Dinuclear versus Mononuclear Zinc Compounds from Reduction of $LZnCl_2$ (L = α-Diimine Ligands): Effects of the Ligand Substituent, Reducing Agent, and Solvent

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Received May 6, 2008

A Zn−Zn-bonded compound, $[K(THF)_2]_2[(L^{iPr})Zn-Zn(L^{iPr})]$ (**2**) and three mononuclear zinc compounds, $[Zn(L^{Me})_2Na_2(Et_2O)_2]$ (**3**), $[Zn(L^{Et})_2Na_2(THF)_2]$ (**4**), and $[Zn(L^{Et})_2K_2]_n$ (**5**), with N-aryl substituted α-diimine ligands L^{iPr}, L^{Me}, and L^{Et} ($L = [(2,6\text{-}R_2C_6H_3)N(Me)C]_2$, R = ^{i}Pr, Me, Et, respectively) have been synthesized from the reduction of the $LZnCl_2$ precursors by the alkali metal Na or K. X-ray structural analyses show that the compounds have a $[Zn_2L_2]^{2-}$ (**2**) or $[ZnL_2]^{2-}$ (**3**−**5**) core incorporating Na^+ or K^+ ions solvated by THF or Et_2O molecules, except for **5**, which displays a 2D polymeric structure formed by intermolecular K−C bonds due to the lack of K−solvent interactions. In compound **2**, the formal Zn^{2+} ion in the precursor is reduced to Zn^+, while in **3**−**5** it remains unreduced. The neutral ligands in the precursor, however, are doubly reduced to a dianion, L^{2-}, in all compounds, as evidenced by the bond lengths of the N–C═C–N moiety of the ligands. Effects of the ligand substituent, reducing agent, and solvent on the products have been studied, which reveal that the steric bulk of the ligand is the most important factor that determines whether the Zn−Zn bond can be formed. DFT computations show that the Zn−Zn bond in **2** is formed mainly by the 4s orbitals of zinc. The results of natural charge and orbital analyses also confirm the reduction of the ligands to their dianionic forms.

Introduction

Metal−metal bonding is an important and fundamental dimension of chemistry.[1] One of the effective approaches for generating metal−metal (multiple) bonds is reduction of suitable metal−ligand−halide precursors with various reducing agents, especially alkali metals. Appropriate protective ligands are often essential in the stabilization of metal−metal bonds, and different ligand substituents can have a great impact on the structures of the products.[2] Zn−Zn-bonded compounds have attracted considerable recent attention since the report of the first Zn−Zn bond in 2004.[3] A variety of supporting ligands have been used for the synthesis of [RZn−ZnR] compounds, including Cp derivatives,[3,4] the β-diketiminate $HC[C(Me)N(C_6H_3\text{-}2,6\text{-}{}^iPr_2)]_2$,[5] terphenyl ligands,[6] and the N-donor ligand η^2-$Me_2Si(NDipp)_2$.[7]

Recently we reported a Zn−Zn-bonded compound, $[Na(THF)_2]_2[(L^{iPr})Zn-Zn(L^{iPr})]$ (**1**; L^{iPr} = $[(2,6\text{-}{}^iPr_2C_6H_3)N(Me)C]_2$), obtained by reduction of L^0ZnCl_2 (L^0 is the neutral α-diimine ligand) with sodium metal. The neutral ligand has been doubly reduced to L^{2-}.[8] A similar compound using another α-diimine ligand, [(dpp-Bian)Zn−Zn(dpp-Bian)] (dpp-Bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), has also been synthesized, in which the ligand is the radical anion L^-.[9] To further explore α-diimine-supported metal−metal bonding, we have examined the reduction of $LZnCl_2$ precursors bearing α-diimine ligands with 2,6-substituents on the *N*-phenyl ring (L^{iPr}, L^{Me}, L^{Et}). Herein we report experimental and

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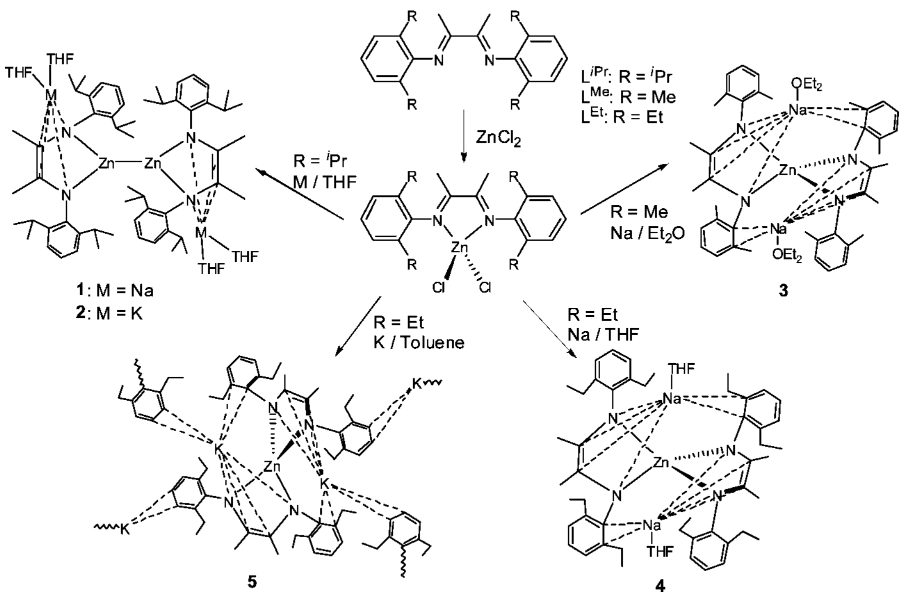
Scheme 1. Synthesis of the Compounds 2−5



theoretical (DFT) studies of the resultant Zn−Zn-bonded compound **2** and the mononuclear Zn compounds **3**−**5**, the latter representing very rare examples of Zn^{II} complexes with two doubly reduced α-diimine ligands (Scheme 1). The influence of ligand system, reducing agent, and solvent on the structure of the product is also discussed.

