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Homoleptic *β*-Diketiminato Complexes of the Alkaline-Earth Metals: Trends in the Series Mg, Ca, Sr, and Ba

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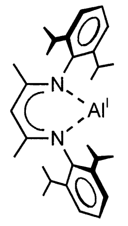
Four homoleptic *β*-diketiminato complexes were prepared and structurally characterized: (DIPP-nacnac)$_2$M with M = Mg, Ca, Sr, and Ba (DIPP-nacnac = (2,6-iPr$_2$C$_6$H$_3$)NC(Me)C(H)C(Me)N(2,6-iPr$_2$C$_6$H$_3$)). The crystal structures show very similar C_2-symmetric monomeric species in which the ligand backbones are nearly planar and the metals are situated out-of-plane. Several C−H···π interactions between the ligands stabilize the complexes substantially and play a role in their solution structures. A dynamic process, which involves inversion of the puckered six-membered metal−N−C−C−C−N ring, leads to exchange of the aryl rings and a reorganization of the C−H···π network. The activation energies (kcal/mol) for this process are metal dependent: Mg 17.8(1), Ca 17.6(1), Sr 16.6(1), and Ba 15.2(1). The NMR chemical shifts point to increased ionicity of the ligand−metal bond along the row Mg < Ca < Sr < Ba. Delocalization of negative charge from the nitrogen sp^2 electron pair into the aryl ring increases along the row Mg < Ca < Sr < Ba.

Introduction

Although the long-known *β*-iminoamine compounds[1] have been used as precursors for monoanionic bidentate ligands as early as 1968,[2] research activities on this unique ligand system tremendously increased over the past decade.[3] This class of ligands combines a number of advantages, among which are easy syntheses, easy variation of substituents, extreme steric bulk, and strong donor properties. The bulkier ligands have been found especially effective in stabilizing low coordination numbers and enabled the isolation of metal complexes with unique coordination geometries (**1**−**3**).[4−6] The ligand also gained popularity as spectator ligand in well-defined single-site polymerization catalysts (**4**; M−R = $[\mathrm{Cr^{III}{-}Me}]^+$,[7] $[\mathrm{V^{III}{-}Me}]^+$,[7,8] $[\mathrm{Ti^{III}{-}Me}]^+$,[7,8] $[\mathrm{Al{-}Me}]^+$,[9] Zn−Me,[10] Mg−alkyl,[11] Mg−OR,[12] Zn−OR,[13] and Sn$^{\mathrm{II}}$−OR[14]) used in the polymerization of a variety of monomers.



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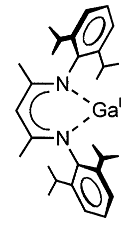

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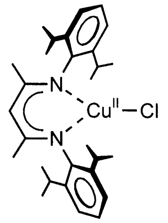

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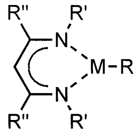

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We are particularly interested in well-defined homoleptic *β*-diketiminato complexes of the heavier alkaline-earth metals. These complexes not only are potential

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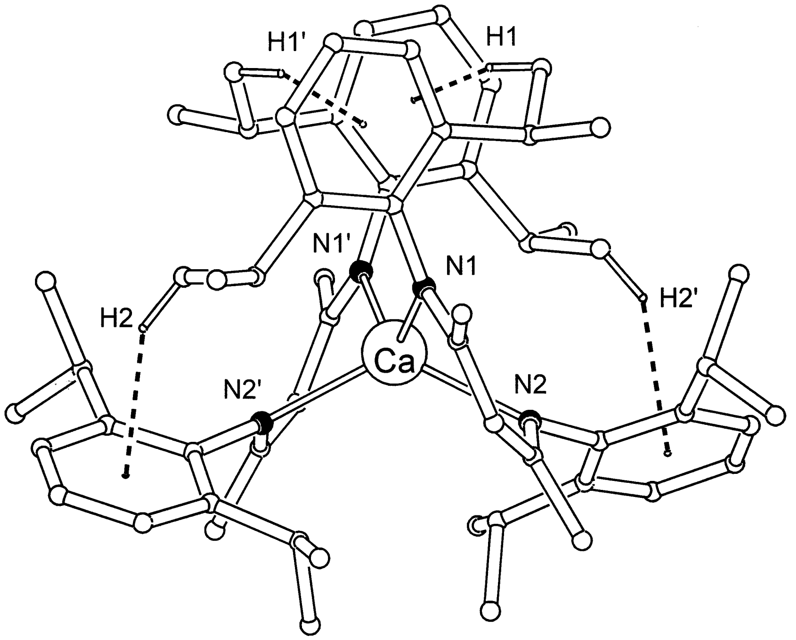
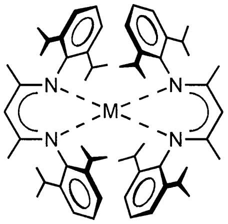


