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Sodium and Magnesium Complexes with Dianionic α-Diimine Ligands

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A series of sodium and magnesium complexes with α-diimine ligands, $[Na_2(L^{iPr})(Et_2O)]_2$ (**1**, L^{iPr} = $[(2,6\text{-}^iPr_2C_6H_3)N(Me)C]_2$), $[Na_2(L^{Mes})(solv)_2]_2$ (L^{Mes} = $[(2,4,6\text{-}Me_3C_6H_3)N(Me)C]_2$, **2a**, solv = Et_2O; **2b**, solv = THF), $[Na_4(L^{Et})_2]_n$ (**3**, L^{Et} = $[(2,6\text{-}Et_2C_6H_3)N(Me)C]_2$), and $[Mg(L^{Mes})(THF)_3]$ (**4**), have been synthesized by reduction of the diimine ligands with sodium or magnesium metal. Single-crystal X-ray diffraction analysis revealed that the sodium complexes have a 2:1 $[Na_2L]$ unit that aggregates to dimeric (**1**, **2a**, **2b**) or polymeric (**3**) structures, while the magnesium complex (**4**) shows a monomeric 1:1 structure. In all compounds **1**−**4**, the ligand is doubly reduced to a dianion. The two Na^+ ions in **1**, **2a**, **2b**, and **3** show different coordination modes, one of which is chelated by the N donors of a ligand with supplementary Na−C bonds to the phenyl ring of another ligand within the $[Na_2L]_2$ dimer, while the other is bonded by the central C_2N_2 core of the ligand and solvent molecules (**1**, **2a**, and **2b**). Compound **3** displays a novel three-dimensional network. The Mg^{2+} ion in **4** is coordinated by a ligand molecule and three THF molecules. Density functional theory (DFT) computations on the sodium and magnesium complexes **1** and **4** confirmed their electronic structures and the dianionic character of the ligands.

Introduction

α-Diimine compounds have been widely used as nitrogen donor ligands in coordination chemistry for both main group and transition metals. Transition metal complexes with diimine ligands are efficient catalysts for a variety of reactions;[1] in particular, the Pd(II) and Ni(II) halide complexes have been found to be highly active olefin polymerization catalysts.[2] The differences of the electronic properties between transition and main group metal atoms could lead to diverse reactivity of their corresponding α-diimine complexes. In 1974, Walther et al.[3] synthesized and characterized (by UV−vis spectroscopy) alkali metal complexes with an α-diimine ligand (M_2L_n·solvent, L = $[PhN(Ph)C]_2$, M = Li, Na, K). Within the past decade, a number of lithium complexes[4] and potassium complexes[5,6] of mono- or dianionic α-diimine ligands have been synthesized. Complexes of group 2 and 13 metals (Be, Mg, Ca, Sr, Ba and Al, Ga, In) with various substituted α-diimine ligands have also been reported.[7,8] Surprisingly, structural studies of the sodium and potassium complexes are very rare, although they have appeared as intermediates in the approaches to other organometallic compounds.[9] Recently, Fedushkin et al.[10] reported the structures of some sodium complexes with the mono- and dianion of an α-diimine-based ligand, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-Bian).

The alkali metal complexes of α-diimine ligands have been used as reducing agents for the synthesis of various organometallic and organic substrates, and it is clear that the ligand properties could affect their performance as electron sink or tank.[5,9,11] Very recently, we synthesized a series of dinuclear

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(Zn−Zn-bonded) and mononuclear Zn compounds by reducing [L^0ZnCl_2] (L^0 denotes the neutral α-diimine ligands) with sodium or potassium metal.[12] In the reaction procedure the neutral ligand L accepted two electrons to form a dianion (L^{2-}). In order to better understand the redox behavior of such α-diimine ligands and to further explore the potential applications of the reduced species as electron donors, we carried out the reduction of a series of α-diimines bearing different substituents on the *N*-phenyl ring, L^{iPr}, L^{Et}, and L^{Mes}, by different reducing agents. Herein we report the crystal structures of the resulting sodium and magnesium complexes, as well as their electronic structures and charge distributions studied by means of density functional computations.

Results and Discussion

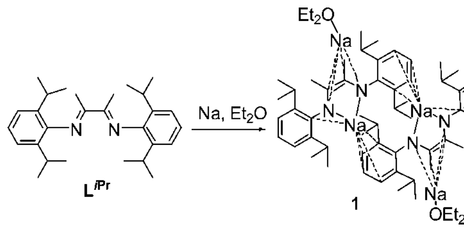
Reduction of the neutral ligand (L^{iPr}, L^{Et}, or L^{Mes}) with sodium or magnesium metal resulted in the isolation of complexes **1**−**4**. The reaction of Na with the ligands in diethyl ether, THF, or toluene yielded the sodium complexes **1**−**3**, while the magnesium compound **4**, [$Mg(L^{Mes})(THF)_3$], was obtained by reaction of L^{Mes} with Mg in THF. These compounds are highly air- and moisture-sensitive, but are thermally quite stable under argon at room temperature and can be stored for several days without decomposition. They are soluble in THF and slightly soluble in diethyl ether and toluene. The formation of **1**−**4** can be readily monitored by the color change of the reaction solution from orange (free ligand) to red (product), from which the complexes could be isolated as red crystals.