Results and Discussion

Synthesis. The LZnCl$_2$ compounds were obtained by the reaction of ZnCl$_2$ with the corresponding ligand L. The precursors were reduced by different reagents such as Li, Na, K, Mg, and Ca in a variety of solvents (THF, diethyl ether, and toluene), which led to mono- or dinuclear Zn compounds with different structures (Scheme 1).

The reduction of (L^{iPr})ZnCl$_2$ by potassium in THF resulted in the Zn−Zn-bonded compound [K(THF)$_2$]$_2$[(L^{iPr})Zn−Zn(L^{iPr})] (**2**), as in the case of the sodium reduction.[8] When the 2,6-dimethyl-substituted precursor (L^{Me})ZnCl$_2$ was used, the reduction by Na in Et$_2$O gave a mononuclear compound, [Zn(L^{Me})$_2$Na$_2$(Et$_2$O)$_2$] (**3**), as yellow crystals. Reaction of the diethyl precursor (L^{Et})ZnCl$_2$ with Na or K also yielded mononuclear zinc compounds. The reduction by Na in THF resulted in the monomeric compound [Zn(L^{Et})$_2$Na$_2$(THF)$_2$] (**4**), which is similar to **3** with L^{Me}. However, using toluene as solvent, the reduction of (L^{Et})ZnCl$_2$ by K led to an orange-red, polymeric compound, [Zn(L^{Et})$_2$K$_2$]$_n$ (**5**). These compounds are highly air- and moisture-sensitive. The compounds **3** and **4** are quite thermally stable up to 80 °C (decomposition), while **2** and **5** slowly decompose upon storage at room temperature for several days under argon. The reduction of the precursors by Li, Mg, or Ca led to a red solution in some cases. Unfortunately, we have not isolated any products from the solutions.

X-ray Crystal Structures. Single crystals suitable for X-ray diffraction studies were obtained in diethyl ether (**3**), THF (**2** and **4**), and toluene (**5**). The molecular structures of **2**−**5** are depicted in Figures 1−4, while the selected bond lengths and angles are given in Tables 1−4.

The compound [K(THF)$_2$]$_2$[(L^{iPr})Zn−Zn(L^{iPr})] (**2**) is indeed isomorphous with its sodium analogue **1**[8] with similar structural features (Figure 1, Table 1), except that the C$_2$N$_2$ planes of the two ligands are nearly coplanar in **2** while they are parallel in **1** (vertical distances of 0.70 and 1.28 Å, respectively). The Zn−Zn bond length in **2** (2.393(1) Å) is almost identical with that in the sodium analogue (2.399(1) Å). As in **1**, the formal divalent Zn^{2+} ion is reduced to Zn^{+}, and the neutral α-diimine ligand is doubly reduced to the dianion [L^{iPr}]$^{2-}$, whose negative charges are further compensated by a solvated K^{+} ion. Notably, the ionic [(L^{iPr})Zn−Zn(L^{iPr})]$^{2-}$ core in the two compounds (**1** and **2**) is significantly different from that of a similar Zn−Zn-bonded compound bearing the α-diimine ligand dpp-Bian, [(dpp-Bian)Zn−Zn(dpp-Bian)], in which the dpp-Bian ligand is only singly reduced to a radical anion, leading to a neutral [LZn−ZnL] compound.[9]

Switching the phenyl ligand substituents from 2,6-diisopropyl to the less crowded 2,6-dimethyl led to the mononuclear compound [Zn(L^{Me})$_2$Na$_2$(Et$_2$O)$_2$] (**3**). The zinc atom is four-coordinated by the nitrogen donors of two L^{Me} ligands in a distorted-tetrahedral geometry (Figure 2). The mean Zn−N bond length (2.05 Å) for **3** is comparable to those in **1** (2.02 Å) and **2** (2.01 Å). The two N−Zn−N bite angles are nearly the same (82.3 and 82.7°), but the N1−Zn−N4 angle of 144.6(1)° is significantly widened. In contrast to the parallel/coplanar arrangement for the two ligand molecules in the Zn−Zn-bonded **1** and **2**, the two C$_2$N$_2$ planes are nearly perpendicular to each other (dihedral angle 84.7°). The zinc

