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Binuclear Magnesium, Calcium, and Zinc Complexes Based on Nitrogen–Nitrogen-Coupled Salicylaldiminate and β-Diketiminate Ligands

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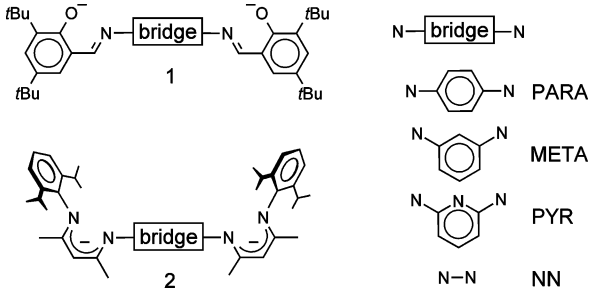
The diprotic bis(salicylaldimine) ligand *N*,*N*′-bis(3,5-di-*t*Bu-salicylidene)diimine, (**1**-NN)H_2, was smoothly deprotonated by reaction with two equivalents of a metal amide M[N(SiMe$_3$)$_2$]$_2$ (M = Mg, Ca or Zn) to form a bimetallic metal amide complex (**1**-NN)[MN(SiMe$_3$)$_2$]$_2$. This heteroleptic complex was only stable in the case of Mg and (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$ was structurally characterized by X-ray diffraction. For Ca and Zn homoleptic products could be obtained: (**1**-NN)Ca·(thf)$_2$ and (**1**-NN)Zn. The latter crystallized as a trimer with approximate C_3-symmetry. The diprotic N–N coupled bis(β-diketimine) ligand [RHN–C(Me)=C–C(Me)=N–N=C(Me)–C=C(Me)–NHR, R = 2,6-di-*i*Pr-C$_6$H$_3$], which is abbreviated as (**2**-NN)H_2, can be deprotonated only under much harsher reaction conditions. Attempted synthesis of (**2**-NN)[Mg(*n*Bu)]$_2$ gave after ligand exchange the homoleptic species (**2**-NN)Mg and Mg(*n*Bu)$_2$. For Ca, the complexes [(**2**-NN)Ca]$_2$ and (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$ both have been prepared and structurally characterized by X-ray diffraction. The latter heteroleptic complex is in benzene solution in equilibrium with [(**2**-NN)Ca]$_2$ and Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$. Reaction of (**2**-NN)H_2 with excess of Et$_2$Zn gave the heteroleptic complex (**2**-NN)[ZnEt]$_2$ and is stable towards ligand exchange reactions. The complex is not active in CO_2/cyclohexene oxide copolymerization.

Introduction

The increasing interest in bimetallic catalysis[1] and in the use of benign and cheap main-group metal catalysts[2] prompted us to introduce various bis(salicylaldiminate)[3] and bis(β-diketiminate)[4] complexes of group 2 metals (Mg, Ca) and the group 12 metal Zn. The *N*,*O*- or *N*,*N*-chelating mono-anionic units in our ligands are connected through a variety of rigid spacers (Scheme 1; ligands are abbreviated according to the bridge). The nature of this bridging spacer not only tunes the metal···metal distances but also the electronic properties.



Scheme 1.

Here we introduce a series of Mg, Ca and Zn complexes in which anionic salicylaldiminate or β-diketiminate units are directly connected through N–N bonding. Lack of a bridging spacer in these ligands, which in their protonated form are abbreviated as (**1**-NN)H_2 and (**2**-NN)H_2 (Scheme 1), could give rise to very small metal···metal distances. The influence of this direct connection on the structures of the metal complexes, and its possible consequences for Schlenk equilibria and for catalytic CO_2/cylohexene oxide copolymerization, are discussed.

Results and Discussion

Bis(salicylaldiminate)metal Complexes

The bis(salicylaldimine) ligand (**1**-NN)H_2 has been prepared according to a literature procedure[5] that involves condensation of two equivalents of 3,5-di-*t*Bu-salicylaldehyde with one equivalent of hydrazine. Such *O*,*N*,*N*,*O*-ligands have been used earlier in the chemistry of various metals (Ti, Ru, Fe, Cu and Zn)[6] but hitherto no binuclear alkaline-earth metal complexes have been described. We are particularly interested in heteroleptic complexes of the type (**1**-NN)[MR]$_2$ in which M is either Mg, Ca or Zn and R is a reactive group (amide or alkyl) for catalytic activity.

Like the other diprotic bis(salicylaldimine) ligands in Scheme 1, (**1**-NN)H_2 reacts smoothly with two equivalents of Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ to the bimetallic heteroleptic

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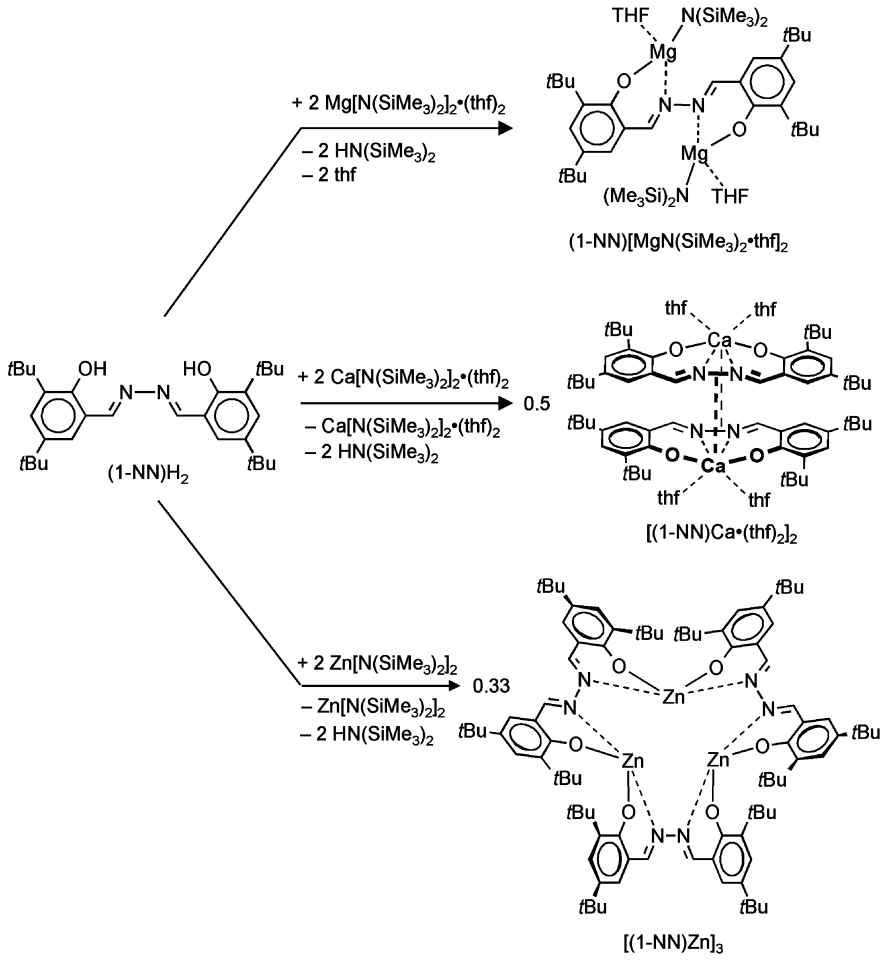