In compounds **1**−**4**, the ligand is doubly reduced to a dianion with a metal-to-ligand ratio of 2:1 (for Na complexes) or 1:1 (for the Mg complex). However, the (singly reduced) radical-anionic form of such ligands is also known. The potassium salt of the monoanion $(L^{iPr})^-$ has been obtained in the reaction of L^{iPr} with KH as an intermediate to other transition metal complexes,[5] and the structure of the sodium salt with a radical-anion, Na[dpp-Bian], has been reported.[10] To check other possible anionic species of the ligands used in this work, we have conducted the reduction of $(L^{iPr})^0$ with various agents, such as K, NaH, etc. A similar color change of the reaction mixture to that of the Na reduction was observed, but we have not isolated any products yet.

Sodium Complex with L^{iPr}, [$Na_2(L^{iPr})(Et_2O)]_2$ (1). The ligand with the isopropyl substituents, 2,6-diisopropylphenyl-2,3-dimethyl-2,3-diazabutadiene (L^{iPr}), previously used to stabilize the Zn−Zn bond,[12] was reduced by sodium metal to give complex **1** (Scheme 1). Single crystals for X-ray diffraction studies were grown from diethyl ether.

The sodium complex **1** consists of a centrosymmetric [$Na_2(L^{iPr})(Et_2O)]_2$ dimer (Figure 1). There are two types of sodium ions in the compound with different coordination modes. One of them (Na(1)) is chelated by the two N donors of a ligand, and its coordination sphere is completed by supplementary Na−C bonding with one of the *ipso* carbon atoms of the same ligand and four carbon atoms of the aryl ring in another ligand (Na−C contact distances range from 2.756 to 3.002 Å, Table 1). The latter four Na−C bonds link two [$Na(L^{iPr})$] units into the dimeric structure. The Na(1) atom is located out of the plane defined by N(1)C(1)C(2)N(2), with a vertical distance of 1.38 Å and a dihedral angle of 45.5° between planes N(1)Na(1)N(2) and N(1)C(1)C(2)N(2). This differs greatly from the situation in Na[dpp-Bian] (Na deviates 6.7°) and Na_2[dpp-Bian] (Na deviates 23.9°).[10]

Scheme 1



The other sodium ion, Na(2), is solvated by a diethyl ether molecule and is η^4-bonded to the N−C=C−N moiety of the ligand. The [$Na(2)(Et_2O)]^+$ unit sits 1.86 Å above the N−C=C−N plane, and the dihedral angle between the chelating plane N(1)Na(2)N(2) and the enediamido N(1)C(1)C(2)N(2) plane is 75.9°. The surrounding environment of Na(2) resembles that

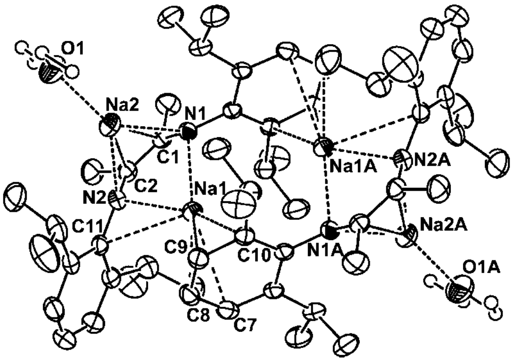


Figure 1. Molecular structure of **1** (thermal ellipsoids are drawn at 30% probability level; H atoms are omitted and C atoms on Et_2O drawn as smaller spheres for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds 1, 2a, and 2b

	1	2a	2b
C(1)−C(2)	1.364(4)	1.356(4)	1.366(4)
C(1)−N(1)	1.420(3)	1.421(4)	1.428(4)
C(2)−N(2)	1.418(4)	1.421(4)	1.411(4)
Na(1)−N(1)	2.417(2)	2.377(3)	2.385(3)
Na(1)−N(2)	2.339(2)	2.334(3)	2.323(3)
Na(1)−C(5)			3.001(3)
Na(1)−C(6)		2.971(4)	2.920(4)
Na(1)−C(7)	2.988(3)	2.829(4)	2.819(4)
Na(1)−C(8)	2.756(3)	2.769(4)	2.798(3)
Na(1)−C(9)	2.758(3)	2.710(4)	2.714(4)
Na(1)−C(10)	3.002(3)	2.829(4)	2.775(3)
Na(1)−C(11)	2.953(3)		
Na(2)−C(1)	2.618(3)	2.657(4)	2.734(3)
Na(2)−C(2)	2.597(3)	2.657(4)	2.736(4)
Na(2)−N(1)	2.376(3)	2.421(3)	2.373(3)
Na(2)−N(2)	2.353(3)	2.399(3)	2.380(3)
Na(2)−O(1)	2.309(3)	2.406(4)	2.329(3)
Na(2)−O(2)		2.390(3)	2.327(3)
Na(1)···Na(2)	3.356(2)	3.360(2)	3.240(2)
Na(1)···Na(1A)	4.139(2)	4.260	4.155
N(1)−Na(1)−N(2)	71.28(9)	73.1(1)	73.47(9)
N(1)−Na(2)−N(2)	71.76(8)	71.21(9)	72.68(9)