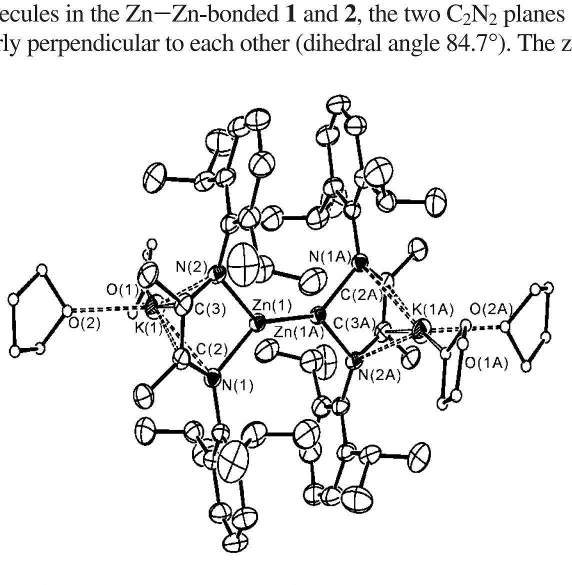


Figure 1. Molecular structure of **2** (thermal ellipsoids at the 20% probability level, with atoms of the solvent THF drawn as smaller spheres and hydrogen atoms omitted for clarity).

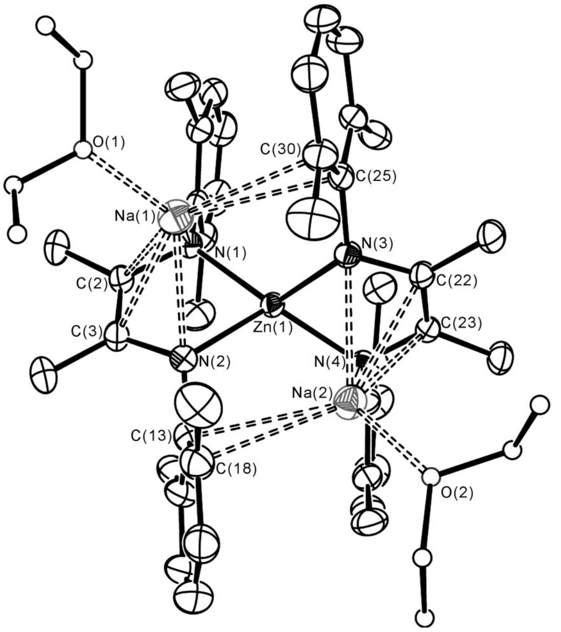


Figure 2. Molecular structure of **3** (thermal ellipsoids at the 20% probability level, with the atoms of Et_2O drawn as smaller spheres and hydrogen atoms omitted).

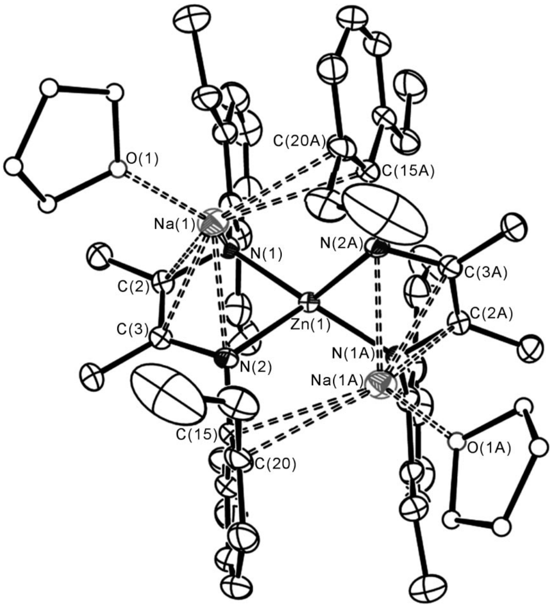


Figure 3. Molecular structure of **4** (thermal ellipsoids at the 20% probability level, with the atoms of THF drawn as smaller spheres and hydrogen atoms omitted).

atom deviates slightly from the C_2N_2 plane (~0.45 Å). Furthermore, compound **3** also incorporates two sodium ions, as in **1** and **2**, but each is solvated by only one Et_2O molecule. The Na atoms are located over the C_2N_2Zn ring and are η^4-bonded by the N–C═C–N moiety with Na−C distances in the range 2.677(4)−2.734(4) Å and Na−N distances in the range 2.488(4)−2.621(3) Å. There are two additional Na−C contacts (Na1−C25, Na1−C30, Na2−C13, and Na2−C18) of each Na atom with the ipso and 2-position carbon atoms of the phenyl ring of another ligand (Figure 2, Table 2). These contacts, although longer (~2.96 Å) than the Na−C(C_2N_2) bonds, drive the two solvated $Na(OEt_2)^+$ units to sit above two triangular faces of the ZnN_4 tetrahedron with a Na−Zn−Na angle of 100.6° and a Na···Na separation of 4.41 Å.

Compounds **4** and **5**, obtained from the 2,6-diethyl-substituted precursor $(L^{Et})ZnCl_2$, which has medium steric bulk between the isopropyl and methyl analogues, also feature the mononuclear $[ZnL_2]^{2-}$ core. The compound $[Zn(L^{Et})_2Na_2(THF)_2]$ (**4**) is structurally similar to **3** with L^{Me}. The Zn^{2+} center is tetrahedrally coordinated by two ligand molecules, with the N1−Zn1−N2 bite angle being 82.4(2)° and the N1−Zn1−N1A angle widened (149.9(3)°) (Table 3). The two N–C═C–N planes in **4** deviate slightly from the orthogonal conformation (dihedral angle 79.2° compared to 84.7° in **3**). The major differences between **3** and **4** are that the latter possesses a *C*2 axis bisecting the N1−Zn−N1A and N2−Zn−N2A angles (while **3** lacks the crystallographically imposed *C*2 symmetry), and the coordination sphere of the Na ions is completed by a THF molecule instead of Et_2O (Figure 3). As in **3**, the additional Na−C(aryl) bonds in **4** resulted in a Na−Zn−Na angle of 95.2° and Na···Na separation of 4.21 Å.