Scheme 2.

magnesium amide complex (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$ (Scheme 2). This complex is, also in benzene solution, stable against ligand exchange by the Schlenk equilibrium. Yellow crystals could be obtained from cold hexane. The crystal structure shows a crystallographically centrosymmetric molecule (Figure 1, a). The center of inversion on the N–N axis renders both nearly flat salicylaldiminate units coplanar and gives rise to a *trans*-geometry. This contrasts with the structure of (**1**-PARA)[MgN(SiMe$_3$)$_2$·thf]$_2$ which crystallized with C_2 symmetry and perpendicularly oriented salicylaldiminate units.[4] Despite this *trans*-conformation, the Mg···Mg′ distance of 5.2276(9) Å in (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$ is shorter than that in (**1**-PARA)[MgN(SiMe$_3$)$_2$·thf]$_2$ [8.186(2) Å]; this is due to lack of a spacer unit. Other selected bond lengths and angles (Table 1) are comparable.

Reaction of (**1**-NN)H$_2$ with two equivalents of Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ in THF gave an immediate colour change from yellow to red and overnight large orange-red crystalline blocks of (**1**-NN)Ca·(thf)$_2$ crystallized. The poor solubility and precipitation of this product directs the Schlenk equilibrium to the homoleptic side. Crystals of (**1**-NN)Ca·(thf)$_2$ are of poor quality and additional twinning problems result in a structure determination that only allows for a qualititative description. The Ca^{2+} ion in this complex is chelated by two O and two N atoms of one single *O*,*N*,*N*,*O*-ligand and solvated by two thf ligands. The (**1**-NN)Ca·(thf)$_2$ molecules dimerize by mutual Ca···N–N bonding (Scheme 2). Although a detailed structure description can not be given at this stage, the eightfold coordination of Ca^{2+} illustrates its considerable size. The latter is responsible for the ligand distribution reactions that often plague organocalcium chemistry[13] and also have been observed for (**1**-PARA)[CaN(SiMe$_3$)$_2$·(thf)$_2$]$_2$.[4]

Likewise, reaction of (**1**-NN)H$_2$ with two equivalents of Zn[N(SiMe$_3$)$_2$]$_2$ gave exclusively access to the homoleptic species (**1**-NN)Zn. Similar problems have been observed for the other bridged salicylaldiminate ligands in Scheme 1. Different than (**1**-PYR)Zn, which through self-organization formed a cyclic tetramer,[4] the current complex crystallized as the cyclic trimer [(**1**-NN)Zn]$_3$ (Figure 1, b–c). The asymmetric unit contains two trimers, which essentially show equal geometries. Although the overall structure is roughly C_3-symmetric, merely crystallographic C_2-symmetry can be observed. The Zn···Zn′ distances, however, are in a very narrow range of 4.8126(8)–4.8483(7) Å [average: 4.8328(8) Å]. Like in [(**1**-PYR)Zn]$_4$, each Zn atom coordinates to two mutual perpendicular *N*,*O*-chelating ligands, a structural motiv that allows for formation of cyclic aggre-

