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Syntheses and Structures of Magnesium Complexes with Reduced α-Diimine Ligands

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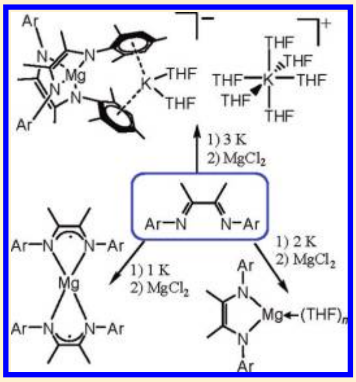
Supporting Information

ABSTRACT: The reduction of neutral α-diimine ligands bearing different substituents on the N-aryl rings by different amounts of potassium metal and subsequent reaction with anhydrous $\mathrm{MgCl_2}$ in THF afforded a series of magnesium compounds, $[(\mathrm{L}^{i\mathrm{Pr}})^{2-}\mathrm{Mg(THF)_2}]\cdot\mathrm{THF}$ (**2**), $[(\mathrm{L}^{\mathrm{Mes}})^{2-}\mathrm{Mg(THF)_3}]$ (**3**), $[(\mathrm{L}^{i\mathrm{Pr}})^{-}{}_2\mathrm{Mg}]\cdot\mathrm{THF}$ (**4**), $[(\mathrm{L}^{\mathrm{Mes}})^{-}{}_2\mathrm{Mg}]$ (**5**), and $[(\mathrm{L}^{\mathrm{Mes}})^{2-}{}_2\mathrm{Mg}(\eta^6{:}\eta^6\text{-}\mathrm{K(THF)_2})][\mathrm{K(THF)_6}]\cdot(\mathrm{THF})_2$ (**6**) ($\mathrm{L}^{i\mathrm{Pr}} = [(2,6\text{-}{}^i\mathrm{Pr_2C_6H_3})\mathrm{NC(Me)}]_2$), $\mathrm{L}^{\mathrm{Mes}} = [(2,4,6\text{-}\mathrm{Me_3C_6H_2})\mathrm{NC(Me)}]_2$). Complexes **2**−**6** have been characterized by single-crystal X-ray diffraction, elemental analysis, NMR spectroscopy, and EPR studies (for **4** and **5**). The noninnocent α-diimine ligands exist as the dianionic form in compounds **2**, **3**, and **6** and as a monoanion in **4** and **5**. Effects of the ligand substituents and the amount of the reducing agent on the structure of the product have been discussed.



INTRODUCTION

Magnesium compounds play indispensable roles in organic and organometallic chemistry, as they can be employed as convenient precursors for the synthesis of other products. The most important class of organomagnesium compounds is Grignard reagents, which have been utilized in numerous synthetic transformations.[1,2] In most organomagnesium complexes, the magnesium metal exhibits the formal oxidation state of +2 because this valence of the alkaline earth metals possesses the stable noble gas configuration. Recently, alkaline earth metal complexes in the +1 valence have been developed. The first stable $\mathrm{Mg^I{-}Mg^I}$-bonded compounds [LMg−MgL] (L = $[(\mathrm{ArN})_2\mathrm{CN}^i\mathrm{Pr}_2]$, or nacnac, $[(\mathrm{ArNCMe})_2\mathrm{CH}]$; Ar = $2,6\text{-}{}^i\mathrm{Pr_2C_6H_3}$) were reported in 2007,[3a] followed by some nacnac analogues.[3b] Another example of the $\mathrm{Mg^I{-}Mg^I}$ bond, $[(\mathrm{L}^{i\mathrm{Pr}})^{2-}\mathrm{Mg{-}Mg}(\mathrm{L}^{i\mathrm{Pr}})^{2-}][\mathrm{K(THF)_3}]_2$ (**1**), which is stabilized by α-diimine ligands, was reported by our group in 2009.[4] The $\mathrm{Mg^I{-}Mg^I}$ bonds in these compounds are kinetically protected by sterically bulky ligands from disproportionation processes.[5] A calcium(I) compound stabilized with an arene system, $[(\mathrm{THF})_3\mathrm{Ca}\{\mu\text{-}\mathrm{C_6H_3}\text{-}1,3,5\text{-}\mathrm{Ph_3}\}\mathrm{Ca(THF)_3}]$,[6] has also been obtained. These results invoked great interest in the study of new magnesium organic compounds.

The structures and reactivity of $\mathrm{Mg^{II}}$ complexes with N-donor ligands, including β-diketiminates (nacnac),[7] bis(arylimino)-acenaphthenes (Ar-BIAN),[8] amidinates,[9] and diazabutadiene (DAB),[10] have been reported previously, such as the homoleptic $\mathrm{L_2Mg}$ and LMg(solvent)$_n$ complexes. However, monomeric magnesium complexes with N-aryl-substituted α-diimine ligands are rather rare considering the wide application of such ligands in the coordination with a variety of metal ions, from transition[11] and rare earth[12] to main group metals.[13] Moreover, these ligands are redox noninnocent and can accept one or two electrons to form the monoanion and dianion, which in turn can serve as reductants in the synthesis of some low-valent complexes.