Figure 1. Crystal structure of (DIPP-nacnac)$_2$Ca (**6**). Hydrogens have been omitted for clarity, except those involved in C−H···π interactions (indicated by dashed lines). The Mg, Sr, and Ba analogues display a similar structure (crystallographic C_2-symmetry is found for M = Ca and Sr; the Mg and Ba complexes show approximate C_2-symmetry).

candidates for application in CVD processes[3e,15] but can also be useful starting materials in the syntheses of heteroleptic initiators for stereoselective styrene polymerization.[16] Here we describe the syntheses and solid state and solution structures of a series of homoleptic β-diketiminato alkaline-earth metal complexes.

Results and Discussion

The complexes **5**−**8** ((DIPP-nacnac)$_2$M with M = Mg, Ca, Sr, Ba) were prepared by reacting the corresponding alkaline-earth iodides (or in the case of Mg the bromide) with 2 equiv of (DIPP-nacnac)K in THF. After reaction, the THF solvent was evaporated and the highly soluble homoleptic complexes were extracted with cyclohexane. Crystals were obtained by concentrating and/or cooling the cyclohexane solutions.



5, M = Mg
6, M = Ca
7, M = Sr
8, M = Ba

The crystal structures of the homoleptic compounds **5**−**8** show comparable features. All compounds crystallize as monomers with 4-fold N-metal coordination. The Ca and Sr complexes crystallize with crystallographic C_2-symmetry, and the Mg and Ba complexes display approximate C_2-symmetry (Figure 1). Selected structural parameters are listed in Table 1. The dihedral angles between the planes N−M−N (nitrogens belonging to one nacnac ligand) and N′−M−N′ do not show large deviations from 90° (Table 1). All complexes, however, show distortion of a tetrahedral coordination geometry. This is due to the bite angle of the nacnac ligand, which deviates considerably from the tetrahedral angle. The bite angles decrease with cation size (average values: Mg 92.97(8)°, Ca 83.09(4)°, Sr 78.67(5)°, and Ba 68.89(5)°). In all structures a typical and remarkably similar puckering of the six-membered metal−N−C−C−C−N ring is observed (Figure 2). The ligand part is slightly deviated from perfect planarity, and the metals are located out-of-plane. The distances to the N−C−C−C−N least-squares planes are as follows: Mg, 0.876(1) and 0.938(1) Å; Ca, 1.291(1) Å; Sr, 1.381(1) Å; Ba, 1.498(1) and 0.946(1) Å. The large difference between the

Table 1. Selected Structural Parameters (distances in Å and angles in deg) for the Crystal Structures of the Homoleptic (DIPP-nacnac)$_2$M Complexes (5−8)

	M =			
	Mg (**5**)	Ca (**6**)	Sr (**7**)	Ba (**8**)
M−N1	2.100(2)	2.374(1)	2.506(2)	2.695(2)
M−N2	2.122(2)	2.384(1)	2.513(2)	2.716(2)
M−N3	2.110(2)			2.695(2)
M−N4	2.112(3)			2.742(2)
<average>	2.111(2)	2.379(1)	2.510(2)	2.712(2)
N1−M−N2	93.05(8)	83.09(4)	78.67(5)	70.70(5)
N3−M−N4	92.90(9)			67.07(5)
<average>	92.97(8)	83.09(4)	78.67(5)	68.89(5)
N1−C(aryl)	1.448(3)	1.437(2)	1.433(3)	1.429(3)
N2−C(aryl)	1.444(3)	1.431(2)	1.429(3)	1.426(3)
N3−C(aryl)	1.456(3)			1.418(3)
N4−C(aryl)	1.445(4)			1.425(3)
<average>	1.448(4)	1.434(2)	1.431(3)	1.425(3)
C−N1−C	115.8(2)	117.6(1)	119.1(2)	115.7(2)
C−N2−C	115.6(2)	117.5(1)	117.9(2)	119.7(2)
C−N3−C	115.1(2)			122.9(2)
C−N4−C	113.9(2)			117.6(2)
<average>	115.1(2)	117.6(1)	118.5(2)	119.0(2)
dihedral angle:				
N−M−N/N′−M−N′	87.4(1)	89.0(1)	88.3(1)	80.3(1)