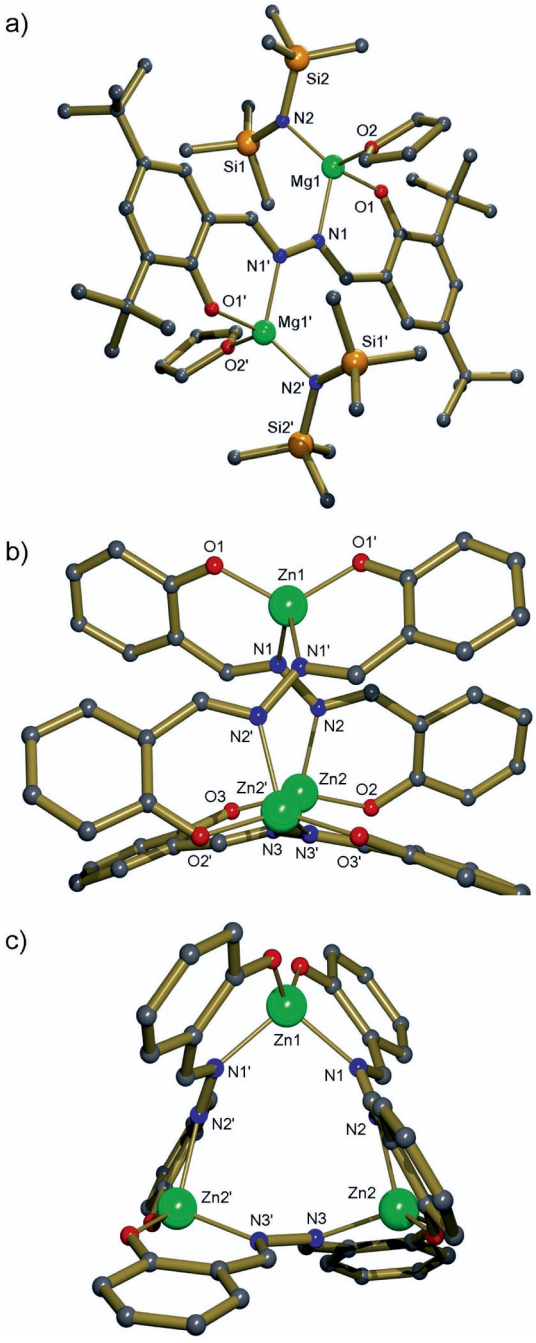


Figure 1. Crystal structures (hydrogen atoms omitted for clarity) of (a) (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$ (b) [(**1**-NN)Zn]$_3$ (*t*Bu groups omitted for clarity); view direction perpendicular on the crystallographic twofold rotation axis and (c) [(**1**-NN)Zn]$_3$; view along the approximate threefold axis. Selected geometric parameters for both structures have been summarized in Table 1.

gates.[7] The average metal–ligand bond lengths and angles in [(**1**-NN)Zn]$_3$, given in Table 1, compare well to those in [(**1**-PYR)Zn]$_4$.

Bis(β-diketiminate)metal Complexes

The *N*,*N*-coupled bis(β-diketimine) ligand (**2**-NN)H$_2$ can be prepared by a standard condensation route also used for the preparation of our previously published bis(β-diketimine) ligands:[4] i.e. stepwise reaction of (2,6-*i*Pr$_2$–C$_6$H$_3$)-N=C(Me)–CH=C(Me)–OH with Et$_3$O$^+$BF$_4^-$ followed by the addition of 0.5 equiv. of the diamine (hydrazine). Although a large variety of connected β-diketimine ligands has been reported,[5,8] this particular linkage of ligands was hitherto unknown.

The crystal structure of (**2**-NN)H$_2$ shows a non-crystallographically centrosymmetric molecule (Figure 2). The acidic hydrogen atoms, which could be located and have been refined, are connected to the outer nitrogen atoms and form strong N–H···N hydrogen bridges to the inner imine nitrogen atoms. This results in extended conjugation (RHN–C=C–C=N–N=C–C=C–NHR) which is responsible for the coplanarity of the two β-diketimine units and the short N–N bond of 1.389(3) Å. The C–N and C–C bond lengths and alternation in (**2**-NN)H$_2$ is comparable to that in the unlinked (2,6-*i*Pr$_2$C$_6$H$_3$)NH–C(Me)=C(H)–C(Me)=N(2,6-*i*Pr$_2$C$_6$H$_3$) (DIPP-nacnacH).[9]

The reaction of the bis(β-diketimine) ligand (**2**-NN)H$_2$ with two equivalents of Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ is very sluggish and, even at elevated temperatures, proceeds slowly. In benzene at 70 °C, we observed after three days only 15% mono-deprotonation. This contrasts strongly with the reactivity of the corresponding unbridged β-diketimine ligand (DIPP-nacnacH) which in toluene at 80 °C was fully deprotonated by Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ overnight.[10] The extended conjugation of C=C and C=N bonds in (**2**-NN)H$_2$ should make this ligand more acidic. Therefore, the reluctance of (**2**-NN)H$_2$ to be deprotonated might be attributed to steric shielding of the acidic N–H. Twofold deprotonation of the ligand with the stronger base (*n*Bu)$_2$Mg gave, instead of (**2**-NN)[Mg(*n*Bu)]$_2$, the homoleptic complex (**2**-NN)Mg.

Even deprotonation of (**2**-NN)H$_2$ with the considerably more reactive Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ is slow: in benzene at 80 °C reaction times of 3 days are needed. Use of the polar solvent THF did not give a significant acceleration of this deprotonation reaction. The desired product, the heteroleptic dinuclear complex (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$, is not stable towards ligands exchange and only homoleptic (**2**-NN)Ca could be isolated as a crystalline product (Scheme 3). Despite the poor crystal quality we have been able to reveal its structure as the dimer [(**2**-NN)Ca]$_2$ (Figure 3, b). This dimer, of approximate D_2 symmetry, does not show any crystallographic symmetry. The N–Ca bonds to the outer N atoms in the ligand [average: 2.375(5) Å] are slightly longer than those to the inner N atoms [2.330(5) Å]. The β-diketiminate units within one ligand are oriented nearly perpendicular in respect to each other [75.2(3)° and 85.6(4)°]. This results in rather long N–N bonds of 1.446(6) and 1.457(7) Å [cf. 1.389(3) Å in (**2**-NN)H$_2$]. The Ca···Ca′ distance measures 4.341(3) Å.

The attempted synthesis of the comparable mononuclear complex (DIPP-nacnac)CaN(SiMe$_3$)$_2$·thf by reaction of a DIPP-nacnacH with Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ also gave impure products on account of ligand distribution reactions.[11] In this case the desired product could be obtained

Table 1. Selected bond lengths [Å] and angles [°] for the bimetallic complexes; numbers given in <brackets> represent average values.