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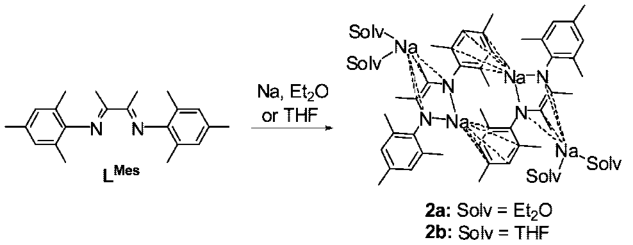
Scheme 2



of the Zn−Zn bonded complex $[Na(THF)_2]_2[(L^{iPr})Zn-Zn(L^{iPr})]$.[12] Moreover, while the solvated $[Na(2)Et_2O]^+$ unit is located in a more terminal fashion, the "bare" Na(1) atom is between the two symmetry-related ligands of the dimer. Despite the differences between Na(1) and Na(2), the Na−N distances of the two sodium ions are comparable (Na(2)−N 2.376(3)/2.353(3) Å; Na(1)−N 2.417(2)/2.339(2) Å, respectively), with the Na(2)−N bonds a little more symmetric. The Na(1)···Na(2) separation (3.36 Å) is considerably longer than that in Na_2[dpp-Bian] (2.96 Å).[10]

Upon reduction, the C(1)−N(1) (1.420(3) Å) and C(2)−N(2) (1.418(4) Å) distances (Table 1) are dramatically elongated compared to those (1.280(3) and 1.279(3) Å) in the neutral ligand L^{iPr}. In contrast, the C(1)−C(2) bond in **1** is shortened to 1.364(4) Å from 1.498(3) Å in the neutral ligand.[13] The C−N bond elongation and C−C bond shortening correspond to electron acquisition (reduction) of the ligand LUMO, as has been reported in similar processes[14,15] and confirmed by our DFT computations (vide infra). Although the ligand in compound **1** appears to have negative valences of −2, as in the dianionic dpp-Bian species, its structure is significantly different from the latter. First, compound **1** is dimeric, while Na_2[dpp-Bian] is a monomer. Second, only Na(2) in compound **1** is coordinated by a diethyl ether molecule and Na(1) is not solvated, while in Na_2[dpp-Bian] the two Na^+ ions are solvated by three Et_2O molecules.[10]

Sodium Complexes with L^{Mes}, $[Na_2(L^{Mes})(solv)_2]_2$ (2a, solv = Et_2O; 2b, solv = THF). The reaction of the mesityl-substituted ligand L^{Mes} with Na also yielded the dimeric complexes (Scheme 2). The crystal structure of **2a** is similar to **1** as a centrosymmetric $[Na_2(L^{Mes})(Et_2O)_2]_2$ compound (Figure 2). The sodium atom Na(1) is coordinated by N donors and aryl C atoms and the solvated Na(2) contacts with the N−C=C−N moiety, both deviating from the plane N(1)C(1)C(2)N(2) (by 1.38 and 1.89 Å, respectively). Upon reduction of the ligand to the dianionic form L^{2-}, the C−N (1.421(4), 1.421(4) Å) distances are also elongated, while C−C (1.356(4) Å) shortened. The Na(1)···Na(2) separation (3.36 Å) is identical to that in **1**. However, the coordination environments of both types of Na atoms in **2a** are different from those in **1**. Besides the Na−N bonds, the Na(1) atom is interacting with five C atoms (instead of four in **1**) of the aryl ring in another ligand (Na−C distances 2.710−2.971 Å). Accordingly, the projection of the Na(1) atom on the contacting aryl ring is closer to the ring centroid (by 0.33 Å) than that in **1** (0.57 Å), which has four Na(1)−C bonds. The Na(1)−C_{ipso} contact found in **1** is absent here. On the other hand, the "terminal" Na(2) is coordinated by two Et_2O molecules instead of only one solvent molecule in **1**. This is apparently due to the larger steric hindrance of the *ortho* isopropyl groups in **1** than the methyl analogue **2a**.

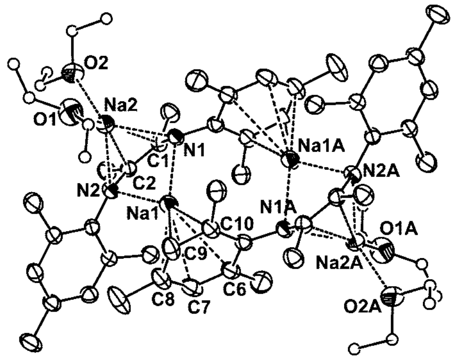


Figure 2. Molecular structure of **2a** (thermal ellipsoids are drawn at 30% probability level; H atoms are omitted and C atoms on Et_2O drawn as smaller spheres for clarity).