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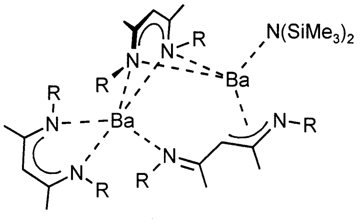
latter two values suggests that steric factors are responsible for this ring puckering. This was also concluded in a study on the structures of heteroleptic (DIPP-nacnac)MgR complexes.[11a]

The N−metal bond distances increase down the group (average values: Mg 2.111(2) Å, Ca 2.379(1) Å, Sr 2.510(2) Å, Ba 2.712(2) Å). The 0.60 Å increase from Mg to Ba is somewhat smaller than the 0.68 Å difference between their ionic radii (Mg^{2+}, 0.66 Å; Ba^{2+}, 1.34 Å).

The average Mg−N bond distance in $(DIPP\text{-}nacnac)_2Mg$ (2.111(2) Å) is slightly longer than the corresponding bond distances in structures of heteroleptic (DIPP-nacnac)MgR complexes (R = Me, 2.076(3) Å; R = *t*Bu, 2.024(3) Å; R = O*t*Bu, 2.048(2) and 2.054(2) Å)[11,12] and also longer than the Mg−N bonds in another homoleptic (β-diketiminato)$_2$Mg complex (2.096(8) and 2.068(8) Å).[3g] The slighly longer Mg−N bond is likely due to the sterical crowding in homoleptic $(DIPP\text{-}nacnac)_2Mg$. This is also reflected in the average C−N−C angle in **5** (115.1°), which is smaller than those in the monomeric heteroleptic (DIPP-nacnac)MgR complexes (values vary from 118.7° to 119.4°).[11,12] Sterical crowding in homoleptic $(DIPP\text{-}nacnac)_2M$ complexes decreases along the row Mg > Ca > Sr > Ba, as can be seen from an increase in the C−N−C angles (Table 1).

No nacnac complexes with Ca and Sr have been published so far; however, one example of a nacnac-Ba complex is known: attempted synthesis of homoleptic $(cyclohexyl\text{-}nacnac)_2Ba$ via deprotonation of the iminoamine with $Ba[N(SiMe_3)_2]_2$ led to an interesting heteroleptic cluster **9**,[3e] which can be considered an intermediate on the reaction pathway. This complex shows three different coordination modes for the nacnac ligand. The Ba−N bond distances for the terminal ligand in **9** (2.635(4) and 2.689(4) Å) are smaller than those in **8**.



9, R = cyclohexyl

All ligands in the complexes **5**−**8** show typical C−C and C−N bond lengths in the backbone, which can be related to delocalization of negative charge (C−N bonds vary from 1.309(2) to 1.351(3) Å and C−C bonds from 1.375(4) to 1.420(4) Å). There is no significant relationship between the geometry of the backbone and the cation.

The structural similarity between $(DIPP\text{-}nacnac)_2Mg$ (**5**) and $(DIPP\text{-}nacnac)_2Ba$ (**8**) is remarkable in light of the enormous difference in ionic radii of Mg^{2+} (0.66 Å) and Ba^{2+} (1.34 Å). Whereas 4-fold coordination is normal for Mg^{2+}, it is exceptional for Ba^{2+}, which is usually found with 6-fold coordination. An increase in coordination number could be realized in a dimeric species with bridging nacnac ligands (cf. **9**) or via aryl-Ba^{2+} coordination. Nevertheless, similar monomeric $(DIPP\text{-}nacnac)_2M$ species are observed throughout the series Mg → Ba.

