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Solvent-Free Alkali and Alkaline Earth Metal Complexes of Di-imine Ligands

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ABSTRACT: *Compound [(dph-BIAN)Mg(THF)]$_2$ (**2**) was prepared by reacting magnesium metal with 1,2-bis[(2-biphenyl)imino]acenaphthene (dph-BIAN) in THF, followed by crystallization from toluene. Reaction of CaI$_2$ with (dpp-BIAN)Li$_2$ in toluene afforded [(dpp-BIAN)Li]$_2$Ca (**3**) (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene). Both complexes **2** and **3** were characterized by single crystal X-ray diffraction. The ^{1}H NMR spectroscopic data obtained for complex **3** in toluene solution indicated an agostic interaction between the methyl groups of the ligand and lithium atoms.* Heteroatom Chem 16:663–670, 2005; DOI 10.1002/hc.20168

INTRODUCTION

Main group metal complexes with ligands possessing a variable “oxidation state” might be a new class of reagents for organic synthesis. Such ligands in metal complexes may act as neutral, radical-anionic, dianionic donors, able to change their “oxidation state” under attack from different substrates, thus acting as electron sink or tank. It is required, however, that with electron transfer, these ligands stay coordinated to the metal. This approach could provide for red/ox active complexes of red/ox nonactive metal ions as, for instance, the group 1 and 2 metals.

In recent years, we have reported the preparation of a series of main group metal complexes with acenaphthene-1,2-di-imines, e.g. dpp-BIAN, dtb-BIAN, and dph-BIAN (Chart 1), which may posses a variable “oxidation state.”

Alkali and alkaline earth metal complexes of these di-imines can be prepared by direct reduction of these compounds with metals of groups 1 and 2. Thus, reactions of dpp-BIAN with metallic Li or Na afford in series mono-, di-, tri-, and tetra-anions of dpp-BIAN [1]. In the case of Mg and Ca, the reactions with dpp-BIAN, dtb-BIAN, or dph-BIAN produce solvated monomeric complexes of dianionic BIAN ligands [2], e.g. (dpp-BIAN)Mg(THF)$_3$ and (dpp-BIAN)Ca(THF)$_4$ [2a]. The BIAN complexes of aluminum [3] and germanium(II) [4], in which the BIAN ligands are present in their radical-anionic or dianionic form, were prepared by exchange reactions of Al and Ge halides with alkali and alkaline earth metal derivatives of the corresponding di-imine ligands.

Recently, we have demonstrated that alkaline earth metal complexes with dianionic BIAN ligands have a unique reactivity toward organic substrates [5–8]. Thus, the electron transfer from (dpp-BIAN)Mg(THF)$_3$ (**1**) to Ph$_2$CO affords the pinacolate product, while the reaction of **1** with 9-(10*H*)-anthracenone yields anthryloxymagnesium derivative (Scheme 1) [5].

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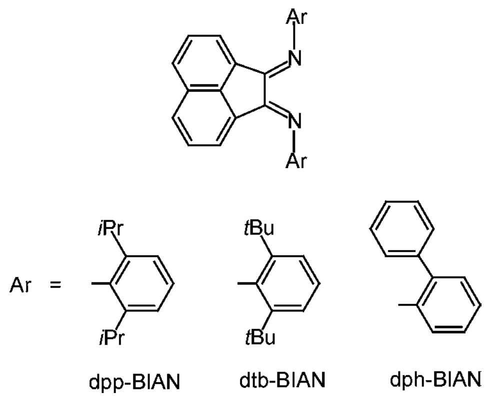


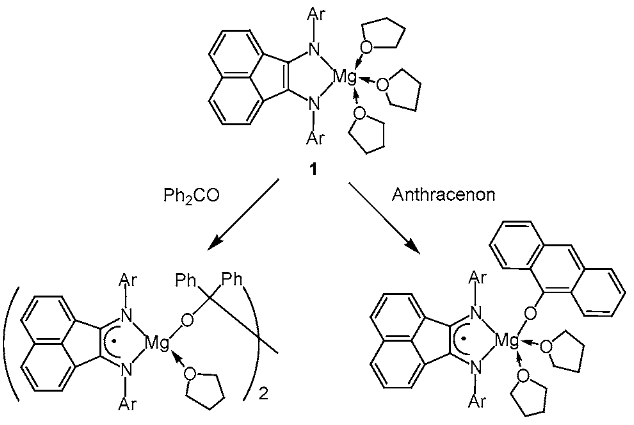
CHART 1

Reactions of complex **1** with Et-X (X = Cl, Br, I) or Me_3SiCl proceed via attack of the ligand by the radical formed by electron transfer from **1** to the organic halide [6] (see Graphic 1). In the case of Me_3SiCl, the reaction involves cleavage of the THF cycle.