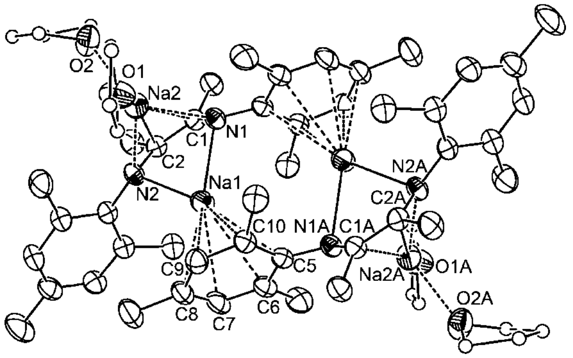
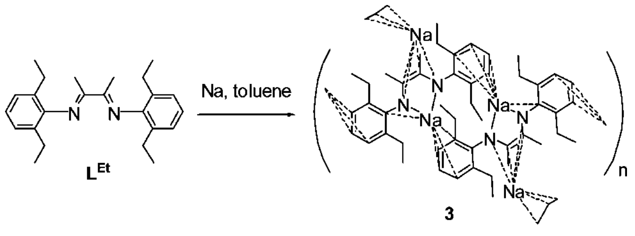


Figure 3. Molecular structure of **2b** (thermal ellipsoids are drawn at 30% probability level; H atoms are omitted and C atoms on THF drawn as smaller spheres for clarity).

Scheme 3



The THF solvate $[Na_2(L^{Mes})(THF)_2]_2$ (**2b**) is isostructural to **2a**, with the Na(2) atom coordinated by two THF molecules (Figure 3). The Na(1) atom interacts with two N atoms and the aryl ring in another ligand (Na−C distances 2.714−3.001 Å). It is noteworthy that the number of Na−C(aryl) bonds for **2b** is six (with all the phenyl C atoms, C5−C10, Table 1) rather than five in **2a**. However, the remaining Na−C(5) separation in **2a** (3.028 Å), which is the shortest nonbonding distance in compounds **1**−**3**, is only slightly longer than the bonding contacts (cutoff ca. 3.01 Å). In accord with the increased Na−C(aryl) bond number, the vertical displacement of the Na(1) atom from the ring centroid (0.23 Å) in **2b** is significantly shorter than that in **2a** (0.33 Å, with five Na−C bonds) and in **1** (0.57 Å, with four Na−C bonds). The Na(1)···Na(2) separation (3.24 Å) is the shortest among the compounds (3.24−3.41 Å).

Polymeric Sodium Complex with L^{Et}, $[Na_4(L^{Et})_2]_n$ (3). The reduction of the diethyl-substituted ligand L^{Et} with sodium metal in toluene led to the polymeric compound **3** (Scheme 3).

The molecular strucure of the $[Na_4(L^{Et})_2]$ unit is similar to the analogues **1** and **2a**/**2b**. The sodium atom Na(1) is bonded

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by the N donors and an adjacent *ipso*-C atom, as well as four carbons from another ligand (Na−C distances 2.756−2.962 Å), while Na(2) is situated over the N−C=C−N moiety and η^4-bonded to these four atoms (Figure 4a). The elongation of C−N (1.402(6), 1.430(6) Å) and shortening of the C−C bond (1.357(6) Å) in the central C_2N_2 moiety are also observed in **3**. The Na(1)···Na(2) separation (3.41 Å) is slightly longer than those in **1** and **2a/2b** (3.36 Å). The most significant structural feature of **3**, however, is the aggregation of the $[Na_4(L^{Et})_2]$ unit into a polymer. In contrast to the solvation of the terminal sodium ions by either one (in **1**) or two (in **2**) Et_2O or THF molecules, the Na(2) atom is not solvated here; instead, its coordination sphere is completed by three short Na−C bonds with the aryl ring in another $[Na_4(L^{Et})_2]$ unit. Thus, each molecule is linked to four adjacent units (Figure 4b), forming a three-dimensional network that possesses higher thermal stability (decomposes at 178 °C) than the dimeric compounds **1** and **2a/2b** (102 and 80/140 °C, respectively).

A comparison of the structures of the three sodium complexes **1**−**3**, as well as with the Zn−Zn-bonded compound,[12] shows some resemblance. All compounds (the repeating unit in **3**) are dimeric with the composition of $[Na_4L_2]$ or $[Na_2Zn_2L_2]$, in which the α-diimine ligand L^0 is reduced to the enediamido dianion L^{2-} and coordinates to a monovalent metal cation (Na^+ or Zn^+) through two M−N bonds. The negative charges of the ligand are further balanced by a solvated (except **3**) Na^+ ion η^4-bonding to the N−C=C−N moiety. The sodium complexes reported here consist of two different types of Na^+ ions, one of which (Na(1)) could be considered roughly as the substitute of the transition metal Zn and the other (Na(2)) has the same function and coordination sphere as the sodium ion in the Zn−Zn-bonded compound. However, the Na(1) center is considerably deviated from the N_2C_2 plane (around 1.4 Å), in contrast to the nearly planar fashion of the matallocycle containing the transition metal Zn^+, N_2C_2Zn. The Na−N bond lengths in **1**−**3** fall in the range 2.334−2.421 Å and the Na−C distances in the range 2.597−3.002 Å (Tables 1 and 2), which are comparable to the similar sodium compounds with dianionic diimine ligands.[10]