Recently we have used α-diimine ligands to synthesize a series of transition and main group binuclear (metal−metal-bonded) and mononuclear metal compounds.[4,11,13] The effects of the ligand substituents and reaction conditions (the reducing agent and amount, solvent, etc.) on the structure of the metal complexes have been investigated. It has been found that the reduced (monoanionic or dianionic) α-diimine ligands can effectively form complexes with many metal ions, both in normal and low oxidation states, with variable structures. Very recently, we reported a series of calcium(II) complexes with reduced α-diimines.[13c] To further explore the coordination chemistry of these noninnocent ligands with group 2 metals, we present herein the syntheses and structures of five new magnesium complexes, $[(\mathrm{L}^{i\mathrm{Pr}})^{2-}\mathrm{Mg(THF)_2}]\cdot\mathrm{THF}$ (**2**), $[(\mathrm{L}^{\mathrm{Mes}})^{2-}\mathrm{Mg(THF)_3}]$ (**3**), $[(\mathrm{L}^{i\mathrm{Pr}})^{-}{}_2\mathrm{Mg}]\cdot\mathrm{THF}$ (**4**), $[(\mathrm{L}^{\mathrm{Mes}})^{-}{}_2\mathrm{Mg}]$ (**5**), and $[(\mathrm{L}^{\mathrm{Mes}})^{2-}{}_2\mathrm{Mg}(\eta^6{:}\eta^6\text{-}\mathrm{K(THF)_2})][\mathrm{K(THF)_6}]\cdot(\mathrm{THF})_2$ (**6**). In contrast to the dimagnesium(I) compound **1**, the magnesium metal shows the oxidation state of +2 in these products. The mononuclear complexes **2**−**5** contain dianionic (**2** and **3**) or

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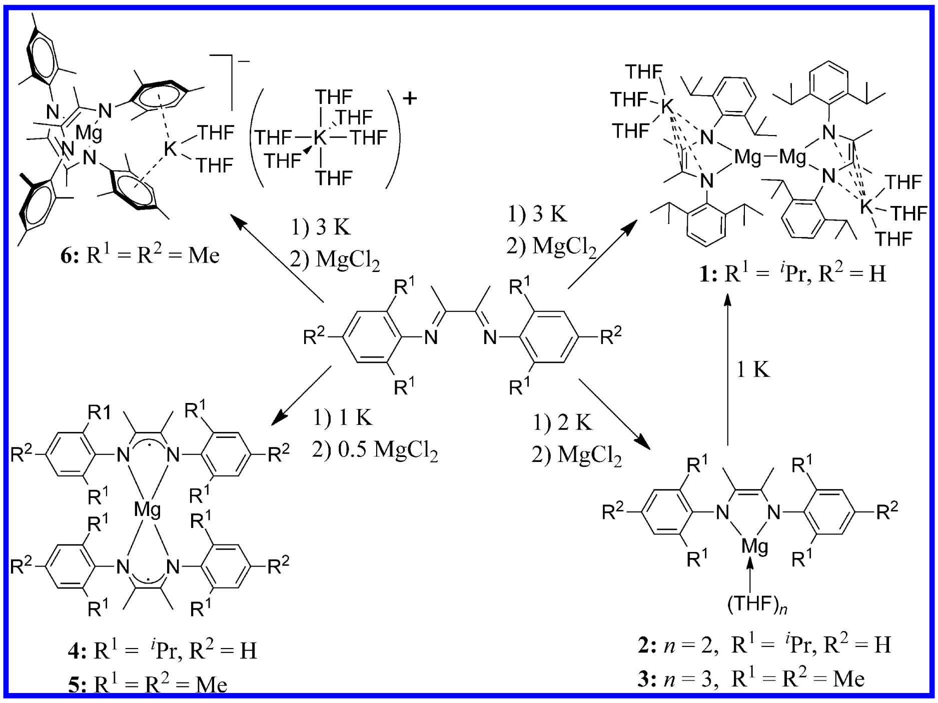
Scheme 1. Synthesis of Compounds 1−6



monoanionic (**4** and **5**) ligands, respectively, while the bimetallic compound **6** features dianionic ligands.

■ RESULTS AND DISCUSSION

Synthesis. The complexes **2**−**6** were obtained from the reaction of the reduced ligands and $\mathrm{MgCl_2}$ (Scheme 1). Reduction of the neutral ligands ($\mathrm{L}^{i\mathrm{Pr}}$ or $\mathrm{L}^{\mathrm{Mes}}$) with one or two equivalents of potassium metal in THF, followed by addition of one equivalent of anhydrous $\mathrm{MgCl_2}$, yielded the compounds **2**−**5**. Compounds $[(\mathrm{L}^{i\mathrm{Pr}})^{2-}\mathrm{Mg}(\mathrm{THF})_2]\cdot\mathrm{THF}$ (**2**) and $[(\mathrm{L}^{\mathrm{Mes}})^{2-}\mathrm{Mg}(\mathrm{THF})_3]$ (**3**) show a metal-to-ligand ratio of 1:1, in which the Mg^{2+} ion is further coordinated by two or three THF molecules. Compound **2** can be converted to **1** by addition of another equivalent of K, accompanied by the reduction of $\mathrm{Mg^{II}}$ to $\mathrm{Mg^{I}}$, while **3** has also been isolated by reduction of $\mathrm{L}^{\mathrm{Mes}}$ with metallic magnesium in THF.[13a] In the compounds $[(\mathrm{L}^{i\mathrm{Pr}})^{-}{}_2\mathrm{Mg}]\cdot\mathrm{THF}$ (**4**) and $[(\mathrm{L}^{\mathrm{Mes}})^{-}{}_2\mathrm{Mg}]$ (**5**), the Mg center is coordinated by two chelating ligands with an M:L ratio of 1:2. Initially, these two products were obtained from the reaction of L and $\mathrm{MgCl_2}$ in a 1:1 stoichiometry. We thus used half an equivalent of anhydrous $\mathrm{MgCl_2}$ in the reaction and, as expected, isolated **4** and **5** in a significantly improved yield. The compound **6**, $[(\mathrm{L}^{\mathrm{Mes}})^{2-}{}_2\mathrm{Mg}(\eta^6{:}\eta^6\text{-}\mathrm{K}(\mathrm{THF})_2)][\mathrm{K}(\mathrm{THF})_6]\cdot(\mathrm{THF})_2$, was prepared by a similar process to the synthesis of **1** (with $\mathrm{L}^{i\mathrm{Pr}}$) with three equivalents of K metal.[4] However, instead of forming a dimagnesium(I) compound like **1**, the divalent Mg complex (**6**) was yielded with two (solvated) K^+ ions incorporated in the structure. This difference may be caused by the smaller ligand $\mathrm{L}^{\mathrm{Mes}}$, which cannot provide sufficient protection for an $\mathrm{Mg^{I}}_2$ core, as also observed for the zinc analogues with such ligands.[11b]