(**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$					
Mg1–N1	2.134(2)	N1–Mg1–O1	90.41(7)	O1–Mg1–O2	100.9(4)[a]
Mg1–N2	1.978(2)	N2–Mg1–O2	115.9(4)[a]	N1–Mg1–O2	94.3(4)[a]
Mg1–O1	1.885(2)	N1–Mg1–N2	121.9(1)		
Mg1–O2	2.041(12)[a]	O1–Mg1–N2	126.5(1)		
[(**1**-NN)Zn]$_3$					
Zn–O	1.872(3)–1.888(3) <1.879(3)>		O–Zn–O′	122.1(1)–123.8(1) <123.1(1)>	
Zn–N	2.018(3)–2.030(3) <2.022(3)>		N–Zn–N′	98.9(1)–101.2(2) <100.0(1)>	
(**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$					
Ca1–N1	2.369(2)	N1–Ca1–N2	82.6(1)	N1–Ca1–O1	131.7(1)
Ca1–N2	2.366(2)	N1–Ca1–N3	113.9(1)	N2–Ca1–O1	98.96(9)
Ca1–N3	2.296(2)	N2–Ca1–N3	140.7(1)	N3–Ca1–O1	95.28(9)
Ca1–O1	2.393(2)				
[(**2**-NN)Ca]$_2$					
Ca1–N1	2.336(5)	Ca2–N3	2.314(5)	N1–Ca1–N5	131.7(1)
Ca1–N2	2.365(5)	Ca2–N4	2.390(5)	N2–Ca1–N6	98.96(9)
Ca1–N5	2.318(5)	Ca2–N7	2.353(5)	N3–Ca2–N7	131.7(1)
Ca1–N6	2.376(5)	Ca2–N8	2.371(5)	N4–Ca2–N8	98.96(9)
(**2**-NN)[ZnEt]$_2$					
Zn1–N1	1.950(2)	Zn2–N3	1.968(2)	N1–Zn1–N2	95.3(1)
Zn1–N2	1.957(2)	Zn2–N4	1.950(2)	Zn1–C35–C36	120.7(4)
Zn1–C35	1.945(5)	Zn2–C37	1.939(5)	N3–Zn2–N4	95.2(1)
				Zn2–C37–C38	123.1(5)

[a] Average value from thf molecule disordered over two positions.

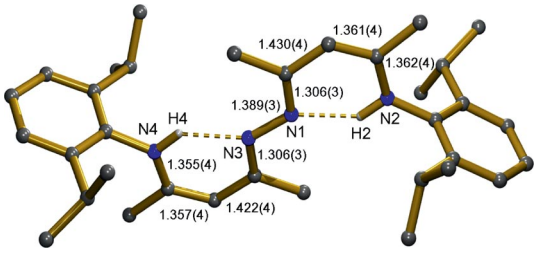
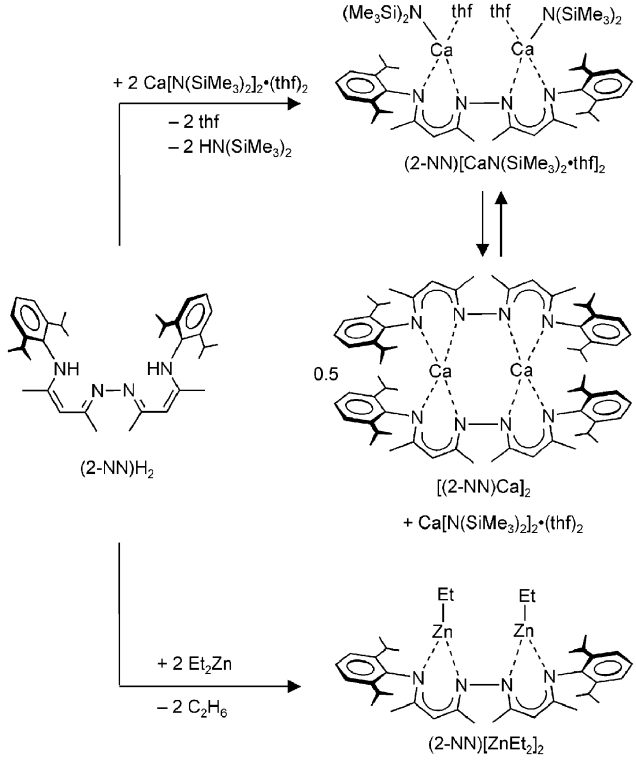


Figure 2. Crystal structure of (**2**-NN)H$_2$; only the NH hydrogen atoms (located and refined) are depicted. The C–C/C–N bond alteration is shown (distances given in Å). Average N–H···N′ hydrogen bond geometry: N···N′ 2.652(3), N–H 0.89(3), H···N′ 1.91(3), N–H···N′ 140(2)°.

by reacting the β-diketimine ligand in THF with two equivalents of KN(SiMe$_3$)$_2$ and one equivalent of CaI$_2$. Similar to this procedure, reaction of (**2**-NN)K$_2$ with two equivalents of KN(SiMe$_3$)$_2$ and two equivalents of CaI$_2$ allowed the isolation of (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$ in the form of orange crystals (37% yield). The crystal structure (Figure 3, a) shows a centrosymmetric heteroleptic complex. The inversion center on the N–N bond results in coplanarity and trans-orientation of the β-diketiminate units. The Ca atoms are considerably bend out of the β-diketiminate plane: the average C(H)–C(Me)–N–Ca torsion angle is 34.8(1)°. This structural feature was also observed in the mononuclear complex (DIPP-nacnac)CaN(SiMe$_3$)$_2$·thf, but to a much smaller extent: the average C(H)–C(Me)–N–Ca torsion angle is 26.5(1)°.[11] It is likely that the *trans*-conformation of



Scheme 3.

the ligand prohibits an in-plane metal position on account of repulsion with the methyl group in the ligand's backbone. The Ca···Ca′ distance measures 5.8291(8) Å.