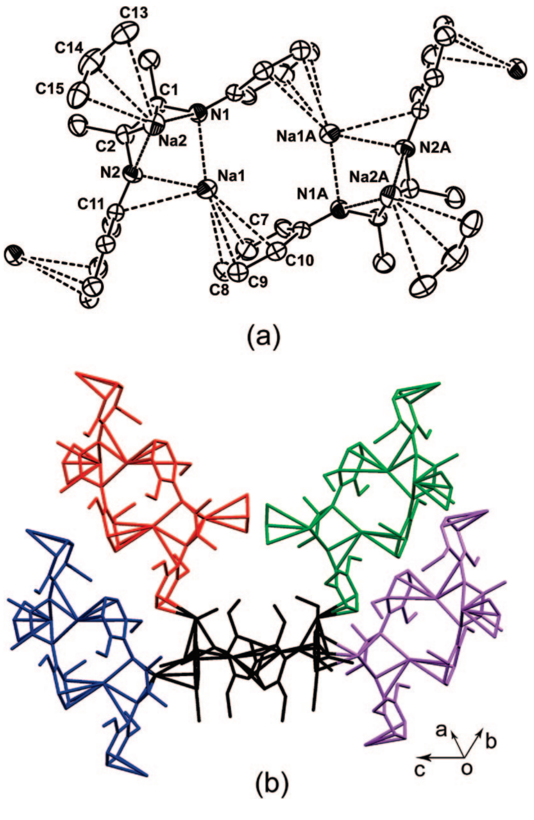
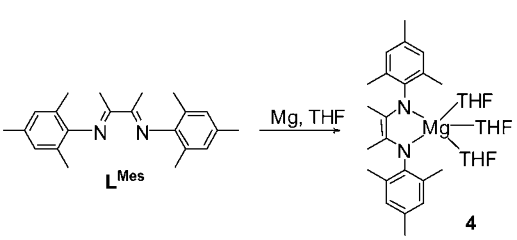


Figure 4. Crystal structure of **3**: (a) One $[Na_4(L^{Et})_2]$ unit (thermal ellipsoids are drawn at 30% probability level; the ethyl groups and hydrogen atoms are omitted for clarity); (b) extended structure showing that one $[Na_4(L^{Et})_2]$ unit (black) is surrounded by four adjacent molecules through $Na-C_{aryl}$ contacts.

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

C(1)−C(2)	1.357(6)	Na(1)−C(11)	2.886(5)
C(1)−N(1)	1.402(6)	Na(2)−C(1)	2.614(5)
C(2)−N(2)	1.430(6)	Na(2)−C(2)	2.644(5)
Na(1)−N(1)	2.381(4)	Na(2)−N(1)	2.379(4)
Na(1)−N(2)	2.373(4)	Na(2)−N(2)	2.393(4)
Na(1)−C(7)	2.928(6)	Na(2)−C(13)	2.969(6)
Na(1)−C(8)	2.756(7)	Na(2)−C(14)	2.664(6)
Na(1)−C(9)	2.759(6)	Na(2)−C(15)	2.766(6)
Na(1)−C(10)	2.962(6)	Na(1)···Na(2)	3.411(3)
Na(1)···Na(1A)	4.161(4)		
N(1)−Na(1)−N(2)	70.4(1)	N(1)−Na(2)−N(2)	70.1(1)

Scheme 4



Magnesium Complex $[(L^{Mes})Mg(THF)_3]$ (4). For a further understanding of the electron acquisition ability of the ligands, we also carried out the reduction of L^{Mes} with the alkaline earth metal Mg (Scheme 4). In contrast to the ease of two-electron reduction of the ligand by sodium metal, the reaction with magnesium is much slower (over a week compared to 2−3 days for Na) with a lower yield.

The magnesium complex **4** is monomeric with a compostition of $[(L^{Mes})Mg(THF)_3]$, in which the Mg center is coordinated by one ligand and three THF molecules with a distorted trigonal-bipyramidal geometry (Figure 5). The oxygen atom O(3) and one nitrogen atom N(1) occupy the axial coordination sites, while the other two O atoms (O1 and O2) and N(2) define the equatorial plane. The axial Mg−O(3) (2.196(2) Å) and Mg−N(1) (2.051(2) Å) bonds are significantly longer than the corresponding equatorial Mg−O (2.08(2) and 2.110(2) Å) and Mg−N(2) bond (2.021(2) Å), respectively (Table 3). The crystal structure of **4** is similar to complex (dpp-Bian)Mg(THF)$_3$.[8] However, the C(2)−N(1) (1.426(3) Å) and C(3)−N(2) (1.406(3) Å) bonds in **4** are longer than those in the latter compound (1.401(6) and 1.378(7) Å), while the C(2)−C(3) bond (1.350(3) Å) is shorter by ∼0.04 Å. The bite angle N(1)−Mg−N(2) of **4** (84.04°) is very close to that in the complex (dpp-Bian)Mg(THF)$_3$ (84.77°).