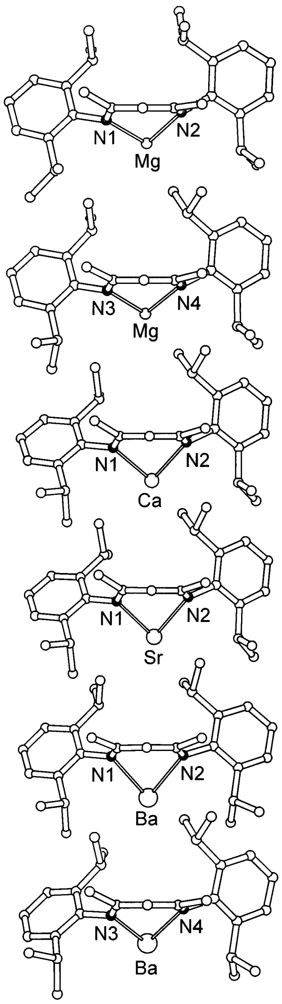


Figure 2. Partial structures viewed along the axis bisecting the C−C−C unit in the ligand backbone. All ligands show backbones with the same deviation from planarity and a remarkable similarity in the orientation of their aryl substituents.

The stability of this particular monomeric structure is possibly due to stabilizing ligand···ligand interactions: closer inspection of all molecular structures shows the presence of C−H···π interactions between the isopropyl group of one ligand and the aryl ring of the other ligand (dashed lines in Figure 1). There are two types of aryl rings: (i) two symmetry-related and nearly parallel rings in the top of the figure which display mutual CH···π interactions (H1) and (ii) the two symmetry-related aryl rings on the far outsides (bottom left and right), which act only as the acceptor in C−H···π interactions (H2). The crystallographical C_2-symmetric Ca and Sr complexes each show four of such stabilizing interactions, the ones involving H1 being shorter than those involving H2 (Ca: C−H1···aryl$_{center}$ = 2.649 Å and C−H2···aryl$_{center}$ = 2.743 Å; Sr: C−H1···aryl$_{center}$ = 2.709 Å and C−H2···aryl$_{center}$ = 2.813 Å). The complexes $(DIPP\text{-}nacnac)_2Mg$ and $(DIPP\text{-}nacnac)_2Ba$ show slight deviations from C_2 symmetry, and only three C−H···π interactions (shorter than 2.90 Å) can be found (Mg, 2.691, 2.792, and 2.865 Å; Ba, 2.653, 2.740, and 2.759 Å). Apparently, the metals Ca^{2+} and Sr^{2+} have the optimal size to fit in a cavity generated by two nacnac ligands that are integrated in a three-dimensional network of C−H···π interactions. The larger Ba^{2+} ion