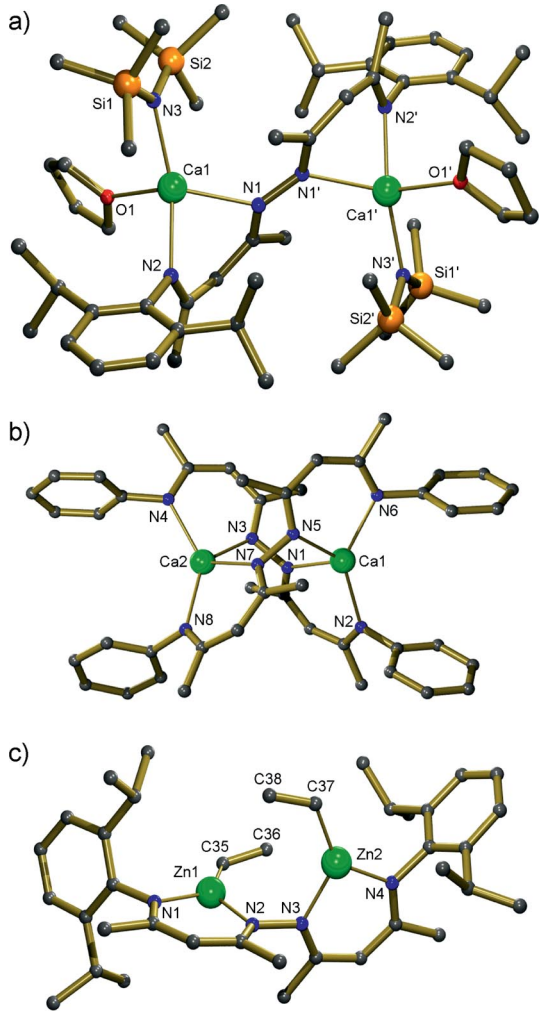


Figure 3. Crystal structures (hydrogen atoms omitted for clarity) of (a) (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$, (b) [(**2**-NN)Ca]$_2$ (*i*Pr groups omitted for clarity), (c) (**2**-NN)[ZnEt]$_2$. Selected geometric parameters for both structures have been summarized in Table 1.

Also the reaction of (**2**-NN)H$_2$ with Zn[N(SiMe$_3$)$_2$]$_2$ is extremely slow. Refluxing these reagents in toluene (1:2 ratio, respectively) gave after two days only mono-deprotonation but no defined products could be isolated. Use of Et$_2$Zn, however, gave under milder reaction conditions (benzene, 70 °C, 2 d) the desired bimetallic complex (**2**-NN)[ZnEt]$_2$ which crystallized as light-yellow blocks from hexane. The crystal structure (Figure 3, c) shows a complex of approximate C_2-symmetry in which the β-diketiminate units within the ligand are oriented nearly perpendicular in respect to each other [angle between least-squares planes: 87.1(1)°]. This originates in a relatively short Zn···Zn′ distance of 3.9676(5) Å and a long N–N bond of 1.442(3) Å. The Zn–N and Zn–C bond lengths are comparable to those in (**2**-PYR)[ZnEt]$_2$[4] or (DIPP-nacnac)ZnEt.[10] The dinuclear complex (**2**-NN)[ZnEt]$_2$ is in a benzene solution also at higher temperatures stable towards ligand exchange.

The availability of a dinuclear Zn complex invited for a preliminary investigation of its catalytic activity. The dinuclear Zn complex (**2**-META)[ZnEt]$_2$ was found to be a highly active catalyst in the copolymerization of cyclohexene oxide (CHO) and CO$_2$. In contrast to the mononuclear catalyst, (DIPP-nacnac)ZnEt, conversion of the ZnEt functionality in an initiating group (ZnOR or ZnO$_2$S) is not needed.[1g,10,12] Under the same conditions, (**2**-NN)[ZnEt]$_2$ was found to be inactive in the CHO/CO$_2$ copolymerization.

Conclusions

The metal amide reagents of Mg, Ca and Zn react fast and efficiently with a N–N coupled bis(salicylaldimine) ligand: (**1**-NN)H$_2$. Only in the case of Mg a well-defined heteroleptic complex, (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$, could be obtained. For Ca and Zn homoleptic products have been isolated and were structurally characterized.

Twofold deprotonation of a N–N-coupled bis(β-diketimine) ligand, (**2**-NN)H$_2$, is not easily accomplished and more reactive reagents combined with harsher reaction conditions are a necessity. This is likely due to a steric shielding of the acidic N–H functionalities [as can be seen in the crystal structure of (**2**-NN)H$_2$]. Heteroleptic complexes of the type (**2**-NN)[MR]$_2$ with M = Mg and Ca are not stable and in Schlenk equilibrium with their homoleptic counterparts. The heteroleptic complex (**2**-NN)[ZnEt]$_2$, however, shows good stability against ligand distribution reactions. In contrast to other bridged β-diketiminate zinc ethyl complexes,[4] (**2**-NN)[ZnEt]$_2$ is not active as a catalyst in the copolymerization of CO$_2$ and cyclohexene oxide. Apparently, this particular ligand geometry is not suitable for the cyclic bimetallic polymerization process. We are currently investigating the use of the here presented stable heteroleptic bimetallic complexes in catalysis and as initiators in the polymerization of other polar monomers.

Experimental Section

General: All manipulations were performed under a dry and oxygen-free atmosphere (argon or nitrogen) using Schlenk line and glove box techniques and freshly dried solvents. Following complexes have been prepared according to literature: (**1**-NN)H$_2$,[5] Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$,[14] Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$,[14] and Zn[N(SiMe$_3$)$_2$]$_2$.[15]

(1-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$: To a solution of Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ (501 mg, 1.02 mmol) in hexane (10 mL) was added (**1**-NN)H$_2$ (238 mg, 512 μmol). Upon heating a yellow solid precipitated. The solid was washed two times with 2 mL of hexane and dried under vacuo. Yield 384 mg, 77%. ^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ = 9.38 (s, 2 H, CC*H*N), 7.75 [d, $^4J_{H,H}$ = 1.2 Hz, 2 H, H$_{Aryl}$], 7.54 [d, $^4J_{H,H}$ = 1.2 Hz, 2 H, H$_{Aryl}$], 3.48 (m, 8 H, thf), 1.72 (s, 18 H, *t*Bu), 1.43 (s, 18 H, *t*Bu), 0.93 (m, 8 H, thf), 0.45 (s, 36 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ = 168.8 (N*C*HC), 167.3 (*C*OMg), 141.8, 137.3, 132.1, 130.3, 117.9 (C$_{Aryl}$), 70.1 (thf), 36.0 (*C*Me$_3$), 34.6 (*C*Me$_3$), 31.9 (C*Me*$_3$), 29.9 (C*Me*$_3$), 24.9 (thf) ppm. Crystals for X-ray measurement were grown by the following procedure: to a solution of Mg[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ (50.1 mg, 102 μmol) in hexane (300 μL) was added (**1**-NN)H$_2$ (23.8 mg, 51.2 μmol). Cooling of the solution to 7 °C, gave yellow single crystals. C$_{50}$H$_{94}$Mg$_2$N$_4$O$_4$Si$_4$ (976.3): calcd. C 61.51, H 9.71; found C 61.84, H 9.87.

