

# First Observation of Zn–CN Bond in “Highly Coordinated” Mixed Organozincates by EXAFS Spectroscopy

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Triorganozincates, symbolized as  $R_3ZnM$  ( $M = Li, Na, etc.$ ), are versatile reagents not only for the construction of carbon–carbon bonds<sup>1</sup> but also for the metalation of aromatic halides<sup>2</sup> or vinyl halides.<sup>3</sup> As a new type of zincates, we reported that “highly coordinated” zincates,  $Me_3Zn(R)Li_2$  ( $R = Me, CN, SCN$ ) are synthetically useful for the metalation of aryl halides and for the selective transference of various organic moieties to carbonyl compounds (Figure 1).<sup>4</sup> On the basis of the excellent chemical yields and the chemoselectivity, these species were considered to be differentiated from ordinary triorganozincates,  $R_3ZnLi$ . However, the reaction mechanism and the real structure of active species are a topic of controversial discussions.

On the other hand, beginning in 1981, Lipshutz *et al.* published a series of papers about “higher order” mixed cuprates,  $R_2Cu(CN)Li_2$ , implying dianionic Cu(I) species containing three covalently bonded ligands on Cu,<sup>5</sup> and the structure of these cuprates has been a controversial issue.<sup>6</sup> However, recent studies on the structure revealed that  $R_2Cu(CN)Li_2$  are not “higher order” cuprates, dianionic Cu(I) salts, but modified Gilman-type cuprates.<sup>7</sup> We now describe primary evidence supporting the existence of “highly coordinated” zincates, namely, tetracoordinated dianionic Zn(II) species, by use of EXAFS, <sup>1</sup>H NMR, and Raman spectroscopic studies.

Extended X-ray absorption fine structure (EXAFS) spectroscopy probes the local structures, *i.e.*, the nature, number, and distance of near neighbors which surround atoms or ions, of a

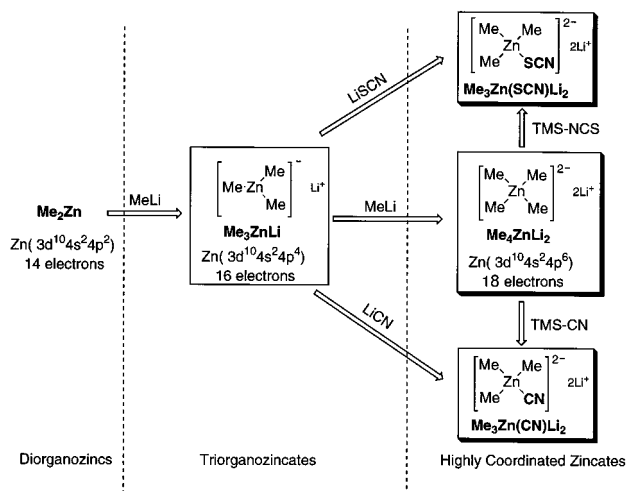


Figure 1. Classification of organozinc reagents.

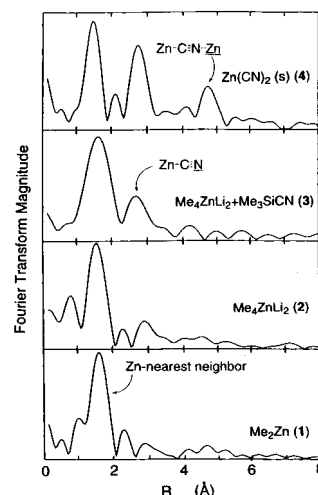


Figure 2. Fourier transform of the EXAFS spectra for compounds 1–4.