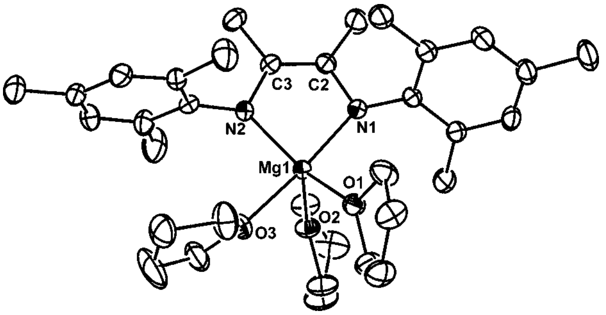


Figure 5. Molecular structure of **4** (thermal ellipsoids are drawn at 30% probability level; H atoms are omitted for clarity).

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

Mg(1)−N(1)	2.051(2)	Mg(1)−O(3)	2.196(2)
Mg(1)−N(2)	2.021(2)	C(2)−C(3)	1.350(3)
Mg(1)−O(1)	2.110(2)	C(2)−N(1)	1.426(3)
Mg(1)−O(2)	2.080(2)	C(3)−N(2)	1.406(3)
N(1)−Mg(1)−N(2)	84.04(9)	O(1)−Mg(1)−O(3)	79.94(8)
N(1)−Mg(1)−O(1)	95.44(9)	O(2)−Mg(1)−O(3)	86.96(8)
N(1)−Mg(1)−O(2)	104.50(8)	N(2)−Mg(1)−O(1)	143.59(9)
N(1)−Mg(1)−O(3)	168.39(8)	N(2)−Mg(1)−O(2)	112.49(9)
O(1)−Mg(1)−O(2)	102.92(8)	N(2)−Mg(1)−O(3)	93.35(9)

Density Functional Theory (DFT) Studies. The full geometry of compound **1** in C_i symmetry has been optimized (Figure S1) at the DFT level of theory, which is very similar to the crystal structure obtained from X-ray diffraction. The theoretical atomic distances of Na1···Na2 (3.261 Å) and Na2···Na2A (4.435 Å) are close to the experimental data (3.357 and 4.139 Å, respectively). The bond order (Wiberg bond index) for the Na···Na contacts (~0.01) ruled out any covalent bond between them. The theoretical bond angles of N1−Na1−N2 (74.04°) and N1−Na2−N2 (73.16°) also match the experimental values (71.76(8)° and 71.28(9)°).

The charge distribution of complex **1** has been studied by the natural bonding orbital (NBO) method,[16] which shows that both Na1 and Na2 have significant positive charge (0.88 and 0.91, respectively). As electron acceptors, the ligand acquires a total of 1.69 electrons. From the theoretical results, the bonding between the Na atoms and the surrounding ligands in complex **1** is largely ionic. The HOMO shows that there is no obvious covalent bonding between the Na atoms and the ligands, and the substantial electron density mainly localizes on the N−C═C−N moiety (Figure 6).

The full geometry of the Mg compound **4** has been optimized (Figure S2). The theoretical Mg−N (2.050 and 2.030 Å) and Mg−O (2.267, 2.137, and 2.195 Å) distances and the N1−Mg−N2 (85.0°) angle are close to the experimental data (Table 2). The NBO analysis shows that the Mg atom has nearly +2 valence (1.80), and the charge of the ligand is −1.82. Similar to the case for **1**, the HOMO electrons are mainly located on the N−C═C−N fragment, and no considerable covalent bonding is available between Mg and the ligands (Figure 7).

The calculated C═C distances (1.385 Å for **1** and 1.376 Å for **4**) are slightly longer than the experimental ones (1.350−1.366 Å for **1**−**4**), while the C−N distances are comparable to the X-ray structural data (Table S1). These values fall in the range for dianionic α-diimines and confirm the double reduction of the ligands in the compounds.[15]

Conclusions

We have obtained a series of sodium and magnesium complexes with α-diimine ligands by reducing the ligands with Na or Mg. In the reduction processes the reducing agents donated two electrons to the neutral diimine N═C−C═N moiety to form a relatively stable dianion, L^{2-}, in the enediamido (N−C═C−N) form. No radical-anionic species was observed under our reaction conditions. While the sodium complexes **1**−**3** are dimeric with two coordinately nonequivalent Na^+ ions, the magnesium analogue **4** is mononuclear. Varying the steric hindrance of the ligand from 2,6-diisopropyl to 2,4,6-trimethyl (in the cases of **1** and **2a**/**2b**) resulted in similar products with slight difference in the number of solvent molecules. Finally, lacking a coordinating solvent, the unsaturated sodium ion in complex **3** formed “intermolecular” Na−C bonds to link the molecules into a three-dimensional structure. Theoretical analyses of the model compounds confirmed the charge distribution and the electronic structure of **1**−**4**.