In contrast to the monomeric manner of **4**, the other compound (**5**) with the L^{Et} ligand exhibits a polymeric structure, $[Zn(L^{Et})_2K_2]_n$. The coordination sphere of the zinc atom in the $[Zn(L^{Et})_2K_2]$ unit resembles that in **3** and **4**, and there is also a 2-fold axis in the $[Zn(L^{Et})_2K_2]$ moiety (Figure 4a). The K atoms are η^4-bonded by the C_2N_2 moiety and are in contact with two additional C atoms of one phenyl ring in another ligand, with a K−Zn−K angle of 104.2° and K···K separation of 5.14 Å (Table 4). However, due to the lack of a coordinating solvent molecule, the "unsaturated" K^+ ion forms two intermolecular K−C bonds with the phenyl 3- and 4-carbons of another unit. Thus, each $[Zn(L^{Et})_2K_2]$ unit is linked to four adjacent molecules, resulting in a two-dimensional network in the *ab* plane (Figure 4b). This aggregation is remarkably different from the other four compounds (**1**−**4**) obtained in either THF or ether. The polymeric zinc(II) complexes $[K(THF)ZnMe(L^{2-})]_n$ and $[K(Et_2O)_{1/2}Zn(CH_2Ph)(L^{2-})]_n$ (L = *t*-BuNCHCHN-*t*-Bu) have been reported; however, both of them show a linear chain structure (one-dimensional), where further extension is prevented by the solvation of the K^+ ion.[10]

The mononuclear compounds (**3**−**5**) and the dinuclear compounds (**1** and **2**) have different charge distributions. The diimine ligands are doubly reduced in all cases, but the zinc remains a formal Zn^{2+} dication in **3**−**5** with a composition of $[Zn^{2+}(L^{2-})_2(M^+)_2]$ (M = Na, K), while in **1** and **2** the Zn^{2+} is reduced to Zn^+, $[(Zn^+)_2(L^{2-})_2(M^+)_2]$. The synthesis of the dinuclear compounds is represented by eq 1, in which 3 equiv of the alkali metal is consumed to provide one electron to the Zn^{2+} center and two electrons to the neutral ligand. The formation of the mononuclear species, on the other hand, is due to the disproportionation of the first formed Zn^I compounds to the Zn^{II} products and zinc metal (eq 2), as confirmed by the observation of Zn metal in the reaction system. To further prove this mechanism, we carried out the reduction of the $(L^{Me})ZnCl_2$ precursor with Na in the presence of equimolar free ligand to convert all Zn to the desired mononuclear product, as shown in eq 3. As expected, only a trace of zinc was formed in this case, indicating a greatly lowered degree of the disproportionation (though this did not completely disappear).

$$2LZn^{II}Cl_2 + 6M \rightarrow [Zn^I{}_2L_2M_2] + 4MCl \tag{1}$$

$$[Zn^I{}_2L_2M_2] \rightarrow [Zn^{II}L_2M_2] + Zn^0 \tag{2}$$

$$LZn^{II}Cl_2 + L + 4M \rightarrow [Zn^{II}L_2M_2] + 2MCl \tag{3}$$

The existence of the ligand as a dianionic species is evidenced by a change in the N═C–C═N moiety. Upon uptake of electrons

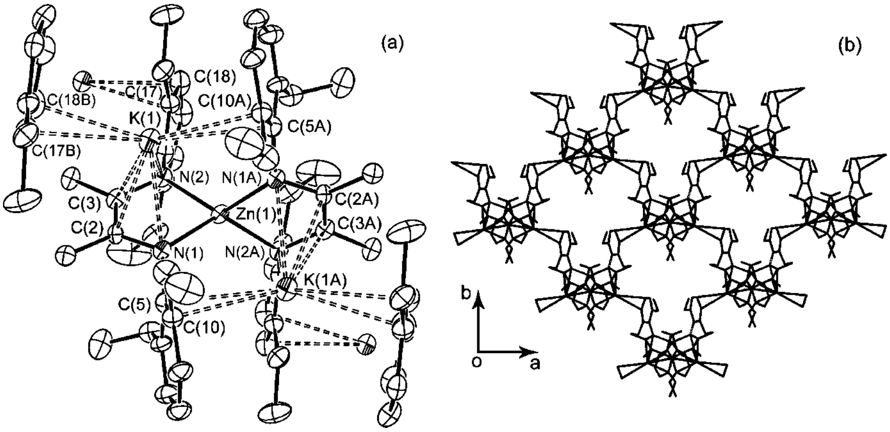


Figure 4. (a) Molecular structure of **5** (thermal ellipsoids at the 20% probability level, with hydrogen atoms omitted). (b) The two-dimensional network in the *ab* plane formed by intermolecular K−C bonds.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 2[a]