These compounds are highly sensitive to air and moisture, but are thermally quite stable under argon at room temperature. They are soluble in THF and diethyl ether and slightly soluble in toluene and hexane. The formation of **1**−**6** can be readily monitored by the color change of the reaction solution from orange (free ligands) to red (potassium salt complexes), and to orange-red (magnesium compounds), from which the complexes could be isolated as red crystals. As mentioned above, the α-diimine ligands $\mathrm{L}^{i\mathrm{Pr}}$ and $\mathrm{L}^{\mathrm{Mes}}$ can take one or two electrons to form the monoanion and dianion, respectively, which can be reflected by the changes of the C−N and C−C bond lengths.[11,13] On going from the neutral ligand to the radical monoanion $\mathrm{L}^{\bullet-}$ and then to the enediamide dianion L^{2-}, the two C=N double bonds are elongated to single bonds via a C−N bond of 1.5 bond order, and the central C−C bond is shortened. As indicated in the crystal structures (see below), in compounds **1**−**3** and **6** the ligands appear as dianions, while in **4** and **5** they are the radical-monoanions.

X-ray Crystal Structures. Single crystals of **2**−**6** suitable for X-ray diffraction studies were obtained by slow evaporation of their THF solutions. The molecular structures of **2**−**6** in the solid state are depicted in Figures 1−4 and 6. Selected bond lengths and angles are listed in Tables 1−3, and the crystal data collection and structure refinement details are given in Table 4.

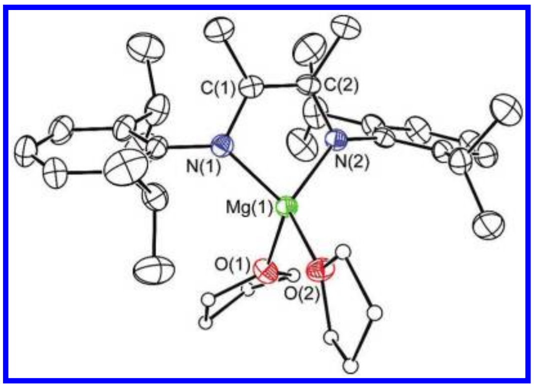


Figure 1. Molecular structure of **2** (thermal ellipsoids at the 20% probability level; H atoms are omitted for clarity; C atoms of THF are drawn as smaller spheres).

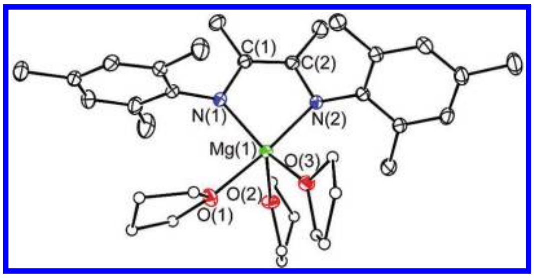


Figure 2. Molecular structure of **3** (thermal ellipsoids at the 20% probability level; H atoms are omitted for clarity; C atoms of THF are drawn as smaller spheres).

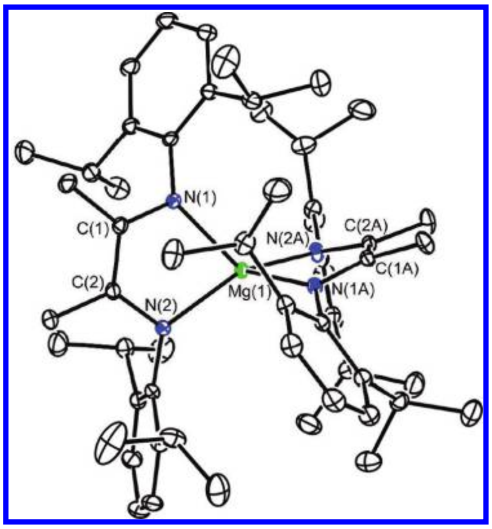


Figure 3. Molecular structure of **4** (thermal ellipsoids at the 20% probability level; H atoms are omitted for clarity).

$[(L^{iPr})^{2-}Mg(THF)_2]\cdot THF$ (2) and $[(L^{Mes})^{2-}Mg(THF)_3]$ (3). In the monomeric complex **2**, the Mg^{II} ion sits in a distorted tetrahedral environment containing one chelating α-diimine ligand and two THF molecules (Figure 1). The two Mg–N bonds (1.966(3) and 1.970(3) Å) and the two Mg–O bonds (2.012(3) and 2.038(2) Å) do not differ markedly in length. The bond angles around the Mg atom display apparent distortion from the ideal value of 109.5°, with the N–Mg–N (88.7°) bite angle and O–Mg–O (93.1°) angle being slightly acute and others widened (116.3–122.2°). The dihedral angle of the coordinate MgN_2 plane and the C_2N_2 plane is 13.1°, and the Mg atom deviates by 0.32 Å from the C_2N_2 plane.