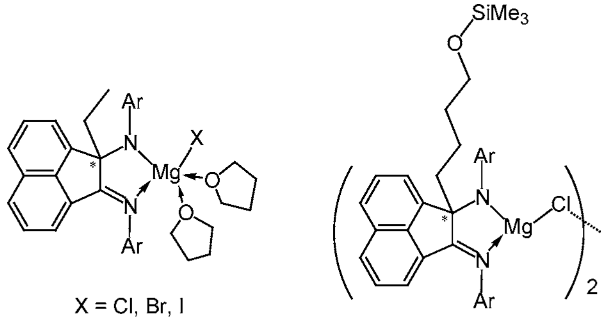
The opposite to the above-discussed reactions, i.e. reduction of the coordinated radical anion to a dianion has also been observed on the organomagnesium complex (dpp-BIAN)$^-$Mg(*i*Pr)(Et_2O). This complex is stable in hydrocarbons and diethyl ether but reductively eliminates an isopropyl radical when dissolved in THF (Scheme 2) [7].

Compound **1** easily adds acidic substances, e.g. phenylacetylene [8a], enolisable ketones [8b], and nitriles [8c]. The high proton affinity of the basic nitrogen atoms in dianionic dpp-BIAN ligand in **1** makes possible the uptake of the hydrogen atom from the substrate to a ligand nitrogen atom and formation of corresponding alkynyl, enolate, and keteniminate derivatives.

One can expect that reactivity of alkaline earth metal complexes of dianionic BIAN ligands may be further extended toward nonacidic and weak electron accepting substrates, for example, alkenes and alkanes. However, in this context one has to provide a free coordination site on the metal bound to the BIAN ligand. We have attempted to prepare coordinatively unsaturated Mg and Ca complexes with dpp-BIAN ligand by elimination of the coordinated THF molecules from (dpp-BIAN)Mg($THF)_3$ and (dpp-BIAN)Ca($THF)_4$ by pumping on the toluene solutions at reflux. In each case, this procedure allowed eradication of only one of the THF molecules coordinated to the metals [2a]. In this paper, we report on the use of this approach to another magnesium complex, as well as the exploitation of noncoordinating solvents in the synthesis of BIAN metal complexes.



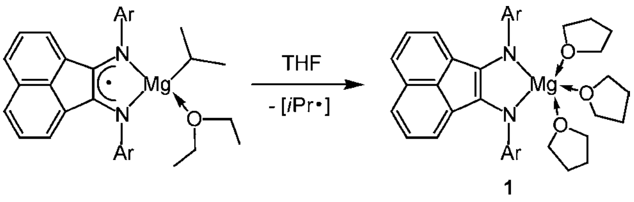
SCHEME 1



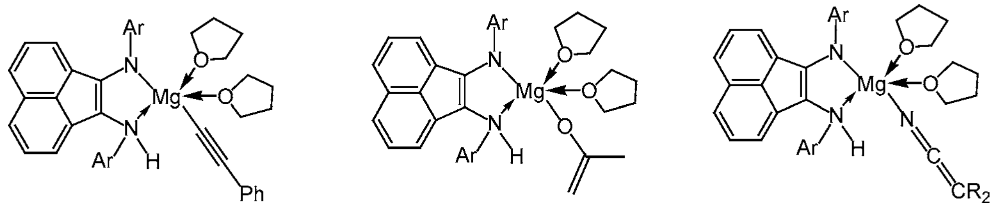
GRAPHIC 1

RESULTS AND DISCUSSION

The reaction of dph-BIAN with activated magnesium metal in THF at reflux resulted in the formation of an emerald green solution within a few minutes. Separation of this solution from unreacted metal and evaporation of the solvent afforded the crystalline magnesium complex (dph-BIAN)Mg($THF)_2$. This crude product was dissolved in toluene by heating, and the solvent was removed in vacuum at elevated temperature. Repetition of this dissolution/evaporation procedure three times resulted in changing the color of mixture from deep green to deep blue and precipitation of black crystalline solid. Crystallization of the product formed from



SCHEME 2



GRAPHIC 2

toluene at ambient temperature gave compound [(dph-BIAN)Mg(THF)]$_2$ (**2**) as deep blue almost black rhombic crystals. Compound **2** was characterized by elemental analysis and IR spectroscopy. Its molecular structure was determined by single crystal X-ray analysis. The ^{1}H NMR spectrum of **2** in C_6D_6 is not informative, as it consists of numerous broadened and overlapping signals in the aromatic region.