Zn(1)−Zn(1A)	2.3934(8)	K(1)−O(2)	2.721(7)
Zn(1)−N(1)	2.015(3)	K(1)−C(2)	2.897(4)
Zn(1)−N(2)	2.005(3)	K(1)−C(3)	2.907(4)
Zn(1)•••K(1)	3.340(1)	C(2)−C(3)	1.363(5)
K(1)−N(1)	2.940(3)	N(1)−C(2)	1.409(5)
K(1)−N(2)	2.950(3)	N(2)−C(3)	1.410(5)
K(1)−O(1)	2.626(4)		
N(1)−Zn(1)−Zn(1A)	138.61(9)	N(2)−Zn(1)−Zn(1A)	137.82(9)
N(1)−Zn(1)−N(2)	82.89(12)		

[a] Symmetry code: (A) 1 − *x*, 2 − *y*, −*z*.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Zn(1)−N(1)	2.014(3)	Na(2)−N(3)	2.621(3)
Zn(1)−N(2)	2.096(3)	Na(2)−N(4)	2.488(4)
Zn(1)−N(3)	2.099(3)	Na(2)−C(22)	2.734(4)
Zn(1)−N(4)	2.001(3)	Na(2)−C(23)	2.677(4)
Zn(1)•••Na(1)	2.850(2)	Na(2)−O(2)	2.282(4)
Zn(1)•••Na(2)	2.879(2)	Na(2)−C(13)	2.945(4)
Na(1)−N(1)	2.502(4)	Na(2)−C(18)	2.912(5)
Na(1)−N(2)	2.571(4)	C(2)−C(3)	1.350(6)
Na(1)−C(2)	2.684(5)	C(22)−C(23)	1.347(5)
Na(1)−C(3)	2.711(5)	N(1)−C(2)	1.410(5)
Na(1)−O(1)	2.266(4)	N(2)−C(3)	1.431(5)
Na(1)−C(25)	2.949(4)	N(3)−C(22)	1.429(5)
Na(1)−C(30)	3.021(5)	N(4)−C(23)	1.424(5)
N(1)−Zn(1)−N(2)	82.3(1)	N(2)−Zn(1)−N(3)	109.7(1)
N(1)−Zn(1)−N(3)	118.6(1)	N(2)−Zn(1)−N(4)	118.8(1)
N(1)−Zn(1)−N(4)	144.6(1)	N(3)−Zn(1)−N(4)	82.7(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 4[a]

Zn(1)−N(1)	1.993(4)	Na(1)−O(1)	2.278(6)
Zn(1)−N(2)	2.103(4)	Na(1)−C(15A)	2.958(6)
Zn(1)•••Na(1)	2.849	Na(1)−C(20A)	2.911(7)
Na(1)−N(1)	2.474(5)	C(2)−C(3)	1.347(8)
Na(1)−N(2)	2.585(5)	N(1)−C(2)	1.418(7)
Na(1)−C(2)	2.644(6)	N(2)−C(3)	1.432(7)
Na(1)−C(3)	2.695(7)		
N(1)−Zn(1)−N(2)	82.4(2)	N(1)−Zn(1)−N(1A)	149.9(3)
N(1)−Zn(1)−N(2A)	115.4(2)	N(2)−Zn(1)−N(2A)	110.3(3)

[a] Symmetry code: (A) 1 − *x*, *y*, 0.5 − *z*.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5[a]

Zn(1)−N(1)	2.090(6)	K(1)−C(5A)	3.171(7)
Zn(1)−N(2)	2.008(5)	K(1)−C(10A)	3.080(8)
Zn(1)•••K(1)	3.256(2)	K(1)−C(17B)	3.30(1)
K(1)−N(1)	2.956(7)	K(1)−C(18B)	3.10(1)
K(1)−N(2)	2.911(6)	C(2)−C(3)	1.36(1)
K(1)−C(2)	2.941(8)	N(1)−C(2)	1.412(8)
K(1)−C(3)	2.956(7)	N(2)−C(3)	1.426(9)
N(1)−Zn(1)−N(2)	83.0(2)	N(1)−Zn(1)−N(1A)	113.0(3)
N(1)−Zn(1)−N(2A)	122.8(3)	N(2)−Zn(1)−N(2A)	135.3(3)

[a] Symmetry codes: (A) 1 − *x*, *y*, 0.5 − z; (B) 0.5 − *x*, *y* − 1.5, 0.5 − *z*.

the C−N bonds are elongated and the central C−C bond shortened from the neutral ligand to monoanion L^{-} and then to the dianion. In the present work, the C−N bond lengths of **1**−**5** fall in the range 1.409−1.431 Å, which are significantly longer than those for the free ligands (1.275−1.283 Å). Meanwhile, the C−C bond is shortened to 1.347−1.358 Å, in comparison to the length in the free ligands (1.498−1.504 Å).[11] These distances correspond to the dianionic enediamido form (N–C=C–N), as is confirmed by the DFT computations described below. In all compounds **1**−**5**, half of the negative charge of the dianion, −1, is compensated by a Na^{+} or K^{+} ion attaching to the N–C=C–N moiety. The average Zn•••Na and Zn•••K contacts are 2.86 and 3.30 Å, respectively. Mononuclear Zn compounds with other diimine ligands in different combinations of the three oxidation states (neutral, radical anionic, and dianionic), e.g. $[Zn^{II}(L^{2-})(L^{-})]^{-}$, $[Zn^{II}(L^{-})_2]$, and $[Zn^{II}(L^{0})(L^{-})]^{+}$, have been reported.[12−14] However, structures of $[Zn(L^{2-})_2]^{2-}$ compounds that contain two dianionic ligands are not yet known.[13]