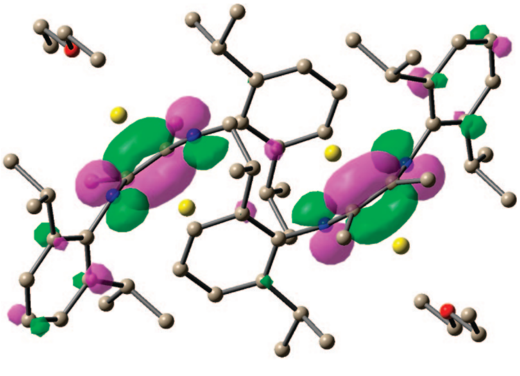


Figure 6. HOMO of $[Na_2L^{iPr}(Et_2O)]_2$ (**1**).

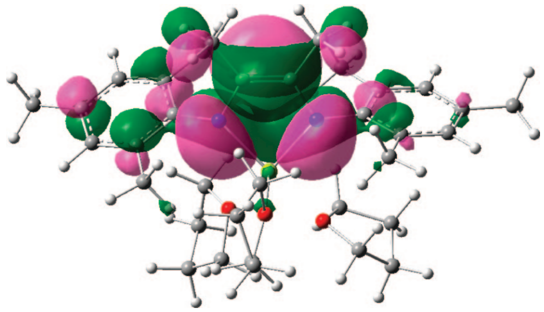


Figure 7. HOMO of $[Mg(L^{Mes})(THF)_3]$ (**4**).

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere using Schlenk tube or drybox techniques. Diethyl ether and tetrahydrofuran were dried by sodium/benzophenone and distilled under argon prior to use. The ligands L^{iPr}, L^{Et}, and L^{Mes} were prepared according to literature procedures.[17] The ^1H NMR spectra were obtained on a Bruker DPX-200 NMR spectrometer (400 MHz).

Synthesis of $[Na_2(L^{iPr})(Et_2O)]_2$ (L^{iPr} = $[(2,6\text{-}^iPr_2C_6H_3)N(Me)C]_2$) (1). L^{iPr} (1.00 g, 2.48 mmol) and sodium (0.20 g, 8.70 mmol) were stirred in 50 mL of Et_2O at ambient temperature for 4 days, and the mixture was filtered. Slow evaporation of the filtrate at ca. −20 °C for several days afforded the product as red crystals (crystal yield: 0.60 g, 24%), which decomposes at 102 °C. ^1H NMR (400 MHz, C_6D_6, δ/ppm): 1.04 (t, 12H, J = 7.2 Hz, $O(CH_2CH_3)_2$), 1.16 (d, 24H, J = 7.2 Hz, $CH(CH_3)_2$), 1.49 (d, 24H, J = 6.8 Hz, $CH(CH_3)_2$), 2.04 (s, 12H, CCH_3), 3.17 (q, 8H, J = 7.2, 13.6 Hz, $O(CH_2CH_3)_2$), 3.62 (m, 8H, $CH(CH_3)_2$), 6.86 (t, 4H, J = 7.2 Hz, *p*-ArH), 7.24 (d, 8H, J = 7.6 Hz, *m*-ArH).

Synthesis of $[Na_2(L^{Mes})(Et_2O)_2]_2$ (2a) and $[Na_2(L^{Mes})(THF)_2]_2$ (2b) (L^{Mes} = $[(2,4,6\text{-}Me_3C_6H_2)N(Me)C]_2$). L^{Mes} (1.00 g, 3.12 mmol) and sodium (0.23 g, 10.00 mmol) were stirred in 50 mL of Et_2O (for **2a**) or THF (for **2b**) at ambient temperature for 3 days. The mixture was filtered, and the filtrate was stored at ca. −20 °C for several days to yield the product as red crystals. **2a**: 0.59 g (37%). Decomp at 80 °C. ^1H NMR (400 MHz, C_6D_6, δ/ppm): 1.09 (t, 24H, J = 6.8 Hz, $O(CH_2CH_3)_2$), 1.92 (s, 6H, CCH_3), 1.93 (s, 6H, *p*-$ArCH_3$), 2.10 (s, 12H, *o*-$ArCH_3$), 2.20 (s, 6H, CCH_3), 2.21 (s, 6H, *p*-$ArCH_3$), 2.31 (s, 12H, *o*-$ArCH_3$), 3.23 (q, 16H, J = 6.8, 14.0 Hz, $O(CH_2CH_3)_2$), 6.82−7.13 (m, 8H, ArH). **2b**: 0.56 g (35%). Decomp at 140 °C. ^1H NMR (400 MHz, C_6D_6, δ/ppm): 1.27 (THF), 1.96 (s, 6H, CCH_3), 1.98 (s, 6H, *p*-$ArCH_3$), 2.08 (s, 12H, *o*-$ArCH_3$),

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[17] Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399.