[(1-NN)Ca·(thf)$_2$]$_2$: To a solution of Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ (60.6 mg, 120 μmol) in THF (0.10 mL) was added (**1**-NN)H$_2$ (28.2 mg, 60.7 μmol). The solution turned red immediately. Over night red crystals precipitated from the solution. The crystals were washed two times with 0.1 mL portions of hexane and dried under vacuo. Yield 26.7 mg, 69%. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 8.00 (s, 2 H, CC*H*N), 7.14 [d, $^4J_{H,H}$ = 1.2 Hz, 2 H, H$_{Aryl}$], 6.74 [d, $^4J_{H,H}$ = 1.2 Hz, 2 H, H$_{Aryl}$], 3.52 (m, 8 H,thf), 1.73 (m, 8 H,thf), 1.46 (s, 18 H, *t*Bu), 1.17 (s, 18 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]THF, 25 °C): δ = 168.4 (N*C*HC), 164.4 (*C*OCa), 139.0, 132.3, 129.2, 127.9, 120.7 (C$_{Aryl}$), 68.8 (thf), 36.0 (*C*Me$_3$), 34.2 (*C*Me$_3$), 32.2 (C*Me*$_3$), 30.4 (C*Me*$_3$), 24.9 (thf) ppm. C$_{76}$H$_{116}$Ca$_2$N$_4$O$_8$ (1294.0): calcd. C 70.55, H 9.04; found C 69.98, H 9.21.

[(1-NN)Zn]$_3$: To a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (46.3 mg, 120 μmol) in toluene (0.20 mL) was added (**1**-NN)H$_2$ (28.2 mg, 60.7 μmol). Cooling of the solution to –27 °C, gave after 96 h single crystals suitable for X-ray diffraction. Yield 16.6 mg, 52%. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 8.17 (s, 2 H, CC*H*N), 7.14 [d, $^2J_{H,H}$ = 2.4 Hz, 2 H, H$_{Aryl}$], 6.36 [d, $^4J_{H,H}$ = 2.4 Hz, 2 H, H$_{Aryl}$], 1.77 (s, 18 H, *t*Bu), 1.17 (s, 18 H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]-THF): δ = 168.0 (N*C*HC), 167.5 (*C*OZn), 141.3, 137.5, 132.0, 128.0, 116.2, (C$_{Aryl}$), 35.9 (*C*Me$_3$), 34.1 (*C*Me$_3$), 31.8 (C*Me*$_3$), 29.9 (C*Me*$_3$) ppm. C$_{90}$H$_{126}$N$_6$O$_6$Zn$_3$ (1584.2): calcd. C 68.24, H 8.02; found C 68.70, H 8.14.

Synthesis of (2-NN)H$_2$: Triethyloxonium tetrafluoroborate (14.1 g, 65.9 mmol) dissolved in dichloromethane (60 mL) was added over a period of 20 min to a stirred solution of 2-hydroxy-4-(2,6-diisopropylphenyl)imino-2-pentene (17.1 g, 65.9 mmol) in dichloromethane (80 mL) under an argon atmosphere. The mixture was stirred overnight. An equimolar portion of triethylamine (6.53 g, 64.5 mmol) was slowly added to the red-brown solution after which the solution turned dark-red. After stirring for 20 min, a solution of hydrazine monohydrate (1.65 g, 32.9 mmol) and triethylamine (25 mL) was added. The mixture was stirred for 80 h at ambient temperature. All volatiles were removed in vacuo and the crude product was washed three times with ethanol (150 mL) to yield (**2**-NN)H$_2$ (8.53 g, 50%) as a yellow powder. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 12.0 (s, 2 H, N*H*), 7.22–7.12 (m, 6 H, C*H*$_{N\text{-}aryl}$), 4.88 (s, 2 H, CH$_3$CNC*H*), 3.43 [m, 4 H, C*H*(CH$_3$)$_2$], 2.23 (s, 6 H, C*H*$_3$CN), 1.66 (s, 6 H, C*H*$_3$CN), 1.22 [d, ^3J(H,H) = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.15 [d, ^3J(H,H) = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ = 161.7 (*C*$_q$), 153.4 (*C*$_q$), 147.6 (*C*$_q$), 136.9 (*C*$_q$), 128.4 (*C*H$_{N\text{-}aryl}$), 124.2 (*C*H$_{N\text{-}aryl}$), 95.7 (CH$_3$CN*C*H), 29.2 [*C*H(CH$_3$)$_2$], 25.7 [CH(*C*H$_3$)$_2$], 23.4 [*C*H-(CH$_3$)$_2$], 20.9 (*C*H$_3$CN), 20.2 (*C*H$_3$CN) ppm. C$_{34}$H$_{50}$N$_4$ (514.8): calcd. C 79.33, H 9.79; found C 79.04, H 9.87.