It would be very instructive to correlate the reaction conditions (e.g., the ligand environment, reducing agent, and solvent) with the products from the reduction of $LZnCl_2$. Generally the electronic factor and steric bulk of the ligands can have a significant effect on the structure of the resulting metal compounds. In the present work the ligand steric effect is dominant and plays a critical role in the formation of the

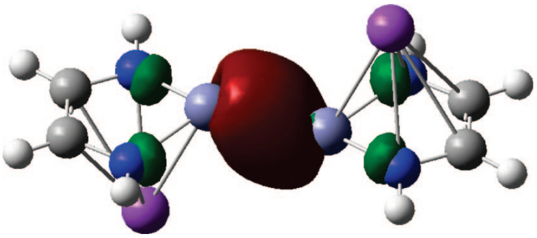


Figure 5. HOMO-2 of the model compound **2H**.

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Table 5. Crystallographic Data and Refinement Details for Compounds 2−5

	2	3	4	5
empirical formula	$C_{72}H_{112}K_2N_4O_4Zn_2$	$C_{48}H_{68}N_4Na_2O_2Zn$	$C_{56}H_{80}N_4Na_2O_2Zn$	$C_{48}H_{64}K_2N_4Zn$
fw	1306.70	844.41	952.59	840.66
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$C2/c$	$C2/c$
a/Å	13.467(2)	11.5189(5)	24.712(9)	16.507(3)
b/Å	20.206(2)	23.1977(9)	12.745(4)	13.602(3)
c/Å	14.077(2)	18.0425(7)	19.001(6)	19.924(4)
β/deg	91.367(2)	96.279(2)	117.492(5)	101.92(3)
V/Å^3	3829.4(8)	4792.3(3)	5309(3)	4377(2)
Z	2	4	4	4
D_{calcd}/g cm^{-3}	1.128	1.170	1.192	1.276
cryst size/mm^3	0.32 × 0.30 × 0.30	0.40 × 0.40 × 0.38	0.48 × 0.40 × 0.30	0.46 × 0.33 × 0.30
F(000)	1392	1808	2048	1792
μ/mm^{-1}	0.779	0.570	0.522	0.789
θ range/deg	1.76−28.28	1.98−26.84	1.85−28.34	1.96−27.93
no. of rflns collected	22 840	28 054	15 081	12 551
no. of indep rflns	8943	10229	6171	4925
R(int)	0.0556	0.0686	0.0777	0.2481
no. of obsd rflns ($I > 2\sigma(I)$)	4395	4988	3048	1475
R1, wR2 ($I > 2\sigma(I)$)	0.0569, 0.1550	0.0590, 0.1439	0.0909, 0.2516	0.0912, 0.2052
R1, wR2 (all data)	0.1326, 0.1951	0.1383, 0.1826	0.1759, 0.2984	0.2626, 0.2698
GOF (F^2)	0.989	0.964	1.007	0.819

metal−metal bond. The isopropyl-substituted ligand L^{iPr} provided proper protection for the Zn−Zn bond in **1** and **2**, while the less crowded L^{Et} and L^{Me} resulted in the mononuclear compounds **3**−**5**, in which Zn^{2+} replaces the $[Zn-Zn]^{2+}$ core. The two alkali metals Na and K as reducing agents led to similar molecular structures with the same ligand (in the cases **1**, **2** and **4**, **5**), although further conclusions are hindered by the absence of the products reduced by other agents. The solvent could affect the aggregation state of the products, as in the case of **4** and **5** with the same L^{Et} ligand. A THF molecule coordinates to the Na^+ ion to form the monomeric **4**, while the nonsolvated K^+ ion in **5** is further bonded by the carbon atoms of another molecule, leading to a two-dimensional polymeric species.

Density Functional Theory (DFT) Studies. Theoretical studies were performed at the DZP BP86 level for the Zn−Zn-bonded compound **2** and the mononuclear zinc compounds **3**−**5**. The model of $K_2[(CHNH)_2Zn-Zn(NHCH)_2]$ (**2H**) is used for **2**, and the results are similar to those for the sodium analogue **1**/**1H**.[8] The theoretical Zn−Zn bond distance (2.396 Å) compares well with that observed for **2** (2.393(1) Å) and is close to that calculated for **1H** (2.373 Å). The HOMO and HOMO-1 for **2H** (see Figure S2 in the Supporting Information) are ligand-based orbitals, and HOMO-2 represents the Zn−Zn σ bond (Figure 5). The Wiberg bond index (WBI) gave a Zn−Zn bond order of 0.64 for **2H** (close to the value 0.69 for **1H**).[8] Similar to the case for **1H**, this σ bond is formed mainly by the 4s orbitals, with 94.7% s, 4.2% p, and 1.1% d character. The natural charges on Zn and K are +0.71 and +0.86, respectively, while each N–C═C–N moiety of the ligand has a total negative charge of −1.58, with the computed C−N and C−C distances (see Table S2 in the Supporting Information) corresponding to a dianionic ligand.[14]