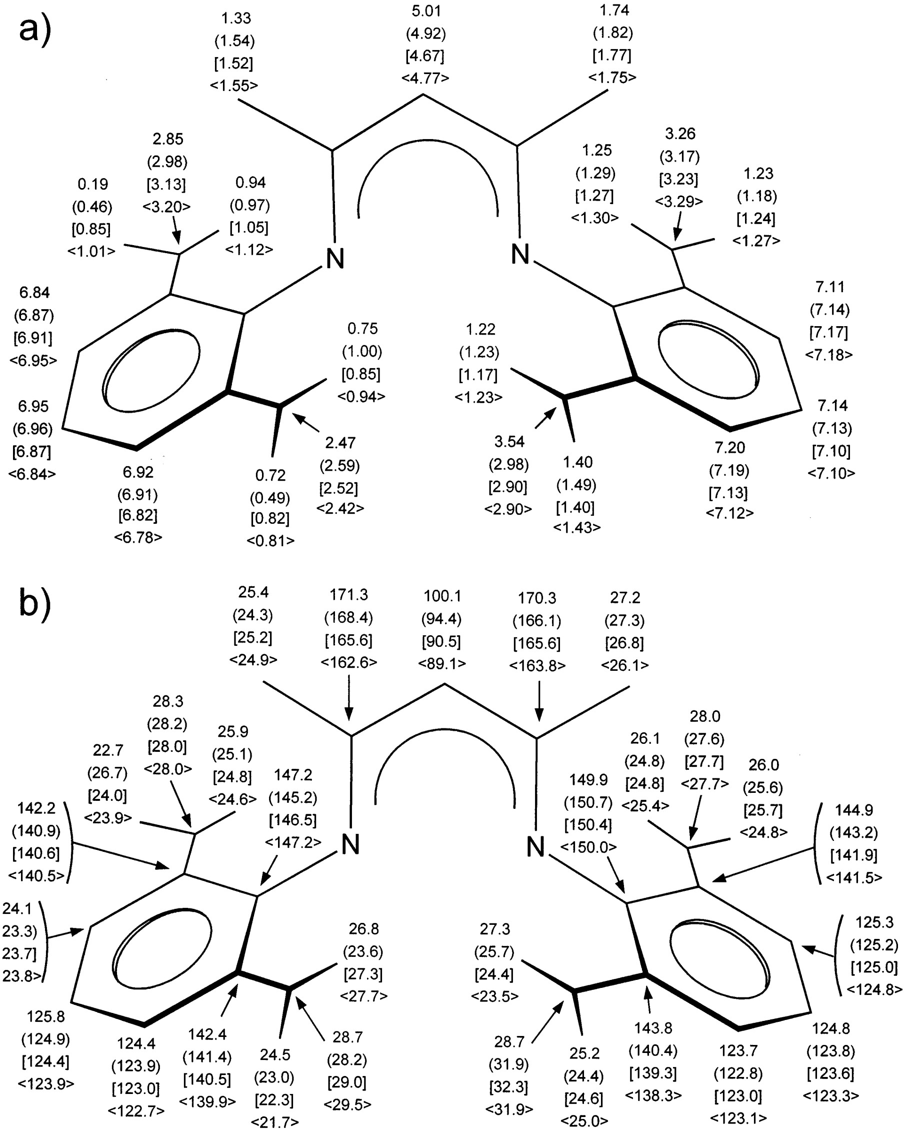


Figure 3. NMR chemical shifts for the (DIPP-nacnac)$_2$M complexes dissolved in toluene-d_8: (a) ^{1}H and (b) ^{13}C. The stacks of numbers represent the values for the Mg, (Ca), [Sr], and <Ba> complexes. The values given in (a) correspond with those given in (b).

partly ruptures the network, and only three C−H···π interactions can be formed. The smaller Mg^{2+} ion brings the nacnac ligands too close, which also partly disturbs the C−H···π network. The importance of C−H···π interactions in three-dimensional structures of DIPP-nacnac complexes has been discussed earlier.[11a]

The complexes **5**−**8** were studied in benzene solution by NMR. ^{1}H NMR spectra show unique chemical shifts for all groups in the ligand (Figure 3); for example, the isopropyl groups give rise to eight doublets and four heptets. Also, two sets of aromatic signals and two singlets for the methyl groups in the backbone are observed. This indicates that the C_2-symmetric solid state structure is retained in solution. The C−H···π interactions observed in the solid state structures also play a role in solution. This can be concluded from the ^{1}H chemical shifts for the *i*Pr methyl groups (Figure 3a): the *i*Pr groups on one aryl susbtituent show substantially lower chemical shifts than the *i*Pr groups on the other aryl substituent. This high-field shift is caused by the ring current effect[17] in the aryl groups and is typical for groups involved in C−H···π interactions. This is in good agreement with the solid state structure in which only one of the 2,6-diisopropyl-phenyl groups is involved as a C−H donor in the C−H···π network (the top aryls in Figure 1) and the other functions only as the acceptor.

Warming of the NMR samples results in broadening and finally coalescence of all signal groups, except the signal for the proton in the backbone. This proton is located in the mirror plane of the nacnac ligand and its signal remains sharp over the whole temperature range. The eight doublets (Me groups of *i*Pr) coalesce in one doublet, the four heptets (CH of *i*Pr) in one heptet, and the two singlets, assigned to the Me groups in the backbone, in one singlet. Therefore, coalescence is due to (i) exchange of the mirror-symmetric sites of the nacnac ligand and (ii) rotation around the N−C(aryl) bond. The first process, exchange of the mirror-symmetric sites of the nacnac ligand, can proceed by rotation of the nacnac ligand around its internal C_2-axis. Such