Synthesis of (2-NN)K$_2$: A solution of (**2**-NN)H$_2$ (2.00 g, 3.89 mmol) and K[N(SiMe$_3$)$_2$] (1.55 g, 7.77 mmol) in benzene (30 mL) was stirred at ambient temperature for 4 h. After removing the solvent under vacuum, pure (**2**-NN)K$_2$ was obtained in quantitative yield. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.04–6.95 (m, 6 H, C*H*$_{N\text{-}aryl}$), 4.36 (s, 2 H, CH$_3$CNC*H*), 3.12 [sept, 2 H, C*H*(CH$_3$)$_2$], 2.67 [sept, 2 H, C*H*(CH$_3$)$_2$], 1.78 (s, 6 H, C*H*$_3$CN), 1.70 (s, 6 H, C*H*$_3$CN), 1.25 [d, ^3J(H,H) = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.11 [d, ^3J(H,H) = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.09 [d, ^3J(H,H) = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.37 [d, ^3J(H,H) = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ = 162.2 (*C*$_q$), 159.0 (*C*$_q$), 151.0 (*C*$_q$), 140.3 (*C*$_q$), 139.7 (*C*$_q$), 125.1 (*C*H$_{N\text{-}aryl}$), 123.5 (*C*H$_{N\text{-}aryl}$), 122.8 (*C*H$_{N\text{-}aryl}$), 86.8 (CH$_3$CN*C*H), 30.4 [*C*H(CH$_3$)$_2$], 27.1 [*C*H(CH$_3$)$_2$], 25.5 [CH(*C*H$_3$)$_2$], 25.2 [CH(*C*H$_3$)$_2$], 24.5 [CH(*C*H$_3$)$_2$], 24.5 [CH(*C*H$_3$)$_2$], 22.9 (*C*H$_3$CN), 21.1 (*C*H$_3$CN) ppm. C$_{34}$H$_{48}$K$_2$N$_4$ (591.0): calcd. C 69.10, H 8.19; found C 69.46, H 8.35.

Synthesis of (2-NN)Mg: A solution of (*n*Bu)$_2$Mg (0.5 M in heptane, 10 mL, 5.0 mmol) was added to a solution of (**2**-NN)H$_2$ (2.13 g, 4.14 mmol) in benzene (12 mL) over a period of one hour. The yellow solution turned to orange-red and was stirred for two hours at ambient temperature. After removing the solvent under vacuum, the crude product was crystallized from hot hexane to obtain (**2**-NN)Mg (1.66 g, 75%) as yellow needless. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.11–6.94 (m, 6 H, C*H*$_{N\text{-}aryl}$), 4.71 (s, 2 H, CH$_3$CNC*H*), 3.17 [m, 2 H, C*H*(CH$_3$)$_2$], 2.56 [sept, 2 H, C*H*(CH$_3$)$_2$], 2.09 (s, 6 H, C*H*$_3$CN), 1.40 (s, 6 H, C*H*$_3$CN), 1.34 [d, ^3J(H,H) = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.17 [d, ^3J(H,H) = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.10 [d, ^3J(H,H) = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.45 [d, ^3J(H,H) = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR {^{1}H} (75 MHz, C$_6$D$_6$, 25 °C): δ = 169.3 (*C*$_q$), 167.3 (*C*$_q$), 150.0 (*C*$_q$), 143.6 (*C*$_q$), 142.3 (*C*$_q$), 126.0 (*C*H$_{N\text{-}aryl}$), 124.8 (*C*H$_{N\text{-}aryl}$), 124.0 (*C*H$_{N\text{-}aryl}$), 93.3 (CH$_3$CN*C*H), 30.1 [*C*H(CH$_3$)$_2$], 29.4 [*C*H(CH$_3$)$_2$], 26.7 [*C*H-(CH$_3$)$_2$], 25.4 [CH(*C*H$_3$)$_2$], 24.9 [CH(*C*H$_3$)$_2$], 24.6 (*C*H$_3$CN), 22.3 (*C*H$_3$CN) ppm. C$_{34}$H$_{48}$MgN$_4$ (537.1): calcd. C 76.04, H 9.01; found C 75.75, H 9.23.

Synthesis of [(2-NN)Ca]$_2$: A solution of (**2**-NN)H$_2$ (1.00 g, 1.94 mmol) and Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ (1.55 g, 7.77 mmol) dissolved in benzene (15 mL) was heated to 80 °C for 70 h. After removing the solvent under vacuum, the crude product was washed with hexane (10 mL) to obtain [(**2**-NN)Ca]$_2$ (680 mg, 63%) as a yellow powder. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.08–6.97 (m, 12 H, C*H*$_{N\text{-}aryl}$), 4.61 (s, 4 H, CH$_3$CNC*H*), 3.12 [sept, 4 H, C*H*(CH$_3$)$_2$], 2.87 [sept, 4 H, C*H*(CH$_3$)$_2$], 2.08 (s, 12 H, C*H*$_3$CN), 1.59 (s, 6 H, C*H*$_3$CN), 1.23 [ps-t, 24 H, CH(C*H*$_3$)$_2$], 1.08 [d, ^3J(H,H) = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 0.50 [d, ^3J(H,H) = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ = 164.7 (*C*$_q$), 162.3 (*C*$_q$), 147.9 (*C*$_q$), 142.6 (*C*$_q$), 142.1 (*C*$_q$), 125.0 (*C*H$_{N\text{-}aryl}$), 124.7 (*C*H$_{N\text{-}aryl}$), 124.4 (*C*H$_{N\text{-}aryl}$), 92.2 (CH$_3$CN*C*H), 29.4 [*C*H(CH$_3$)$_2$], 29.3 [*C*H(CH$_3$)$_2$], 26.2 [CH(*C*H$_3$)$_2$], 25.1 [CH(*C*H$_3$)$_2$], 25.0 [CH(*C*H$_3$)$_2$], 24.3 [CH(*C*H$_3$)$_2$], 24.1 (*C*H$_3$CN), 21.9 (*C*H$_3$CN) ppm. C$_{68}$H$_{96}$Ca$_2$N$_8$ (1105.7): calcd. C 73.87, H 8.75; found C 73.36, H 8.39.

Synthesis of (2-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$: A suspension of (**2**-NN)K$_2$ (455 mg, 770 μmol), CaI$_2$ (445 mg, 1.51 mmol) and K[N(SiMe$_3$)$_2$] (311 mg, 1.56 mmol) in THF (10 mL) was stirred at ambient temperature for 18 h. After centrifugation, the solvent was removed under vacuum. The reddish brown residue was extracted with hexane (20 mL). The hexane solution was concentrated to 5 mL and slowly cooled to –28 °C. (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$ was obtained as orange crystals (760 mg, 37%). ^{1}H NMR studies in C$_6$D$_6$ showed a highly complex mixture of signals in which those of the homoleptic complexes [(**2**-NN)Ca]$_2$ and Ca[N(SiMe$_3$)$_2$]$_2$·(thf)$_2$ could be recognized. Therefore, (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$ is in solution not stable on account of the Schlenk equilibrium. The ratio between homoleptic and the heteroleptic species is circa 1/2. C$_{54}$H$_{100}$Ca$_2$N$_6$O$_2$Si$_4$ (1057.9): calcd. C 61.31, H 9.53; found C 60.98, H 9.67.