Switching the ligand substituents from 2,6-diisopropyl to the less crowded 2,4,6-trimethyl also led to a mononuclear compound (**3**). The Mg^{II} center is coordinated by one ligand and three THF molecules in a distorted trigonal-bipyramidal geometry (Figure 2), which is different from the tetrahedral coordination of the Mg atom in **2** with one less THF. This structure was reported previously by us (but it was obtained from a different synthetic method).[13a] Compared to **2**, the Mg–N bonds (2.021(2) and 2.051(2) Å) and Mg–O bonds (2.196(2), 2.080(2), and 2.110(2) Å) in **3** are longer, and the N–Mg–N bite angle (84.04°) is smaller (88.70° in **2**). The Mg atom is more coplanar (deviating 0.19 Å) with the C_2N_2 plane.

Some similar magnesium or calcium complexes with related ligands, such as (dpp-Bian)$Mg(THF)_3$, (dpp-Bian)$Ca(THF)_4\cdot(THF)_{1/2}$, and (dph-Bian)$Ca(THF)_3$, have been reported in the literature.[8] We have also synthesized the calcium complex

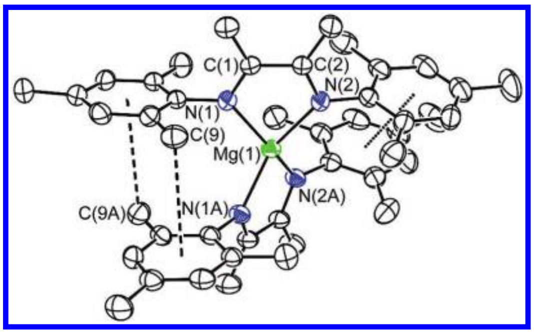


Figure 4. Molecular structure of **5** (thermal ellipsoids at the 20% probability level; H atoms are omitted for clarity).

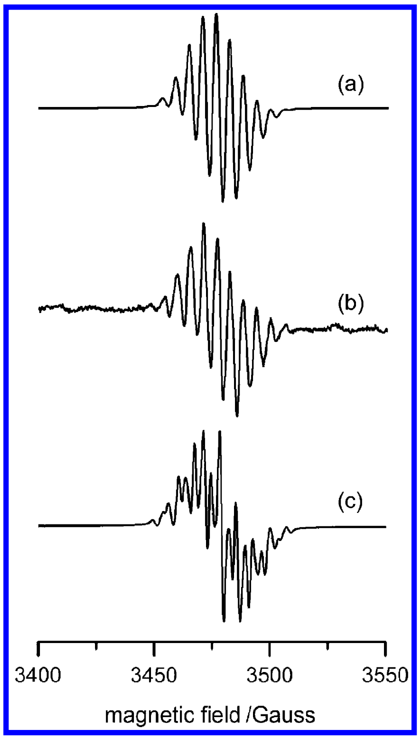


Figure 5. Room-temperature EPR spectra recorded in THF solution: (a) simulated; (b) experimental spectrum for **4**; and (c) experimental spectrum for **5**.

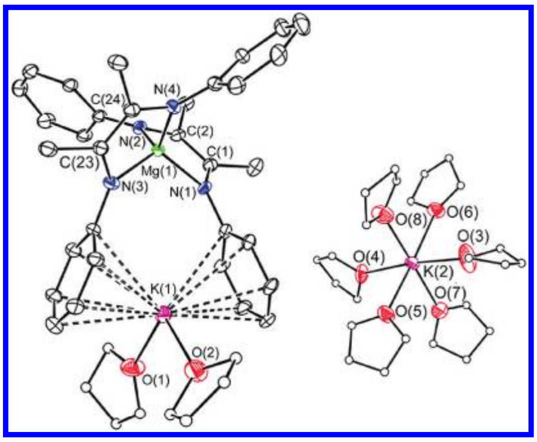


Figure 6. Molecular structure of **6** (thermal ellipsoids at the 20% probability level; ^{i}Pr groups and H atoms are omitted for clarity; C atoms of THF are drawn as smaller spheres).

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 2 and 3

	2	3
C(1)−C(2)	1.366(5)	1.350(3)
C(1)−N(1)	1.416(4)	1.406(3)
C(2)−N(2)	1.432(4)	1.426(3)
Mg(1)−N(1)	1.966(3)	2.021(2)
Mg(1)−N(2)	1.970(3)	2.051(2)
Mg(1)−O(1)	2.012(3)	2.196(2)
Mg(1)−O(2)	2.038(2)	2.080(2)
Mg(1)−O(3)		2.110(2)
N(1)−Mg(1)−N(2)	88.70(12)	84.04(9)
N(1)−Mg(1)−O(1)	116.29(12)	93.35(9)
N(1)−Mg(1)−O(2)	122.21(12)	143.59(9)
N(1)−Mg(1)−O(3)		112.49(9)
N(2)−Mg(1)−O(1)	117.87(12)	168.39(8)
N(2)−Mg(1)−O(2)	121.25(12)	95.44(9)
N(2)−Mg(1)−O(3)		104.50(8)
O(1)−Mg(1)−O(2)	93.12(11)	79.94(8)
O(1)−Mg(1)−O(3)		86.96(8)
O(2)−Mg(1)−O(3)		102.92(8)

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4 and 5

	4	5
C(1)−C(2)	1.403(5)	1.460(3)
C(1)−N(1)	1.358(4)	1.344(3)
C(2)−N(2)	1.367(4)	1.342(3)
Mg(1)−N(1)	2.078(2)	2.080(2)
Mg(1)−N(2)	2.094(3)	2.070(2)
N(1)−Mg(1)−N(2)	81.54(10)	79.38(8)
N(1)−Mg(1)−N(1A)	128.50(15)	108.18(14)
N(1)−Mg(1)−N(2A)	114.67(10)	149.78(9)
N(2)−Mg(1)−N(2A)	143.76(16)	109.16(14)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 6