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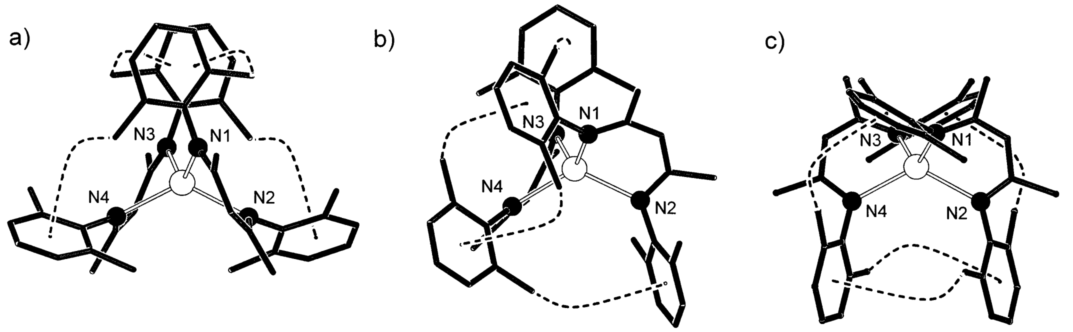
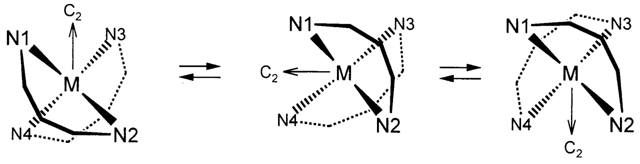


Figure 4. Conformational changes in (DIPP-nacnac)$_2$M complexes. The isopropyl groups are not fully shown, and C$-$H$\cdots\pi$ interactions are depicted by dashed curves (note that the positions of the nitrogen atoms do not change). (a) Starting position: the C_2-axis bisects N1$-$M$-$N3, and the 2,6-diisopropylphenyl groups attached to N1 and N3 are active as C$-$H donors; (b) ring puckering of the ligand N1$-$C$-$C$-$C$-$N2 inversed: the C_2-axis bisects N3$-$M$-$N4, and the 2,6-diisopropylphenyl groups attached to N3 and N4 are active as C$-$H donors; (c) ring puckering of both ligands inversed: the C_2-axis bisects N2$-$M$-$N4, and the 2,6-diisopropylphenyl groups attached to N2 and N4 are active as C$-$H donors. The structures (a) and (b) are mirror images and not superimposable. The structures (a) and (c) are identical and superimposable.

Scheme 1



a process goes through a highly crowded transition state in which the metal would have a 4-fold planar coordination geometry. A better alternative to explain the coalescence phenomena is a simple inversion of the ring puckering in the six-membered N$-$C$-$C$-$C$-$N-metal ring; that is, the metal swings to the other side of the N$-$C$-$C$-$C$-$N plane (Scheme 1). Inverting the ring puckering of one nacnac ligand results in another C_2-symmetric complex, which is the mirror image of the original conformation (the object is chiral). The C_2-axis, however, is tilted by 90° with respect to its original orientation. Inversion of the other ligand's ring puckering again results in a C_2-symmetric complex with a 90° tilt of the C_2-axis. This conformation is superimposable on the first conformation (under exchange of N1 and N2 and exchange of N3 and N4). The dynamic process described in Scheme 1 results in a reorganization of the C$-$H$\cdots\pi$ network (details of the different conformations are shown in Figure 4). This leads to complete exchange of the diisopropyl-phenyl groups: the active C$-$H donors now become inactive and function only as acceptors in C$-$H$\cdots\pi$ bonding (and vice versa). Additional rotation of the aryl rings around the C$-$N bond results in complete scrambling of all *i*Pr groups.

The coalescence temperatures (coalescence of singlets assigned to Me groups in the backbone) and activation energies (kcal/mol; given in parentheses) are dependent on the metal: Mg at 95 °C (17.8(1)), Ca at 85 °C (17.6(1)), Sr at 65 °C (16.6(1)), and Ba at 35 °C (15.2(1)). This can be explained by release of steric stress within the (DIPP-nacnac)$_2$M complex along the row M = Mg > Ca > Sr > Ba. Also, conformational changes likely involve some stretching of the metal$-$N bonds. Thus, activation energies are dependent on the metal$-$N bond strengths, which decrease along the row M = Mg > Ca > Sr > Ba.