Crystals of **2** formed from C_6D_6 in the NMR tube were found suitable for single crystal X-ray analysis. The molecular structure of **2** is depicted in Fig. 1. The crystal data collection and structure refinement data for **2** are listed in Table 1. The molecule of **2** is centrosymmetric dimer formed from two (dph-BIAN)Mg(THF) subunits with the inversion center located at the middle point between Mg(1) and Mg(1a) (Mg(1)–Mg(1a) 3.009(1) Å). In the subunits, each magnesium atom is bound to two nitrogen atoms of the chelating dph-BIAN ligand and to the oxygen atom of the THF molecule. Aggregation of two subunits occurred through interactions Mg(1)–N(2a) and Mg(1)–C(2a), and their symmetry related equivalents. Due to the different bonding modes of two N atoms, the Mg(1)–N(1) and Mg(1)–N(2) distances differ significantly from each other (2.035(1) and 2.159(1) Å, respectively). Note that the interaction Mg(1)–N(2a) (2.121(1) Å), which causes dimer formation, is even shorter than the distance Mg(1)–N(2) (2.159(1) Å). The fact that atoms N(2) and N(2a), in contrast to N(1) and N(1a), bridge magnesium atoms explains the difference of C—N bond distances within the di-imine skeleton: the bond distance N(1)–C(1) (1.401(2) Å) is shorter than N(2)–C(2) (1.437(1) Å). In the four-coordinate monomeric complex (dpp-BIAN)Mg(THF)$_2$, the relevant N(1)–C(1) and N(2)–C(2) distances are fairly the same (1.393(1) and 1.395(1) Å) [2a].

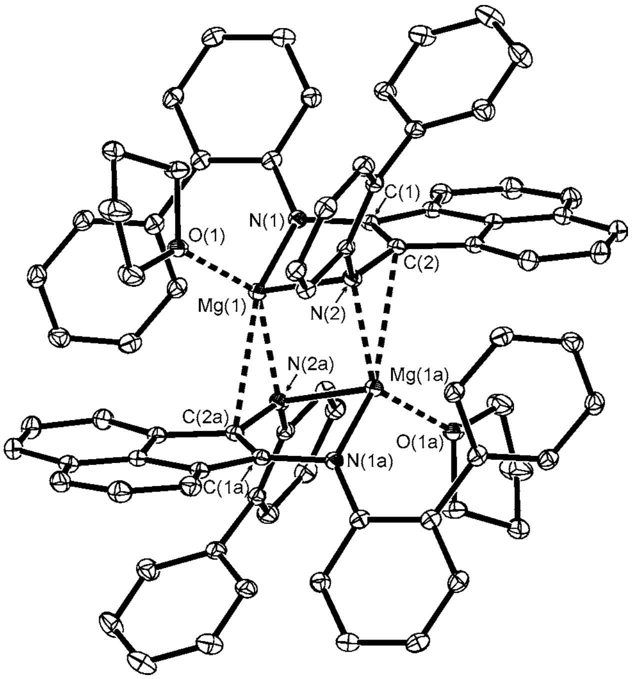


FIGURE 1 ORTEP view of **2** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å: Mg(1)–O(1) 2.0021(12), Mg(1)–N(1) 2.0351(13), Mg(1)–N(2) 2.1588(14), Mg(1)–N(2a) 2.1205(13), Mg(1)–C(1) 2.6938(16), Mg(1)–C(2) 2.7582(16), Mg(1)–Mg(1a) 3.0091(10), N(1)–C(1) 1.401(2), N(2)–C(2) 1.4363(19), C(1)–C(2) 1.384(2).

The color of BIAN group 1 and 2 metal complexes arises from the anionic di-imine ligand. The Mg and Ca complexes, in which the metal cations M^{2+} are symmetrically chelated by dianionic BIAN ligand, are green in color. In contrast, compound **2** has deep blue color. The same blue color has been observed in a number of magnesium complexes, which however consist of two cations $(RMg)^+$ and H^+; each bound to two different N atoms of the di-imine ligand [8a–c]. Another blue-colored derivative of BIAN ligand is the complex (dpp-BIAN)(Mg-*i*Pr)$_2$(Et$_2$O). Although this compound consists of two same cations $(i\text{PrMg})^+$, they are asymmetrically coordinated to two N atoms of the ligand [7]. Taking this into account, one may conclude that blue color of BIAN dianions emerges from the charge transfer between two nonequivalent nitrogen atoms of dianionic BIAN ligands. Comparison of the molecular structures of compounds **2** and (dpp-BIAN)Mg(THF)$_2$ shows that after loss of the THF ligands, which provide the coordinative saturation of the metal cation, the complexes restore saturation by recruiting electrons from the BIAN ligand.