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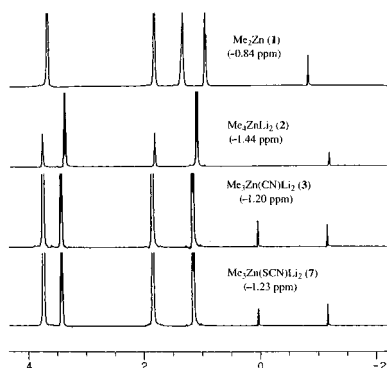
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chosen element within noncrystalline systems.<sup>8</sup> The laboratory X-ray spectrometer employed for the XAFS measurements has been described previously<sup>9</sup> as well as the details of the analysis procedure. The Fourier transform of the EXAFS data for THF solutions (*ca.* 0.2 M) of  $Me_2Zn$  (1),  $Me_4ZnLi_2$  (2), and  $Me_4ZnLi_2 + Me_3SiCN$  (3), and  $Zn(CN)_2$  (4) in the solid phase are shown in Figure 2. The spectra give a pseudoradial distribution function around the absorbing atom (Zn). Peak positions in the Fourier transform are shifted by about 0.5 Å due to phase shift. Only one and similar principal feature is observed for both 1 and 2. These peaks are attributed to Zn–C nearest neighbors. On the other hand, the Fourier transform for 3 which were prepared by the reaction of  $Me_4ZnLi_2$  (2) with  $Me_3SiCN$  in a THF solution, *i.e.*,  $Me_3Zn(CN)Li_2$  shows a second feature in addition to the nearest neighbor peak. A new peak is considered to be attributed to Zn–C–N next nearest neighbors. To be more precise, the presence of the feature indicates that the CN ligand is on the Zn atom in  $Me_3Zn(CN)Li_2$ . FEFF6 calculations have been carried out using the following model; a Zn atom is surrounded by four tetrahedrally coordinated carbon atoms, one of which is CN and the others are methyl. The observed spectrum was almost reproduced

(8) See, for example: *X-ray Absorption: Principles, Applications, and Techniques of EXAFS, SEXAFS and XANES*; Prins, R., Koningsberger, D., Eds.; Wiley: New York, 1988.

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**Figure 3.**  $^1\text{H}$  NMR spectra of organozincates in THF ( $-20\text{ }^\circ\text{C}$ ).

when Zn–C nearest neighbors and Zn–C–N next nearest neighbors distances were set to 1.96 and 3.10 Å, respectively (Supporting Information). The CN distance is calculated to be 1.14 Å, which is very close to that observed in  $\text{Zn}(\text{CN})_2$ .<sup>10</sup> Indeed, the Fourier transform for  $\text{Zn}(\text{CN})_2$  (s) (**4**) of which cyanide is coordinated to the Zn atom, have similar peaks. Moreover, a second outer shell peak is also observed for **4** (s). This peak can be assigned Zn  $\cdots$  Zn (Zn–C–N–Zn) EXAFS, since the crystal structure of  $\text{Zn}(\text{CN})_2$  is known.<sup>10</sup> Also, the existence of this peak supports that  $\text{Zn}(\text{CN})_2$  (s) is oligomeric structure, as previously reported.<sup>10</sup>

In order to obtain additional information about the structures of “highly coordinated” zincates, we measured  $^1\text{H}$  NMR and Raman spectra of organozinc reagents and other organometallic reagents. The methyl signals of  $\text{Me}_2\text{Zn}$  (**1**),  $\text{Me}_4\text{ZnLi}_2$  (**2**),  $\text{Me}_3\text{ZnLi}$  (**5**), and  $\text{MeLi}$  (**6**) in THF at  $-20\text{ }^\circ\text{C}$  were observed as sharp singlets at  $-0.84$ ,  $-1.44$ ,  $-1.08$ , and  $-1.96$  ppm, respectively (Figure 3).<sup>4a,11</sup> High-field shift of **2** from the value of **5** is considered to indicate the more anionic character of the “highly coordinated” zincates. Indeed, the crystal structure of **2** is known to be a tetracoordinated, dianionic zinc structure.<sup>12</sup> Furthermore, the methyl signals of cyano- and thiocyno-substituted “highly coordinated” zincates,  $\text{Me}_3\text{Zn}(\text{CN})\text{Li}_2$  (**3**) and  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**), prepared by the addition of 1 equiv of  $\text{Me}_3\text{SiCN}$  or  $\text{Me}_3\text{SiNCS}$  to  $\text{Me}_4\text{ZnLi}_2$  (**2**) in a THF solution, were observed as sharp singlets ( $-1.20$  ppm for **3** and  $-1.23$  ppm for **7**) together with the signal of newly generated  $\text{Me}_4\text{Si}$ .<sup>13</sup> Measurement at  $-78\text{ }^\circ\text{C}$  gave very similar results with

(10) For recent discussion on the structure of  $\text{Zn}(\text{CN})_2$ , see: Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.