Mg(1)−N(1)	2.045(4)	C(24)−N(4)	1.417(7)
Mg(1)−N(2)	2.066(4)	K(1)−O(1)	2.681(5)
Mg(1)−N(3)	2.035(4)	K(1)−O(2)	2.690(5)
Mg(1)−N(4)	2.065(4)	K(2)−O(3)	2.660(7)
C(1)−C(2)	1.340(8)	K(2)−O(4)	2.691(5)
C(1)−N(1)	1.430(7)	K(2)−O(5)	2.702(6)
C(2)−N(2)	1.409(7)	K(2)−O(6)	2.744(6)
C(23)−C(24)	1.368(7)	K(2)−O(7)	2.753(8)
C(23)−N(3)	1.411(7)	K(2)−O(8)	2.697(8)
N(1)−Mg(1)−N(2)	83.04(17)	N(1)−Mg(1)−N(3)	120.67(18)
N(3)−Mg(1)−N(4)	83.24(17)	N(2)−Mg(1)−N(4)	126.10(16)

$[(L^{iPr})^{2-}Ca(THF)_3]$ and obtained the preliminary structure that demonstrated the presence of three THF molecules. Unfortunately, further refinement of the structure was unsuccessful due to the poor crystal quality.[14] A comparison of these structures clearly indicates that the ionic radius of the metal ion (Mg^{II} or Ca^{II}) and the steric bulk of the ligand are the key factors that determine the number of THF molecules coordinated to the metal. The larger calcium atom tends to accommodate more THF molecules, and the bulkier *i*Pr-substituted ligand prefers less solvent molecules than the L^{Mes} ligand as in the cases of **2** and **3**.

Moreover, it is known that the reduced *α*-diimines can function as reducing agents for the synthesis of other organometallic compounds.[4,11,13] We have previously carried out the reaction of $ZnCl_2$ with the in situ generated $[(L^{iPr})^{2-}Na_2]$ and obtained the desired compound $[(L^{iPr})^{-}Zn-Zn(L^{iPr})^{-}]$. The dianion $(L^{iPr})^{2-}$ acted as an electron donor and reduced the initial divalent Zn^{II} ion to the Zn^{I} in the product, while the ligand itself was oxidized to the monoanion $(L^{iPr})^{-}$.[11c] In this work, the similar reaction of $[(L^{iPr})^{2-}K_2]$ with $MgCl_2$, however, did not produce the M−M-bonded complex but resulted in the mononuclear complex **2**, and no redox process occurred. In addition, the reaction of the doubly reduced ligands with $CaCl_2$ also did not cause the reduction of the divalent Ca^{II} ion.[13c] These results demonstrate the difference of the electropositive nature and reduction ability of the metal ions.

$[(L^{iPr})^{-}{}_2Mg]\cdot THF$ (4) and $[(L^{Mes})^{-}{}_2Mg]$ (5). Compounds **4** and **5** have similar compositions and structures, in which the Mg center is coordinated by two *α*-diimine ligands, forming a distorted tetrahedron. The ^{i}Pr-substituted compound **4** crystallizes in the monoclinic space group *P*2/*c* (Figure 3) with a lattice THF molecule. The Mg atom deviates by 0.661 Å from the C_2N_2 plane, and the average dihedral angle of the C_2N_2 plane and the N_2Mg plane is 22.1°. The two metallo C_2N_2Mg planes are nearly perpendicular to each other (with a dihedral angle of 79.7°).

The mesityl analogue **5** crystallizes in the orthorhombic space group *Fdd*2 with half of the molecule in the asymmetric unit, and the remaining part can be generated by a C_2 axis (Figure 4). The major difference of the structure of **5** from **4** is that the five-membered chelate ring C_2N_2Mg is nearly planar, with the Mg atom deviating only by 0.038 Å from the C_2N_2 plane (compared to 0.661 Å in **4**). Moreover, the relative orientation of the two C_2N_2Mg planes is "flattened" (with a dihedral angle of 46.9°) in a way that is between the tetrahedral and square-planar geometries, which is in contrast to the nearly perpendicular situation of tetrahedral geometry (79.7°) in **4**. These differences can be attributed to the larger steric repulsion of the L^{iPr} than the L^{Mes} ligand. The reason that complex **5** tends to adopt a flattened (instead of tetrahedral) structure may be that such an arrangement allows for two symmetry-related, rather strong C−H···*π* interactions between one of the methyl groups (C9) and the aryl ring of another ligand at one side of the molecule (C···centroid distance 3.528 Å, shown in dashed lines in Figure 4), as well as a *π*···*π* stacking interaction between the two aryl rings at the other side (dihedral angle 2.16°, centroid···centroid distance 3.953 Å, dotted line in Figure 4).

The 1:2 (metal-to-ligand) complexes **4** and **5** are similar to the mononuclear alkaline earth metal compounds with related ligands, such as $[(dpp\text{-}Bian)_2Mg]$,[8g] $(dipp\text{-}nacnac)_2Mg$, and $(dipp\text{-}nacnac)_2Ca$.[7b] For both **4** and **5**, the bond lengths of Mg−N (2.078(2)/2.094(3) Å in **4** and 2.080(2)/2.070(2) Å in **5**) are comparable to those in $(dipp\text{-}nacnac)_2Mg$ (2.100(2)/2.122(2) Å)[7b] and $[(dpp\text{-}Bian)_2Mg]$ (2.111(1)/2.102(1) Å).[8g] The bond lengths of C−C (1.403(5) Å in **4** and 1.460(3) Å in **5**) and C−N (1.358(4)/1.367(4) Å in **4** and 1.344(3)/1.342(3) Å in **5**) of the central C_2N_2 moieties indicate that the ligands are the *π* radical monoanions $(L)^{\bullet-}$ and the Mg is a divalent cation.