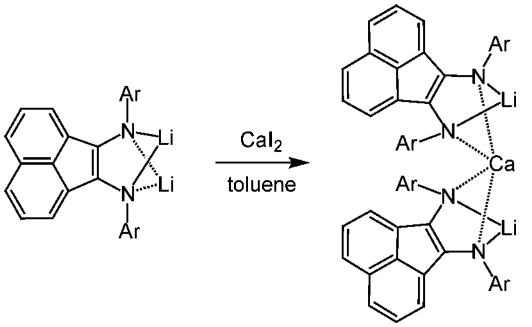
TABLE 1 Crystal Data and Structure Refinement Details for **2, 3,** and **4**

	2	**3**	**4**
Empirical formula	$C_{86}H_{70}Mg_2N_4O_2 \times 2C_6H_6$	$C_{72}H_{80}CaLi_2N_4 \times 4C_7H_8$	$C_{72}H_{80}MgN_4$
Formula weight	1369.3	1423.90	1025.71
Temperature (K)	100(2)	100(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C2/c*	*Cc*	*Pbcn*
Unit cell dimensions (Å, ○)	$a = 27.2065(18)$ $b = 12.9168(9)$ $c = 21.4597(14)$ $\beta = 91.6900(10)$	$a = 12.3693(9)$ $b = 28.150(2)$ $c = 22.9605(17)$ $\beta = 90.285(2)$	$a = 17.6110(9)$ $b = 15.4931(8)$ $c = 21.6442(11)$
Volume ($Å^3$)	7538.1(9)	7994.7(10)	5905.6(5)
Z	8	4	4
ρ_{calc} (g cm^{-3})	1.230	1.183	1.154
μ (mm^{-1})	0.088	0.130	0.076
$F(000)$	2952	3064	2208
Crystal size (mm^3)	0.63 × 0.59 × 0.24	0.30 × 0.25 × 0.20	0.42 × 0.36 × 0.14
$\theta_{min}/\theta_{max}$	1.75/25.06	1.70/25.00	1.75/22.50
Index ranges	$-32 \leq h \leq 32$ $-13 \leq k \leq 15$ $-20 \leq l \leq 25$	$-14 \leq h \leq 14$ $-28 \leq k \leq 33$ $-27 \leq l \leq 24$	$-18 \leq h \leq 18$ $-13 \leq k \leq 16$ $-23 \leq l \leq 20$
Reflections collected	19,833	22,048	24,643
Independent reflections	6663	12748	3863
R_{int}	0.0313	0.0219	0.0410
Completeness to θ_{max} (%)	99.7	99.9	99.8
Absorption correction	SADABS	SADABS	SADABS
Max./min. transmission	0.9793/0.9469	0.9745/0.9621	0.9894/0.9688
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6663/0/642	12748/54/902	3863/0/508
GOF on F^2	1.014	1.049	1.044
Final R indices [I ¿ 2 $\sigma(I)$]	$R_1 = 0.0387$ $wR_2 = 0.0968$	$R_1 = 0.0590$ $wR_2 = 0.1573$	$R_1 = 0.0391$ $wR_2 = 0.0935$
R indices (all data)	$R_1 = 0.0539$ $wR_2 = 0.1048$	$R_1 = 0.0705$ $wR_2 = 0.1656$	$R_1 = 0.0549$ $wR_2 = 0.1004$
Largest diff. peak/hole (e $Å^{-3}$)	0.302/−0.245	0.851/−0.440	0.262/−0.138

The above given results together with those recently published [2a] led us to the conclusion that once being used in the synthesis of BIAN metal complexes, the coordinating solvent (e.g. THF) cannot be completely removed from the metal coordination sphere of the obtained complexes. Keeping this in mind, we decided to exclude the coordinating solvent in the synthesis. However, metallic magnesium and calcium activated with iodine do not react with dpp-BIAN in toluene, even at reflux. However, we found that the exchange reaction between CaI_2 and dilithium salt of dpp-BIAN, obtained in toluene, independent of the reagent ratio, gives the solvent-free dpp-BIAN-Ca derivative, in which the Li cations are still present [(dpp-BIAN)Li]$_2$Ca (**3**) (Scheme 3).