The model compound $ZnL_2Na_2(H_2O)_2$ (**3H**; L = PhNCHCH-NPh) was used to theoretically examine the electronic structure of the mononuclear zinc compounds, and this model gave a minimum structure with *C*2 symmetry (Figure S3, Supporting Information). This is the case for **4** and **5**; but compound **3** lacks the *C*2 symmetry. The theoretical C−N (1.401, 1.412 Å) and C−C (1.385 Å) bond distances are close to the crystal structure data for **3**−**5** (C−N, 1.410−1.432 Å; C−C, 1.347−1.358 Å) (Table S5, Supporting Information), which clearly indicate a formal doubly reduced ligand, as is also confirmed by the natural charges on L (−1.72). The ligand-based orbitals HOMO and HOMO-1 (Figure S4, Supporting Information) show the π-bond character between the two carbon atoms of the N–C═C–N moiety. As mentioned above, the zinc atom bears a formal +2 valence (natural charge +1.55) and the charge on Na is +0.94.

Conclusions

We have described here the structures of a series of di- and mononuclear zinc compounds (**2**−**5**) of α-diimine ligands bearing different N-aryl substituents from the reduction of the $LZnCl_2$ precursors by the alkali metal Na or K. The proper steric bulk of the substituents on the aryl ring (2,6-diisopropyl groups in this work) is crucial for the stabilization of the zinc−zinc bond, and the utilization of different solvents can vary the aggregation state of the products. In the Zn−Zn-bonded compounds **1** and **2**, the formal Zn^{2+} ion in the precursor is reduced to Zn^+, while in the mononuclear compounds **3**−**5** the +2 valence remains. However, in all compounds, the reducing agent donates two electrons to the neutral ligand to form a relatively stable dianion, L^{2-}. DFT computations reveal that the Zn−Zn bond in **2** contains mainly the 4s orbitals of zinc. The existence of the dianionic ligands in **1**−**5** is confirmed by the natural charge analysis (charges on L: −1.58 for **2H** and −1.72 for **3H**) as well as the frontier molecular orbitals, which show the C═C double-bond character of the N–C═C–N moiety of the ligands.

Experimental Section

General Considerations. All manipulations with air- and moisture-sensitive compounds were carried out under argon with standard Schlenk or drybox techniques. The solvents (toluene, Et_2O, and THF) were dried using appropriate methods and were distilled under argon prior to use. Benzene-d_6 was dried over Na/K alloy. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene-d_6. Elemental analyses were performed with an Elementar VarioEL III instrument. The complexes $LZnCl_2$ were prepared according to published procedures.[15]

$[K(THF)_2]_2[(L^{iPr})Zn-Zn(L^{iPr})]$ (2). $(L^{iPr})ZnCl_2$ (1.00 g, 1.85 mmol) and potassium (0.22 g, 5.56 mmol) were combined with 40

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mL of THF at room temperature. The mixture was stirred for 7 days and filtered to yield a dark red solution, which was concentrated to about 10 mL and stored at ca. −20 °C. Orange crystals (0.75 g, 31%) were isolated after 2 weeks. ^{1}H NMR (400 MHz, C_6D_6): δ 1.05 (d, 24H, J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.29 (m, 24H, J = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.38 (t, 16H, J = 6.4 Hz, THF), 2.11 (s, 12H, CCH$_3$), 3.55 (t, 16H, J = 6.4 Hz, THF), 3.90 (m, 8H, C*H*(CH$_3$)$_2$), 6.54 (t, 4H, J = 7.6 Hz, *p*-ArH), 6.89 ppm (d, 8H, J = 7.6 Hz, *m*-ArH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 16.1 (CH$_3$), 22.7 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 25.7 (THF), 28.1 (*C*H(*C*H$_3$)$_2$), 67.7 (THF), 118.0 (*m*-C_6H_3), 120.0 (*p*-C_6H_3), 123.0 (*o*-C_6H_3), 144.7 (*i*-C_6H_3), 154.8 ppm (N−*C*CH$_3$). Anal. Calcd for $C_{72}H_{112}K_2N_4O_4Zn_2$ (1306.70): C, 66.18; H, 8.64; N, 4.29. Found: C, 66.36; H, 8.58; N, 4.42.