Since complexes **4** and **5** contain the monoanionic ligands, their EPR spectra have been studied at both room temperature and low temperature. The room-temperature spectra of **4** and **5** recorded in THF and the simulated spectrum for them are shown in Figure 5. The simulation gave identical hyperfine

Table 4. Crystallographic and Structure Refinement Data for 2−6

	2	3	4	5	6
empirical formula	$C_{40}H_{64}N_2O_3Mg$	$C_{34}H_{52}N_2O_3Mg$	$C_{60}H_{88}N_4OMg$	$C_{44}H_{56}N_4Mg$	$C_{84}H_{136}N_4O_{10}MgK_2$
fw	645.24	561.09	905.65	665.24	1464.48
cryst syst	orthorhombic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	*Pbca*	$P\bar{1}$	*P*2/*c*	*Fdd*2	$Pna2_1$
a/Å	18.5135(16)	9.9238(7)	13.4746(17)	20.497(6)	26.701(3)
b/Å	20.2977(18)	10.9398(7)	12.1227(15)	26.472(7)	12.6843(16)
c/Å	21.0200(18)	16.2205(11)	20.8669(19)	14.723(4)	25.711(3)
α/deg	90.00	74.7420(10)	90.00	90.00	90.00
β/deg	90.00	76.3520(10)	125.462(5)	90.00	90.00
γ/deg	90.00	82.9480(10)	90.00	90.00	90.00
V/Å^3	7898.9(12)	1647.46(19)	2776.3(6)	7989(4)	8707.9(19)
Z	8	2	2	8	4
D_{calcd}/g cm^{-3}	1.085	1.131	1.083	1.106	1.117
cryst size/mm^3	0.30 × 0.25 × 0.25	0.25 × 0.20 × 0.20	0.25 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.25
F(000)	2832	612	992	2880	3192
μ/mm^{-1}	0.081	0.088	0.074	0.079	0.171
θ range	1.78−25.07	2.06−25.00	1. 68−24.77	1.87−25.05	1.95−24.74
reflns collected	38 520	11 048	177 76	12 999	54 019
indep reflns	6977	5687	4726	3529	14 631
obsd reflns [$I > 2\sigma(I)$]	3421	4637	2663	2318	8737
R_{int}	0.0808	0.0188	0.0461	0.0417	0.0686
R_1, wR_2 [$I > 2\sigma(I)$]	0.0653, 0.1765	0.0493, 0.1369	0.0668, 0.1862	0.0429, 0.0971	0.0751, 0.1854
R_1, wR_2 (all data)	0.1424, 0.2283	0.0604, 0.1481	0.1248, 0.2294	0.0820, 0.1132	0.1417, 0.2260
GOF (F^2)	1.004	1.029	1.034	1.021	1.053

coupling constants, $a^N = a^H = 5.58$ G, which are very close to those (5.59 G) of $[(L^{iPr})^-Mg(\mu\text{-Me})]_2$ with the same $(L^{iPr})^-Mg$ fragment.[8e] The spectrum of **4** is well resolved and can be explained as originating from the superimposition of overlapping quintets (due to two equivalent ^{14}N nuclei, $I = 1$) and septets (due to six equivalent ^1H nuclei of two methyl groups, $I = 1/2$). Since the a^N and a^H couplings are identical, the spectrum of **4** appears as an asymmetric 11-lined signal with ratios 1: 2: 3: 5: 8: 9: 8: 5: 3: 2: 1, which results from the overlap of the quintets of septets splitting. The experimental result of **4** is in good agreement with the simulated one and is also similar to literature reports on related systems.[8e] In the case of compound **5**, reduced overlap and more splitting was observed (Figure 5). The differences between the hyperfine coupling of **4** and **5** may be attributed to the subtle differences of their structures. Compound **4** (with the larger L^{iPr} ligand) shows a slightly distorted tetrahedral coordination geometry, and the two ligand radicals are nearly orthogonal to each other. In contrast, compound **5** adopts a flattened structure, which leads to more asymmetric environments for the N atoms and methyl groups (Figure 4) and results in the reduced overlap of lines in the EPR spectrum. Nevertheless, the *g* values (2.0037 for **4** and **5**) and coupling patterns suggest that the electrons are highly delocalized over the ligands, which are consistent with related compounds containing radical anionic diimine ligands.[8d−f,10,c,c]

The frozen solution (toluene, 150 K) EPR spectra of compounds **4** and **5** (Figures S1 and S2) further confirmed that these compounds are biradical species with one unpaired electron localized on each ligand. From the zero-field splitting parameters (*D*, 196 and 185 G), the distances between the geometric centers of the localization of the unpaired electrons were calculated to be 5.21 and 5.31 Å. These values are consistent with the distances of 5.48 and 5.62 Å between the imino carbon atoms C(1)−C(1A) and C(2)−C(2A) in **4** and **5**, respectively, in the crystal structures and are also comparable to those in $[(\text{dpp-Bian})_2Mg]$ (5.28 and 5.65 Å from EPR[8d] and X-ray data,[8g] respectively). Moreover, evidence for the biradical nature of **4** and **5** was also obtained from their half-field ($\Delta M_s = 2$) transitions (Figure S1). The extremely weak half-field transitions ($\Delta M_s = 2$) characteristic of the $S = 1$ triplet ground state were observed at 1680 and 1685 G (see Figure S3), respectively, which indicate that the two $S = 1/2$ spins are only weakly coupled and the unpaired electrons are primarily localized on the NCCN backbone.[8h]