The NMR data of (DIPP-nacnac)$_2$M complexes, summarized in Figure 3, point out several trends in the Mg to Ba series. The ^{1}H chemical shifts for the C$-$H group in the backbone decrease steadily along the row Mg > Ca > Sr > Ba. This chemical shift is highly sensitive toward the electron density in the perpendicular p-orbital: a decrease in chemical shift on going from Mg to Ba reflects an increase in charge in this position. Similar trends are observed in the ^{13}C chemical shifts for the carbons in the backbone. This reflects an increase in ionicity on going from (DIPP-nacnac)$_2$Mg to (DIPP-nacnac)$_2$Ba. Interestingly, also trends in the ^{13}C chemical shifts for the *ortho*- and *para*-carbons in the aryl rings are observed: the chemical shifts decrease along the row Mg > Ca > Sr > Ba. This can be explained by delocalization of negative charge from the nitrogen sp^2 electron pair into the aryl ring.[18] Apparently, charge delocalization increases with ionicity: Mg < Ca < Sr < Ba. This should also effect the N$-$C(aryl) bond distances: delocalization leads to N$-$C(aryl) bond shortening, and therefore these bonds should decrease along the row Mg < Ca < Sr < Ba. Although this trend in N$-$C(aryl) bond distances is indeed observed (Table 1), the differences within the series of complexes are too small to be significant. Apparently, N$^{\delta-}$ → aryl charge delocalization is not as important as CH$_2^-$ → aryl charge delocalization in benzyl anions. The effect, however, partly explains why (DIPP-nacnac)$_2$K in the solid state[19] forms a coordination polymer with interactions between K$^+$ and aryl groups of neighboring molecules. The significant trends observed in the NMR spectra of **5**$-$**8** underscore the importance of this technique in the analyses of charge distributions.

Conclusions

The series of homoleptic (DIPP-nacnac)$_2$M, with M = Mg, Ca, Sr, and Ba, show very similar monomeric C_2-symmetric crystal structures. All structures show close

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[18] The N$^{\delta-}$ → aryl charge delocalization is comparable to CH$_2^-$ → aryl charge delocalization in benzyl anions; see for references: Feil, F.; Harder, S. *Organometallics* **2000**, *19*, 5010.

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Table 2. Selected Crystal Data for (DIPP-nacnac)$_2$M Complexes (5−8)

	M =			
	Mg (**5**)	Ca (**6**)	Sr (**7**)	Ba (**8**)
cryst syst	trigonal	monoclinic	monoclinic	triclinic
a (Å)	22.044(6)	19.483(2)	19.564(1)	11.468(1)
b (Å)	22.044(6)	12.491(1)	12.648(2)	13.207(1)
c (Å)	19.949(6)	22.082(2)	22.143(2)	20.607(2)
α (deg)	90	90	90	81.817(7)
β (deg)	90	100.302(8)	100.455(6)	89.601(8)
γ (deg)	120	90	90	68.020(8)
V (Å^3)	8395(4)	5287.2(9)	5388(1)	2861.0(5)
space group	$P\bar{3}$	$C2/c$	$C2/c$	$P\bar{1}$
formula	$C_{58}H_{82}N_4Mg(C_6H_{12})_{0.66}$	$C_{58}H_{82}N_4Ca$	$C_{58}H_{82}N_4Sr$	$(C_{58}H_{82}N_4Ba)(C_6H_{12})_{0.5}$
M	943.75	875.36	922.90	1014.68
Z	6	4	4	2
ρ_{calcd} (g cm^{-3})	1.120	1.100	1.159	1.178
μ(Mo Kα) (mm^{-1})	0.071	0.158	1.059	0.733
T (°C)	−120	−90	−90	−120
measd reflns	15762	5943	5170	11440
indep reflns	9931	5789	5029	11127
R_{int}	0.069	0.020	0.018	0.015
obsd reflns with $I > 2.0\ \sigma(I)$	6571	4672	4170	10405
R_1	0.060	0.039	0.034	0.026
wR_2	0.178	0.108	0.084	0.067
GOF	1.04	1.05	1.08	1.05
no. of params	921	449	449	911
resid electron dens	−0.25/+0.60	−0.28/+0.25	−0.35/+0.34	−0.52/+0.50