[Zn(L^{Me})$_2$Na$_2$(Et$_2$O)$_2$] (3). (L^{Me})ZnCl$_2$ (1.00 g, 2.30 mmol) and sodium (0.16 g, 6.90 mmol) were stirred in 50 mL of Et_2O at room temperature for 6 days. The mixture was filtered, and the dark red filtrate was concentrated to about 10 mL and stored at ca. −20 °C to yield yellow crystals of the product (0.58 g, 28%) after 1 week. ^{1}H NMR (400 MHz, C_6D_6): δ 0.98 (d, 12H, J = 6.8 Hz, Et_2O), 1.36 (s, 12H, ArCH$_3$), 1.64 (s, 6H, ArCH$_3$), 1.93 (s, 6H, ArCH$_3$), 2.03 (s, 6H, CCH$_3$), 2.12 (s, 6H, CCH$_3$), 3.60 (m, 8H, Et_2O), 6.78 (t, 4H, J = 6.8 Hz, *p*-ArH), 7.01 ppm (d, 8H, J = 6.8 Hz, *m*-ArH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 15.0 (C*C*H$_3$), 15.3 (Et_2O), (CH(*C*H$_3$)$_2$), 15.9 (C*C*H$_3$), 20.2 (ArCH$_3$), 20.4 (ArCH$_3$), 21.1 (ArCH$_3$), 21.7 (ArCH$_3$), 25.3 (Et_2O), 65.5 (Et_2O), 68.3 (Et_2O), 115.7 (*p*-C_6H_3), 119.4 (*p*-C_6H_3),120.2 (*m*-C_6H_3), 121.7 (*m*-C_6H_3), 127.3 (*m*-C_6H_3), 128.6 (*i*-C_6H_3), 130.5 (*m*-C_6H_3), 131.2 (*o*-C_6H_3), 135.3 (*o*-C_6H_3), 139.2 (*o*-C_6H_3), 140.3 (*o*-C_6H_3), 154.1 (N−*C*CH$_3$), 156.2 ppm (N*C*CH$_3$). Anal. Calcd for $C_{48}H_{68}N_4Na_2O_2Zn$ (844.41): C, 68.27; H, 8.12; N, 6.63. Found: C, 68.31; H, 8.28; N, 6.67.

[Zn(L^{Et})$_2$Na$_2$(THF)$_2$] (4). (L^{Et})ZnCl$_2$ (1.00 g, 2.06 mmol) and sodium (0.14 g, 6.20 mmol) were stirred in 50 mL of THF at room temperature for 6 days. The mixture was filtered, and the filtrate was concentrated to about 10 mL and stored at ca. −20 °C for several days to give yellow crystals of the product (0.47 g, 24%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.08 (t, 24H, J = 8.0 Hz, CH$_2$C*H*$_3$), 1.40 (t, 8H, J = 6.0 Hz, THF), 2.08 (s, 12H, CCH$_3$), 2.38 (m, 16H, C*H*$_2$CH$_3$), 3.58 (t, 8H, J = 6.0 Hz, THF), 7.02−7.10 ppm (m, 12H, ArH). ^{13}C NMR (100.6 MHz, C_6D_6): δ 14.0 (CH$_2$*C*H$_3$), 25.3 (*C*H$_2$CH$_3$), 25.8 (THF), 67.8 (THF), 124.0 (*m*-C_6H_3), 126.7 (*o*-C_6H_3), 130.7 (*p*-C_6H_3), 148.1 (*i*-C_6H_3), 168.1 ppm (N−*C*CH$_3$). Anal. Calcd for $C_{56}H_{80}N_4Na_2O_2Zn$ (952.59): C, 70.60; H, 8.46; N, 5.88. Found: C, 70.43; H, 8.70; N, 5.94.

[Zn(L^{Et})$_2$K$_2$]$_n$ (5). (L^{Et})ZnCl$_2$ (0.50 g, 1.03 mmol) and potassium (0.20 g, 5.15 mmol) were combined with 40 mL of toluene at ambient temperature. The mixture was stirred for 15 days and filtered to yield a dark red solution, which was concentrated to about 10 mL and stored at ca. −20 °C for several days to yield orange-red crystals (0.25 g, 19%). The NMR spectra of **5** are not available due to its poor solubility. Anal. Calcd for $C_{48}H_{64}K_2N_4Zn$ (840.66): C, 68.58; H, 7.67; N, 6.66. Found: C, 68.55; H, 7.99; N, 6.45.

X-ray Crystal Structure Determination. Diffraction data for the complexes **2**−**5** were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). An empirical absorption correction using SADABS was applied for all data.[16] The structures were solved by direct methods using the SHELXS program.[17] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 by the use of the program SHELXL.[17] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement details for **2**−**5** are given in Table 5.

Crystallographic data for the compounds of this work have been deposited with the Cambridge Crystallographic Data Centre with reference numbers CCDC 684906−684909. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 3360333; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Computational Methods.[18] The DFT computations were performed at the DZP BP86 level of theory with the Gaussian 94 program. The model compound K$_2$[(CHNH)$_2$Zn−Zn(NHCH)$_2$] (**2H**), where the *N*-2,6-diisopropylphenyl group and the methyl group on the central carbon atoms are replaced by hydrogen atoms, is used for the dinuclear compound **2**, and the simplified model ZnL$_2$Na$_2$(H$_2$O)$_2$ (**3H**; L = PhNCHCHNPh) is used for the mononuclear compounds. The Cartesian coordinates and structures of the optimized geometry, selected theoretical bond lengths, and frontier orbitals are given in the Supporting Information.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (NSFC Grant No. 20771103), the “Bairen Jihua” project of Chinese Academy of Sciences, and the 111 Project (No. B07012) in China and by the U.S. National Science Foundation (No. CHE-0749868). We thank the reviewers for helpful suggestions.

Supporting Information Available: CIF files, giving X-ray structural data for complexes **2**−**5**, Tables S1 and S3, giving the Cartesian coordinates of the optimized geometry for **2H** and **3H**, Tables S2 and S4, giving the theoretical bond distances and angles for **2H** and **3H**, Table S5, giving a comparison of the experimental and theoretical bond parameters, Figures S1 and S3, showing the optimized structures of **2H** and **3H**, and Figures S2 and S4, showing the selected frontier orbitals of **2H** and **3H**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800405M

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