$[(L^{Mes})^{2-}{}_2Mg(\eta^6{:}\eta^6\text{-}K(THF)_2)][K(THF)_6]\cdot(THF)_2$ (6). In order to gain more insights into the chemistry of the magnesium compounds with α-diimine ligands, a similar process employed to synthesize the Mg−Mg-bonded species **1** was adopted in the reaction of the less bulky L^{Mes} and anhydrous $MgCl_2$ with three equivalents of potassium metal. Interestingly, the compound $[(L^{Mes})^{2-}{}_2Mg(\eta^6{:}\eta^6\text{-}K(THF)_2)][K(THF)_6]\cdot(THF)_2$ (**6**) was isolated.

Compound **6** contains an anionic $[(L^{Mes})^{2-}{}_2MgK(THF)_2]^-$ unit and a $[K(THF)_6]^+$ cation (Figure 6), the former involving alkali metal cation−π interactions between potassium and substituted arene groups, which recently emerged as an important bonding force.[15] In the anionic fragment, the Mg^{2+} center is coordinated by four N atoms of two α-diimine ligands in a distorted tetrahedral geometry similar to **4** and **5**. The Mg atom deviates by 0.652 and 0.693 Å from the two C_2N_2 planes. The average Mg−N bond length (2.040 Å) is shorter than that in **4** and **5**. There is one potassium ion (K1) in the anionic moiety, which is η^6-sandwiched by two flanking N-phenyl rings from each of the α-diimine ligands and is also coordinated by two THF molecules, which is different from the situation in compound **1** (where the K^+ ion contacts with the C_2N_2 backbone of the dianionic ligand).[4] The K−C distances vary between 3.127 and 3.259 Å, which are comparable with the K–C bond lengths found in $[(\eta^6{:}\eta^6\text{-K(THF)}(\eta^6{:}\eta^6\text{-K-(THF)}_2)][\text{Mg}\{\eta^2\text{-Me}_2\text{Si(Ndipp)}_2\}_2]$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) (2.968(3)–3.298(3) Å) and $[\{(\text{THF})_2\text{K}(\mu\text{-N(Ph)}^i\text{Pr})_2\}_2\text{Ca}]$ (3.156(2)–3.259(2) Å) with the slipped η^6-coordination.[15] The average distance of K···phenyl ring is about 2.861 Å, while the Mg···K separation is 4.669 Å. In the countercation fragment, the K(2)$^+$ ion is coordinated by six THF molecules in an octahedral arrangement with K–O distances ranging from 2.660(7) to 2.753(8) Å. The carbon atoms of the THF molecules are disordered and have been refined using two split positions and geometrical constraints. The average bond lengths of C–C (1.354 Å) and C–N (1.434 Å) in **6** confirm the dianionic character of the ligand.

A similar complex of the congener calcium, $[(\text{L}^{i\text{Pr}})^{2-}{}_2\text{CaK}_2(\text{THF})]_n$,[13c] reported by us also shows a Ca:K:L ratio of 1:2:2 as in compound **6**. However, its structure is significantly different. Although the main structural motif is the tetrahedral [L$_2$M] core in both the magnesium compound **6** and the calcium analogue $[(\text{L}^{i\text{Pr}})^{2-}{}_2\text{CaK}_2(\text{THF})]_n$, the location and coordination mode of the two K$^+$ ions are different. In the calcium compound, one of the K$^+$ ions is sandwiched by two phenyl rings in two separated $[(\text{L}^{i\text{Pr}})^{2-}{}_2\text{Ca}]$ units, while the other K$^+$ cation is η^3-coordinated by the phenyl rings from two ligands within one $[(\text{L}^{i\text{Pr}})^{2-}{}_2\text{Ca}]$ unit. As a result, an infinite left-handed 2$_1$ helical chain is formed.[13c] In the magnesium species **6**, one potassium ion is encapsulated by two phenyl rings within one $[(\text{L}^{i\text{Pr}})^{2-}{}_2\text{Mg}]$ unit, but the other K$^+$ ion is isolated and does not form any contacts with the diimine ligand; instead, it is solvated by six THF molecules. Thus a discrete rather than infinite structure results.

CONCLUSION

A series of magnesium complexes with reduced α-diimine ligands have been synthesized by the reaction of the neutral ligand, MgCl$_2$, and potassium metal. By varying the equivalents of K (to L), the α-diimine ligands accepted one or two electrons and formed the dianion (in **2**, **3**, and **6**) or the monoanion (in **4** and **5**) in the resulting complexes. However, the initial divalent magnesium ion retained its oxidation state of +2, which is different from the case of the Mg$^\text{I}$–Mg$^\text{I}$-bonded compound. Variable structures were obtained upon changing the amount of the reducing agent K and ligand substituents, and the effects of these factors have been discussed.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under an inert atmosphere of argon using standard Schlenk or drybox techniques. Tetrahydrofuran was dried by sodium/benzophenone and distilled under argon prior to use. Anhydrous MgCl$_2$ was purchased from Alfa Aesar. Benzene-d_6 was dried over Na/K alloy. The reduced ligands, LK$_n$ (L = L$^{i\text{Pr}}$ or L$^\text{Mes}$; n = 1 or 2), were prepared as previously described.[13a] ^{1}H NMR spectra were obtained on a Bruker DPX-200 NMR spectrometer. Elemental analyses were performed with an Elementar VarioEL III instrument. EPR spectra were recorded on a Bruker EMX-10/12 spectrometer.