to planar ligand backbones with the metals situated out-of-plane. Several C−H···π interactions between the ligands stabilize the complex substantially and also play a role in the solution structure. A dynamic process, which involves inversion of the puckered six-membered metal−N−C−C−C−N ring, leads to reorganization of the C−H···π network. The activation energies for such a process decrease along the row Mg > Ca > Sr > Ba. The NMR chemical shifts point to increased ionicity of the ligand−metal bonding along the row Mg < Ca < Sr < Ba and to some delocalization of negative charge from the nitrogen sp^2 electron pair into the aryl ring.

Experimental Section

General Comments. All experiments were carried out under argon using predried solvents and Schlenk techniques. Crystal structures were solved with DIRDIF[19] and refined with SHELXL-97.[20] Geometry calculations and graphics were done with PLATON.[21] The complex (DIPP-nacnac)K was prepared according to literature (note that in the experimental part the quantities of KN(SiMe$_3$)$_2$ and the nacnac ligand have been interchanged).[3d]

Synthesis of the (DIPP-nacnac)$_2$M Complexes 5−8. All complexes were prepared by reacting the corresponding alkaline-earth iodides (or in the case of Mg the bromide) with 2 equiv of (DIPP-nacnac)K[3d] in THF. After stirring overnight, the THF solvent was evaporated and the highly soluble homoleptic complexes were extracted with cyclohexane. Crystals were obtained by concentrating and/or cooling the cyclohexane solutions. Crystal form and yields (in parentheses) are as follows: (DIPP-nacnac)$_2$Mg, light yellow plates (62%); (DIPP-nacnac)$_2$Ca, light yellow blocks (52%); (DIPP-nacnac)$_2$Sr, light yellow blocks (54%); (DIPP-nacnac)$_2$Ba, light yellow blocks (43%). The crystals for the barium compound were hard to obtain. The compound is extremely soluble in alkanes. Highly concentrated solutions were cooled gradually to −80 °C without any sign of crystallization. Leaving the solution at room temperature for several days yielded large crystals. Elemental analyses of crushed crystals freed from volatiles under high vacuum (0.001 Torr): $C_{58}H_{82}N_4Mg$ (calc C 81.04 and H 9.62, found C 80.89 and H 9.51); $C_{58}H_{82}N_4Ca$ (calc C 79.58 and H 9.44, found C 78.88 and H 9.21); $C_{58}H_{82}N_4Sr$ (calc C 75.48 and H 8.96, found C 74.67 and H 8.69); $C_{58}H_{82}N_4Ba$ (calc C 71.62 and H 8.50, found C 70.94 and H 8.21). The low carbon values are a frequent problem in elemental analyses of alkaline-earth complexes.[22] The melting points of all compounds are higher than 275 °C.

Crystal Structure Data. Selected data are summarized in Table 2. All hydrogens have been found and were refined isotropically in the structure determinations of (DIPP-nacnac)$_2$Ca and (DIPP-nacnac)$_2$Sr. For the other structures, most of the hydrogens were found and refined isotropically and some have been placed at calculated positions. The structure of (DIPP-nacnac)$_2$Mg was refined with a disorder model for one of the *i*Pr groups. The crystal structures of (DIPP-nacnac)$_2$Mg and (DIPP-nacnac)$_2$Ba contain cocrystallized cyclohexane. This solvent was ordered in the (DIPP-nacnac)$_2$Ba structure and located on the center of inversion. The (DIPP-nacnac)$_2$Mg structure contains cyclohexane molecules in three different positions: two ordered cyclohexanes are found on the 3_1 axis, and a completely disordered cyclohexane was found on the 3 axis. This disorder was treated with the SQUEEZE procedure incorporated in PLATON.[21]

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Supporting Information Available: Atomic fractional coordinates, bond distances and angles, hydrogen atom positions, anisotropic thermal parameters, and ORTEP plots with numbering schemes for the complexes **5**−**8**, ^{1}H NMR spectra of the new compounds, and some variable-temperature spectra are available free of charge via the Internet at http://pubs.acs.org.

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