Compound **3** crystallizes from toluene as deep blue crystals. The solution behavior of **3** was investigated by ^{1}H NMR spectroscopy, and its crystal structure (Fig. 2 and Table 1) was determined by X-ray diffraction analysis on crystals obtained from toluene.

In the solid state, complex **3** exhibits a metallocene-like structure, in which two anionic



SCHEME 3

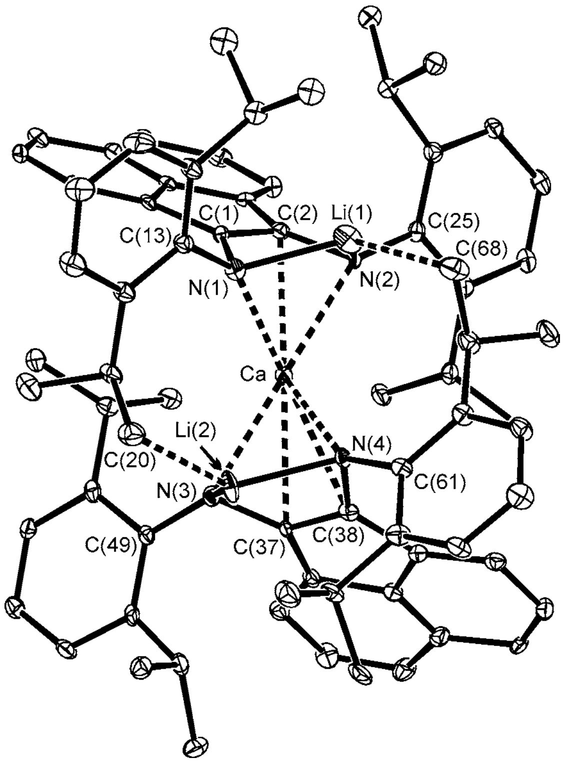


FIGURE 2 ORTEP view of **3** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å): Ca(1)–N(1) 2.434(2), Ca(1)–N(2) 2.420(2), Ca(1)–N(3) 2.417(2), Ca(1)–N(4) 2.423(2), Ca(1)–C(1) 2.663(2), Ca(1)–C(2) 2.636(3), Ca(1)–C(37) 2.647(2), Ca(1)–C(38) 2.665(3), Ca(1)–Li(1) 2.948(5), Ca(1)–Li(2) 2.946(5), Li(1)–N(1) 2.011(6), Li(1)–N(2) 2.013(5), Li(2)–N(3) 2.012(5), Li(2)–N(4) 2.033(5), Li(2)–C(20) 2.391(5), Li(1)–C(68) 2.403(6), Li(1)–C(1) 2.528(5), Li(1)–C(2) 2.538(5), N(1)–C(1) 1.407(3), N(1)–C(13) 1.434(3), C(1)–C(2) 1.404(3), Li(2)–C(38) 2.523(5), Li(2)–C(37) 2.538(5), N(2)–C(2) 1.405(3), N(2)–C(25) 1.415(3), N(3)–C(37) 1.419(3), N(3)–C(49) 1.426(3), N(4)–C(38) 1.411(3), N(4)–C(61) 1.443(3), C(37)–C(38) 1.381(3).