Synthesis of $[(\text{L}^{i\text{Pr}})^{2-}\text{Mg(THF)}_2]\cdot\text{THF}$ (2). Anhydrous MgCl$_2$ (0.070 g, 0.741 mmol) was added to a rigorously stirred solution of $[(\text{L}^{i\text{Pr}})^{2-}\text{K}_2]$ in THF [prepared in situ from L$^{i\text{Pr}}$ (0.300 g, 0.741 mmol) and two equivalents of potassium (0.058 g, 1.48 mmol)]. The mixture was stirred for 3 days at room temperature. It was then filtered, and the filtrate was concentrated to ca. 5 mL. Slow evaporation of the solution at −20 °C for several days gave the product **2** as red crystals (0.16 g, 38%). ^{1}H NMR (400 MHz, C$_6$D$_6$, δ/ppm): 1.20 (d, 24H, CH(C*H*$_3$)$_2$), 1.29 (THF), 2.03 (s, 6H, CCH$_3$), 3.50 (m, 4H, C*H*(CH$_3$)$_2$ and THF), 6.99–7.14 (m, 6H, ArH). Anal. Calcd for C$_{36}$H$_{56}$N$_2$O$_2$Mg·THF (645.24): C, 74.45; H, 9.99; N, 4.34. Found: C, 74.63 ; H, 10.15 ; N, 4.21.

Synthesis of $[(\text{L}^\text{Mes})^{2-}\text{Mg(THF)}_3]$ (3). Method A. Complex **3** was prepared by a similar procedure to that employed for **2**, from MgCl$_2$ (0.089 g, 0.936 mmol), L$^\text{Mes}$ (0.300 g, 0.936 mmol), and K (0.073 g, 1.87 mmol). Red crystals (0.309 g, 59%) were isolated. ^{1}H NMR (400 MHz, C$_6$D$_6$, 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). **Method B.** As reported previously by us.[13a]

Synthesis of $[(\text{L}^{i\text{Pr}})^{-}{}_2\text{Mg}]\cdot\text{THF}$ (4) and $[(\text{L}^\text{Mes})^{-}{}_2\text{Mg}]$ (5). Complexes **4** and **5** were also prepared by the same method as described above. For **4**: MgCl$_2$ (0.059 g, 0.62 mmol), L$^{i\text{Pr}}$ (0.500 g, 1.24 mmol), and K (0.050 g, 1.24 mmol). Red crystals (0.11 g, 22%). Anal. Calcd for C$_{56}$H$_{80}$N$_4$Mg·THF (905.65): C, 79.57; H, 9.79; N, 6.18. Found: C, 79.30; H, 9.71; N, 6.10. For **5**: MgCl$_2$ (0.074 g, 0.78 mmol), L$^\text{Mes}$ (0.500 g, 1.56 mmol), and K (0.061 g, 1.56 mmol). Red crystals (0.11 g, 22%). Anal. Calcd for C$_{44}$H$_{56}$N$_4$Mg·THF (741.38): C, 77.76; H, 8.70; N, 7.56. Found: C, 77.22 ; H, 8.22 ; N, 8.06.

Synthesis of $[(\text{L}^\text{Mes})^{2-}{}_2\text{Mg}(\eta^6{:}\eta^6\text{-K(THF)}_2)][\text{K(THF)}_6]\cdot(\text{THF})_2$ (6). Three equivalents of potassium (0.180 g, 4.69 mmol) were added to a THF solution of L$^\text{Mes}$ (0.500 g, 1.56 mmol) at room temperature. The mixture was stirred for 24 h, and anhydrous MgCl$_2$ (0.150 g, 1.56 mmol) was added. Further reaction for 2 days and subsequent workup yielded red crystals of **6** (0.38 g, 37%). ^{1}H NMR (400 MHz, C$_6$D$_6$, δ/ppm): 1.40 (m, 32H, THF), 1.54 (s, 6H, CCH$_3$), 2.01 (broad, 12H, o-ArCH$_3$), 2.33 (s, 6H, p-ArCH$_3$), 3.56 (s, 6H, THF), 6.70 (m, 4H, ArH). Anal. Calcd for C$_{80}$H$_{128}$K$_2$MgN$_4$O$_8$·THF (1392.40): C, 69.01; H, 9.26; N, 4.02. Found: C, 69.43; H, 9.07; N, 4.32.

X-ray Crystal Structure Determination. Diffraction data for compounds **2**–**6** were collected on a Bruker SMART APEX II diffractometer at 296 K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data. The structures were solved by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL. 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 and refinement details are listed in Table 4.

ASSOCIATED CONTENT

Supporting Information

EPR spectra of compounds **4** and **5** and detailed information on the X-ray crystal structure analysis of compounds **2** and **4**–**6** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Unpublished results. Preliminary crystal data for $[(L^{iPr})^{2-}Ca(THF)_3]$: $C_{80}H_{128}N_4O_6Ca_2$, fw = 1322.02, monoclinic, space group $P2_1/n$, $a = 9.8968(9)$ Å, $b = 38.527(3)$ Å, $c = 22.576(2)$ Å, $\beta = 93.157(2)°$, $V = 8595.1(1)$ Å^3, $Z = 4$, $D_c = 1.022$ g cm^{-3}, $F(000) = 2896$, $m = 0.179$ mm^{-1}, 296(2) K, 6902 unique reflections [$R_{int} = 0.0915$], $R_1 = 0.1232$, $wR_2 = 0.3463$ [$I > 2\sigma(I)$].

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