by the C1, I1, N1 and N2 atoms with the bond angle N1–Cd1–N2 of 145.13(11)° and C1–Cd1–I1 of 145.13(11)°. The I1a atom occupies the apical position and its distance from the square base plane is 3.4356(3) Å (0.5410(3) Å for the Cd1 atom). The overall geometry of **1** is similar to that found in organocadmium iodine [$ArCd(\mu-I)$]₂ stabilized by sterical bulky organic ligand {2,6-(2,6-^{*i*}Pr₂-C₆H₃)₂C₆H₃}[–] [2].

In **2**·C₇H₈, the cadmium atom of monomeric unit L^2CdI is further coordinated by iodine atom I2 (Cd1–I2 = 2.8042(6) Å) of LiI that was formed during the reaction. As the result, the Cd1 atom is five-coordinated by two $N \rightarrow Cd$ interactions with distances 2.566(4) Å (Cd1–N1) and 2.626(4) Å (Cd1–N2), one carbon atom (Cd1–C1 2.157(4) Å) and two iodine atoms with distances (Cd1–I1 2.8039(6) Å). The Cd1 atom shows a distorted trigonal-bipyramidal environment with the C1, I1, I2 atoms located in equatorial positions while the N1 and N2 atoms occupy the axial positions similarly to **1**. The N1–Cd1–N2 bond angle of 142.53(12)° and the I1–Cd1–I2 angle of 100.38(2)° represent the largest deviation from an ideal shape. Both Cd–I distances in **2**·C₇H₈ are similar that is in contrast to different Cd–I bond distances found in **1** (2.7870(4)/2.9288(5) Å). The overall composition of **2**·C₇H₈ can be defined as close contact ion pair consisting of Li cation and organocadmium [L^2CdI_2][–] anion. The presence of two similar Cd–I bonds can be result of the negatively charged cadmium atom in [L^2CdI_2][–] moiety. Although the Cd–I bond lengths are equal, the bond lengths of Li to I1 and I2 are significantly different (2.820(9)/2.765(9) Å). The coordination sphere of the Li cation is completed by two THF molecules. The bonding situation found in **2**·C₇H₈ closely resembles those stabilized by 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene (NacNacH) ligand in the complex $NacNacCd(\mu-I)_2 \cdot Li(OEt_2)_2$ [13]. The Cd–I bond distances (2.7518(7)/2.7920(7) Å) in the latter



Scheme 1. Synthesis of $N \rightarrow Cd$ organocadmium iodides **1** and **2**.

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