(11) The  $\delta$  (ppm) values are relative to  $\beta$ -methylene proton (1.85 ppm) to THF.

(12) (a) Weiss E.; Wolfrum, R. *Chem. Ber.* **1968**, *101*, 35–40. (b) Weiss E.; Plass, H. *J. Organomet. Chem.* **1968**, *14*, 21–31. (c) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501–1523.

(13) On the other hand, the methyl signal of  $\text{Me}_3\text{SiCN}$  (0.38 ppm) or  $\text{Me}_3\text{SiNCS}$  (0.40 ppm) was not observed in the mixture.

a slightly higher field shift of each signals. Methyl signals of free  $\text{Me}_3\text{ZnLi}$  (**5**) and  $\text{MeLi}$  (**6**) were not observed in a THF solution of  $\text{Me}_3\text{Zn}(\text{CN})\text{Li}_2$  (**3**) or  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**);<sup>14</sup> however, we do not have enough evidence to neglect the possibility of the fast exchange on the NMR time scale.

These present results, *i.e.*, EXAFS and  $^1\text{H}$ -NMR studies of the  $\text{Me}_3\text{Zn}(\text{CN})\text{Li}_2$  (**3**) solution, lead us to the conclusion that the cyanide and all of the methyl groups are coordinated to the Zn atom in  $\text{Me}_3\text{Zn}(\text{CN})\text{Li}_2$ , that is, the existence of a “highly coordinated” zincate is confirmed.

Our next interest was focused on the structure of the  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**). We measured Raman spectra of  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**) and  $\text{LiSCN}$  (**8**) (Supporting Information). In the spectrum of  $\text{LiSCN}$  (top trace), a single strong band, which is assignable to the C–S stretching vibration of SCN on the Li atom or free  $\text{SCN}^-$  ion, appears at  $779\text{ cm}^{-1}$ . On the other hand,  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**) shows no band at the  $779\text{ cm}^{-1}$  (bottom trace). Namely, free  $\text{LiSCN}$  (or  $\text{SCN}^-$  ion) do not exist in a THF solution of  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**). From the  $^1\text{H}$  NMR study, it is also evident that  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**) is a new species of zincate. Therefore, no peak at  $779\text{ cm}^{-1}$  for  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**) solution provides support for the SCN ligation on the Zn atom, *i.e.*, the existence of “highly coordinated” zincate.

In conclusion, the combination of the results obtained from extended X-ray absorption fine structure (EXAFS),  $^1\text{H}$  NMR, and Raman spectroscopies of cyano- and thiocyno-substituted “highly coordinated” zincates strongly support that  $\text{Me}_3\text{Zn}(\text{CN})\text{Li}_2$  (**2**) and  $\text{Me}_3\text{Zn}(\text{SCN})\text{Li}_2$  (**7**) are tetracoordinated, dianionic zinc structures, namely, “highly coordinated” zincates, and the CN or SCN ligand is directly coordinated to the Zn atom in these zincates. The conclusion is also consistent with the fact that highly coordinated zincates have a higher and unique reactivity compared to triorganozincates.<sup>4</sup> Further studies on the structural analyses and the theoretical approach with the help of *ab initio* calculations of the highly coordinated organozincates are underway in addition to the investigation of the applications for organic syntheses.

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**Supporting Information Available:** Details of sample preparation for the zincates, conditions used for EXAFS measurements, EXAFS analyses,  $k^3$ -weighted EXAFS spectra, FEFF6 simulations, and Raman spectra (6 pages). See any current masthead page for ordering and Internet access instructions.

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(14) Addition of one more equivalent of  $\text{MeLi}$  to the  $\text{Me}_4\text{ZnLi}_2$  solution showed a broad singlet signal at  $-1.49$  ppm at  $-20\text{ }^\circ\text{C}$  which separated at  $-78\text{ }^\circ\text{C}$  into two signals corresponding to  $\text{MeLi}$  and that of  $\text{Me}_4\text{ZnLi}_2$ .