Table 4. Crystallographic Data and Refinement Details for Compounds 1−4

	1	**2a**	**2b**	**3**	**4**
empirical formula	$C_{64}H_{100}N_4Na_4O_2$	$C_{60}H_{96}N_4Na_4O_4$	$C_{60}H_{88}N_4Na_4O_4$	$C_{48}H_{64}N_4Na_4$	$C_{34}H_{52}MgN_2O_3$
fw	1049.44	1029.37	1021.30	788.99	561.09
cryst syst	monoclinic	monoclinic	monoclinic	tetragonal	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P4_12_12$	$P\bar{1}$
a/Å	17.091(2)	13.751(1)	10.415(1)	12.366(3)	9.919(2)
b/Å	11.026(1)	11.157(1)	20.699(3)	12.366(3)	10.934(2)
c/Å	18.646(2)	21.709(2)	14.609(2)	29.154(8)	16.185(3)
α/deg	90	90	90	90	74.76(3)
β/deg	113.231(2)	106.525(2)	107.828(2)	90	76.25(3)
γ/deg	90	90	90	90	82.97(3)
V/Å^3	3228.7(6)	3193.0(5)	2998.1(7)	4458(2)	1641.7(6)
Z	2	2	2	4	2
D_{calc}/g cm^{-3}	1.079	1.071	1.131	1.176	1.135
cryst size/mm^3	0.26 × 0.25 × 0.24	0.28 × 0.25 × 0.22	0.38 × 0.30 × 0.27	0.39 × 0.30 × 0.27	0.47 × 0.39 × 0.30
F(000)	1144	1120	1104	1696	612
μ/mm^{-1}	0.09	0.09	0.10	0.10	0.09
θ range	2.08−28.30	1.58−28.31	1.76−28.53	1.79−28.33	1.93−27.89
reflns collected	19 250	18 978	18 220	27 177	9629
indep reflns (R_{int})	7658 (0.082)	7536 (0.064)	7269 (0.049)	5525 (0.208)	6981 (0.024)
obsd reflns [$I > 2\sigma(I)$]	2569	2710	2812	1720	3603
R_1; wR_2 [$I > 2\sigma(I)$]	0.0621; 0.1307	0.0696; 0.1782	0.0678; 0.1979	0.0640; 0.1363	0.0607; 0.1727
R_1; wR_2 (all data)	0.2145; 0.1840	0.1976; 0.2383	0.1785; 0.2621	0.2655; 0.2040	0.1082; 0.2014
GOF (F^2)	0.934	0.980	0.982	0.910	0.926

2.21 (s, 6H, CCH_3), 2.26 (s, 6H, p-$ArCH_3$), 2.35 (s, 12H, o-$ArCH_3$), 6.72−7.10 (m, 8H, ArH).

Synthesis of $[Na_4(L^{Et})_2]_n$ (L^{Et} = $[(2,6\text{-}Et_2C_6H_3)N(Me)C]_2$) (3). L^{Et} (1.00 g, 2.87 mmol) and sodium (0.23 g, 10.00 mmol) were stirred in 50 mL of toluene at ambient temperature for 3 days. The resulting mixture was filtered and the filtrate concentrated to about 30 mL and stored at ca. −20 °C for several days to yield the product as red crystals (0.64 g, 28%). Decomp at 178 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.06 (m, 12H, CH_2CH_3), 1.21 (d, 12H, J = 7.6 Hz, CH_2CH_3), 1.30 (s, 12H, CCH_3), 2.27 (m, 8H, CH_2CH_3), 2.72 (m, 8H, CH_2CH_3), 7.01−7.13 (m, 12H, ArH).

Synthesis of $[Mg(L^{Mes})(THF)_3]$ (L^{Mes} = $[(2,4,6\text{-}Me_3C_6H_3)N(Me)\text{-}C]_2$) (4). L^{Mes} (0.50 g, 1.56 mmol) and finely divided magnesium (0.15 g, 6.25 mmol) were stirred in 50 mL of THF at ambient temperature for 10 days. The resulting mixture was filtered, and the filtrate was concentrated to about 10 mL and stored at ca. −20 °C for several days to yield the product as red crystals (0.10 g, 11%). Decomp at 128 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.29 (THF), 2.13 (s, 6H, CCH_3), 2.42 (s, 6H, p-$ArCH_3$), 2.48 (s, 12H, o-$ArCH_3$), 3.50 (THF), 7.13 (s, 4H, m-ArH).

X-ray Crystal Structure Determination. Diffraction data for the complexes **1**−**4** were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS[18] was applied for all data. The structures were solved by direct methods using the SHELXS program.[19] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL.[19] The 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 for **1**−**4** are listed in Table 3.

Density Functional Theory (DFT) Studies. The structure optimization and NBO bonding analysis of the complexes $[Na_2(L^{iPr})(Et_2O)]_2$ (**1**) and $[Mg(L^{Mes})(THF)_3]$ (**4**) were carried out at the DFT (B3LYP) level of theory with a DZP basis set using the Gaussian 03 program.[20] The optimized structures are depicted in Figures S1 and S2, while selected frontier molecular orbitals are given in Figures 6 and 7.

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Supporting Information Available: Detailed information on the X-ray crystal structure analysis of compounds **1**−**4** (CIF files), the DFT-optimized structures of complexes **1** and **4** (Figures S1 and S2), and the full citation of the Gaussian 03 program. This material is available free of charge via the Internet at http://pubs.acs.org.

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