metallocycles (virtual analogs of the cyclopentadienyl rings) are coordinated to calcium atom. All four Li–N distances fall into narrow range of 2.01–2.03 Å (Li(1)–N(1) 2.011(6), Li(1)–N(2) 2.013(5), Li(2)–N(3) 2.012(5), Li(2)–N(4) 2.033(5) Å). The Ca–N distances are also very close and differ only within estimated standard errors (Ca(1)–N(1) 2.434(2), Ca(1)–N(2) 2.420(2), Ca(1)–N(3) 2.417(2), Ca(1)–N(4) 2.423(2) Å). Again, the Ca–Li(1) and Ca–Li(2) distances are fairly the same (2.948(5) and 2.946(5) Å). These parameters indicate that both Li-metallocycles are equally coordinated by calcium atom—a virtual, noncrystallographical inversion center. The N—C bond lengths within both Li-metallocycle are practically identical, and their parameters reflect the dianionic character of the dpp-BIAN ligands in **3**. At first sight, the lack of the C—N bond alternations within the di-imine moiety upsets the above hypothesis about the relationship between the nonequivalence of nitrogen atoms in the dianionic dpp-BIAN ligand and blue color of its metal complexes. However, detailed inspection of the X-ray diffraction data reveal that there is no default plane of symmetry bisecting the N–Li–N angles in both Li-metallocycle because the interaction of CH$_3$-group of one of the four isopropyl susbtituents in each dpp-BIAN ligand with Li cation in each [(dpp-BIAN)Li] anion. The distances Li(1)–C(68) and Li(2)–C(20) are 2.403(6) and 2.391(5) Å, respectively. This strong agostic CH$_3$...Li interactions cause some lengthening of N—C(ipso) bond length (N(1)–C(13) 1.434(3) and N(4)–C(61) 1.443(3) Å) compare to other N—C(ipso) bonds (N(2)–C(25) 1.415(3) and N(3)–C(49) 1.426(3) Å). These agostic interactions are retained in solution, as shown by the ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of **3** (Fig. 3) shows four septets of four different methine protons (δ, 3.84, 3.62, 3.50, and 3.00 ppm) and eight doublets of nonequivalent CH$_3$ groups (δ, 1.23, 1.17, 1.10, 1.03, 0.87, 0.76, 0.60, 0.35 ppm) of isopropyl substituents.

The calcium complex **3** is related to structurally characterized solvent-free complex (dpp-BIAN)$_2$Ca, which consists of two radical-anionic dpp-BIAN ligands [9]. The synthesis and ESR characterization of its magnesium analog (dpp-BIAN)$_2$Mg (**4**) has also been reported [9], but its molecular structure was not determined until recently. We were interested in the determination of the molecular structure of **4** because it is a solvent-free dpp-BIAN magnesium complex, and owing to the differences in Mg^{2+} and Ca^{2+} ionic radii, it may form a different structure due to the steric crowding imposed by bulky dpp-BIAN ligands. The molecular structure of **4** is depicted in Fig. 4.

As in complex (dpp-BIAN)$_2$Ca, two di-imine ligands chelate the magnesium atom, which is located on the crystallographic inversion center. The Mg-N distances (Mg–N(1) 2.111(1) and Mg–N(2) 2.102(1) Å) are ca. 0.27 Å shorter than in (dpp-BIAN)$_2$Ca (Ca–N(1) 2.371(3) and Ca–N(2) 2.378(3) Å) and compare well with the difference in ionic radii of Ca^{2+} and Mg^{2+} (1.00 and 0.72 Å, respectively for six-coordinate ions [10]). In both molecules, **4** and (dpp-BIAN)$_2$Ca the dpp-BIAN ligands are twisted relative to each other, thus resulting the interligand angles of ca. 45° in both the molecules. For four-coordinate Mg and Ca complexes, one may expect rather tetrahedral (90°) than square planar geometry (0°). We believe that the interligand twist in **4** and (dpp-BIAN)$_2$Ca is caused by minimization of the

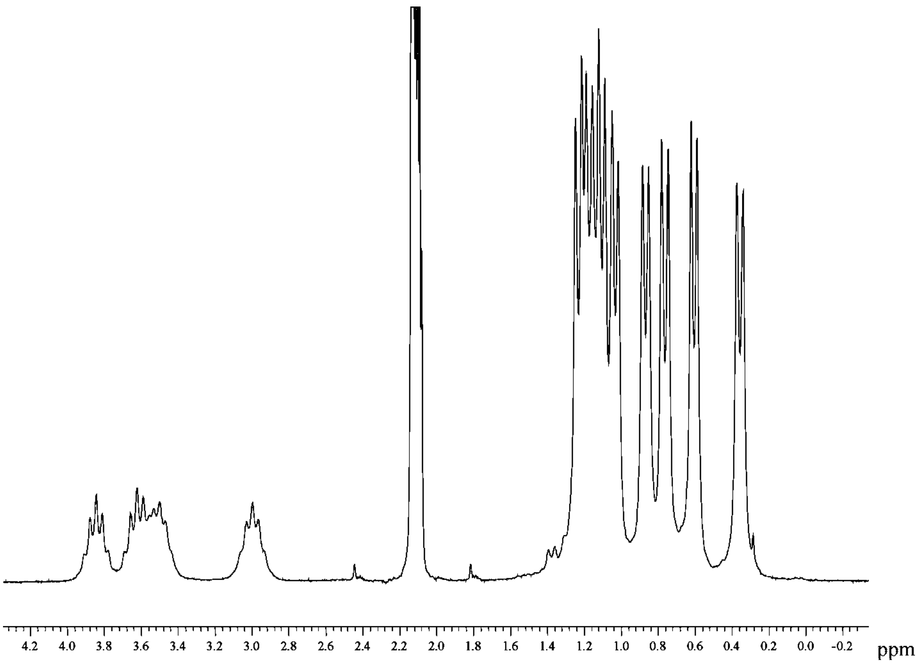


FIGURE 3 ^{1}H NMR spectrum of **3** in toluene-d_8 (200 MHz, 294 K). The aromatic region is not shown.

steric repulsion between two ligands, namely, their isopropyl groups. The N—C bond distances within two Mg metallacycles in **4** indicate the monoanionic nature of the ligands because the N—C distances (N(1)–C(1) 1.338(2) Å, N(2)–C(25) 1.340(2) Å) are elongated relative to those in the free neutral ligand (both N—C 1.282(4) Å) but shortened compare to its dianion as, for instance, in **2** and **3**.

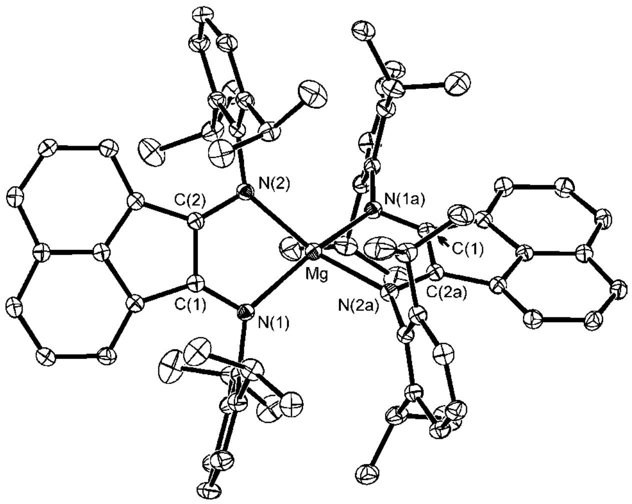


FIGURE 4 ORTEP view of **4** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted. Selected bond lengths (Å): Mg(1)–N(1) 2.1107(15), Mg(1)–N(2) 2.1017(15), Mg(1)–C(2) 2.8378(18), Mg(1)–C(1) 2.8420(18), N(1)–C(1) 1.338(2), N(2)–C(2) 1.340(2), C(1)–C(2) 1.430(3).

EXPERIMENTAL SECTION

General Remarks

All manipulations were carried out under vacuum using Schlenk ampoules. Solvents THF and toluene were dried by distillation from sodium and benzophenone. The toluene-d_8 used for the NMR measurements was dried with sodium and benzophenone at ambient temperature, and just prior to use, condensed under vacuum into the NMR tubes already containing the compound **3**. Melting points were measured in sealed capillaries. The IR-spectra were recorded on a FTIR FSM-1201 spectrometer ("Monitoring Ltd"); the ^{1}H NMR spectra were obtained on a Bruker DPX-200 NMR spectrometer. Solvent-free CaI_2 was obtained reacting calcium metal with CH_2I_2 in THF. The precipitate of $CaI_2(THF)_x$ was extracted from unreacted metal with THF. Evaporation of the solvent from the extract and drying the solid in vacuum at 100°C for 2 h and then at 200°C for 4 h gave nonsolvated CaI_2.

*[(dph-BIAN)Mg(THF)]$_2$***2**

Magnesium shavings (2.4 g, 100 mmol) and CH_2I_2 (0.8 g, 2.98 mmol) were placed in a Schlenk-like ampoule (ca. 100 mL volume) equipped with a teflon stopcock. After evacuation of the ampoule (10^{-1} Torr within ca. 1 min), THF (40 mL) was added by condensation and the mixture was stirred for 2 h. The

$MgI_2(THF)_n$ formed was decanted together with the solvent, and the residual metal was washed three times with THF (40 mL). A suspension of dph-BIAN (0.48 g, 1.0 mmol) in THF (30 mL) was then added to the activated magnesium metal, and the mixture was refluxed. In the course of about 10 min reflux, the reaction mixture turned deep green. The solution was then cooled to ambient temperature and decanted from the excess of magnesium. The solvent was evaporated in vacuum, and the residue was dried in vacuum at 80°C. To the residual crystalline solid, toluene (40 mL) was added. Heating the mixture to 80°C gave a deep-green solution, which was evaporated under reduced pressure. To the residue the toluene was added again, and this procedure was repeated three times. Finally, the mixture turned deep blue and black crystals precipitated yielding 0.63 g (91%) of **2**×$2C_6H_6$. mp >205°C. Anal. calcd (found) for $C_{86}H_{70}Mg_2N_4O_2 \times 2C_6H_6$: C, 84.30% (83.91%), H, 5.92 (5.82%). IR (Nujol): 3040 m, 1581 s, 1484 s, 1425 s, 1327 s, 1308 m, 1261 s, 1210 w, 1182 w, 1100 s, 1030 s, 920 w, 862 w, 847 w, 819 s, 803 s, 770 s, 751 s, 712 m, 699 s, 667 w, 613 w, 534 w cm^{-1}.

[(dpp-BIAN)Li]$_2$Ca **3**

Lithium pieces (0.38 g, 54 mmol) were placed in a Schlenk-like ampoule (ca. 100 mL volume) equipped with a teflon stopcock and containing the magnet stirrer. In the evacuated ampoule, a suspension of dpp-BIAN (0.75 g, 1.5 mmol) in toluene (50 mL) was added. The mixture was stirred at ambient temperature until it turned deep blue (ca. 1 h). The solution formed was decanted from the excess of lithium and treated with CaI_2 (0.22 g, 0.75 mmol). The reaction mixture was refluxed for 1 h. No color change was observed in the course of reflux. The mixture was cooled to ambient temperature and filtered off. Concentration of the solution to 15 mL by evaporation of the solvent in vacuum at ambient temperature resulted in precipitation of deep blue crystals. The formed crystalline solid was dissolved again at heating. In 48 h, the large block-like deep blue crystals of **3**×$4C_7H_8$ were collected after decantation of the mother liquor and drying in vacuum. Yield 0.61 g (57%). mp >245°C. Anal. calcd (found) for $C_{72}H_{80}CaLi_2N_4 \times 4C_7H_8$: C, 84.35% (83.26%), H, 7.93 (8.11%). ^{1}H NMR (toluene-d_8) 7.3–6.7 (m, 10H, H-C$_{\mathrm{arom}}$), 6.46 (d, 1H, H-C$_{\mathrm{arom}}$), 6.02 (d, 1H, H-C$_{\mathrm{arom}}$), 3.84 (spt, 1 H, C*H*Me$_2$), 3.62 (spt, 1H, C*H*Me$_2$), 3.50 (spt, 1 H, C*H*Me$_2$), 3.00 (spt, 1H, C*H*Me$_2$), 1.23 (d, 3 H, CH(C*H*$_3$)$_2$), 1.17 (d, 3H, CH(C*H*$_3$)$_2$), 1.10 (d, 3H, CH(C*H*$_3$)$_2$), 1.03 (d, 3H, CH(C*H*$_3$)$_2$), 0.87 (d, 3H, CH(C*H*$_3$)$_2$), 0.76 (d, 3H, CH(C*H*$_3$)$_2$), 0.60 (d, 3H, CH(C*H*$_3$)$_2$), 0.35 (d, 3H, CH(C*H*$_3$)$_2$). IR (Nujol): 3058 m, 3023 m, 1614 m, 1605 m, 1584 s, 1518 w, 1496 m, 1427 m, 1371 w, 1354 w, 1295 s, 1254 m, 1236 s, 1203 w, 1186 m, 1160 w, 1142 w, 1115 s, 1081 w, 1051 m, 1036 m, 1001 s, 926 m. 914 m, 881 w, 849 m, 817 s, 804 w, 797 m, 769 s, 758 s, 750 w, 728 s, 694 s, 684 w, 667 w, 626 m, 615 m, 600 w, 552 w, 542 w, 509 w, 465 s, 418 s cm^{-1}.

Single Crystal X-Ray Structure Determination of **2, 3,** *and* **4**

The crystal data and details of data collection are given in Table 1. The data were collected on a Bruker SMART APEX diffractometer (graphite-monochromated Mo Kα radiation, ω- and φ-scan technique, $\lambda = 0.71073$ Å) at 100 K. The structures were solved by direct methods using SHELXS-97 [11] and were refined on F^2 using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **2** and **4** were found by the Fourier synthesis and refined isotropically. The hydrogen atoms in **3** were placed in calculated positions and refined in the "riding-model". SADABS [13] was used to perform area-detector scaling and absorption corrections. The geometrical aspects of the structures were analyzed by using the PLATON program [14].

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