Synthesis of (2-NN)[ZnEt]$_2$: A solution of (**2**-NN)H$_2$ (853 mg, 1.66 mmol) and diethylzinc (1 M in hexane, 4.5 mL, 4.5 mmol) in benzene (10 mL) was stirred at 70 °C for 42 h. After removing the solvent under vacuum, pure (**2**-NN)[ZnEt]$_2$ was obtained in quantitative yield as a yellow powder. Light coloured yellow crystals suitable for X-ray analysis could be obtained by slowly cooling a hot hexane solution to 5 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 7.10 (s, 6 H, C*H*$_{N\text{-}aryl}$), 4.75 (s, 2 H, CH$_3$CNC*H*), 3.15 [sept, 4 H, C*H*(CH$_3$)$_2$], 1.96 (s, 6 H, C*H*$_3$CN), 1.64 (s, 6 H, C*H*$_3$CN), 1.37 [t,

^3J(H,H) = 8.1 Hz, 6 H, CH_2CH_3], 1.22 [d, ^3J(H,H) = 7.0 Hz, 12 H, $CH(CH_3)_2$], 1.17 [d, ^3J(H,H) = 7.0 Hz, 6 H, $CH(CH_3)_2$], 1.14 [d, ^3J(H,H) = 6.9 Hz, 6 H, $CH(CH_3)_2$], 0.49 [q, ^3J(H,H) = 8.1 Hz, 4 H, CH_2CH_3] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 166.3 (C_q), 166.2 (C_q), 145.4 (C_q), 142.3 (C_q), 142.1 (C_q), 126.4 ($CH_{N\text{-}aryl}$), 124.3 ($CH_{N\text{-}aryl}$), 123.9 ($CH_{N\text{-}aryl}$), 93.1 (CH_3CNCH), 28.8 [$CH(CH_3)_2$], 28.7 [$CH(CH_3)_2$], 24.8 [$CH(CH_3)_2$], 24.7 [$CH(CH_3)_2$], 23.8 [$CH(CH_3)_2$], 23.6 [$CH(CH_3)_2$], 23.4 (CH_3CN), 21.5 (CH_3CN), 12.9 (CH_2CH_3), –1.54 (CH_2CH_3) ppm. $C_{38}H_{58}N_4Zn_2$ (701.7): calcd. C 65.05, H 8.33; found C 64.74, H 8.27.

Crystal Structure Determinations: All data were collected on a Siemens SMART CCD APEX II diffractometer (Table 2). The structures have been solved by direct methods (SHELXS-97)[16] and were refined with SHELXL-97.[17] The geometry calculations and graphics have been performed with PLATON.[18]

The crystal structure solution of [(**1**-NN)Zn]$_3$ was complicated by cocrystallized toluene molecules. A total of 4.5 toluene molecules per asymmetric unit, i.e. per trimeric [(**1**-NN)Zn]$_3$, has been estimated. Two of these molecules were relatively ordered and could be refined, the remaining 2.5 molecules were completely disordered

Table 2. Crystal data.

	(**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$	[(**1**-NN)Zn]$_3$	(**2**-NN)H$_2$
Formula	$C_{50}H_{94}Mg_2N_4O_4Si_4$	$C_{90}H_{126}N_6O_6Zn_3\cdot(C_7H_8)_2$	$C_{34}H_{50}N_4$
MW	976.27	1768.41	514.78
Crystal size [mm^3]	0.45 × 0.15 × 0.10	0.1 × 0.1 × 0.1	0.3 × 0.3 × 0.3
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a [Å]	10.2419(5)	31.5897(17)	17.2928(8)
b [Å]	12.4802(5)	24.4156(13)	13.1564(7)
c [Å]	13.5319(6)	32.8376(17)	16.0570(7)
α	111.806(2)	90	90
β	101.290(2)	112.964(3)	114.996(2)
γ	99.473(2)	90	90
V [Å^3]	1520.39(12)	23320(2)	3311.0(3)
Z	1	8	4
ρ [g cm^{-3}]	1.066	1.138[a]	1.033
μ (Mo-K_α) [mm^{-1}]	0.159	0.658	0.060
T [°C]	–70	–70	–100
θ (max.)	26.0	26.1	25.4
Reflections total, unique	51246, 5967	383583, 23089	13341, 6040
R_{int}	0.045	0.129	0.036
Obsd. reflections [$I > 2\sigma(I)$]	4605	11976	3613
Parameters	458	1089	411
R_1	0.0541	0.0610	0.0679
$wR2$	0.1595	0.1650	0.2088
GOF	1.05	0.95	1.06
Min./max. residual e$^-$ density [e Å^{-3}]	–0.43/0.46	–0.44/0.50	–0.21/0.14
Compound	(**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$	[(**2**-NN)Ca]$_2$	(**2**-NN)[ZnEt]$_2$
Formula	$C_{54}H_{100}Ca_2N_6O_2Si_4\cdot(C_6H_6)_2$	$C_{68}H_{96}Ca_2N_8$	$C_{38}H_{58}N_4Zn_2$
MW	1214.14	1105.69	701.62
Crystal size [mm^3]	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.3	0.5 × 0.3 × 0.3
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a [Å]	13.9606(4)	9.563(5)	15.2419(3)
b [Å]	15.5500(5)	22.047(12)	16.6230(3)
c [Å]	17.9974(5)	31.120(15)	15.7753(3)
α	90	90	90
β	101.808(2)	90	94.796(1)
γ	90	90	90
V [Å^3]	3824.3(2)	6561(6)	3982.9(1)
Z	2	8	4
ρ [g cm^{-3}]	1.054	1.119	1.170
μ (Mo-K_α) [mm^{-1}]	0.253	0.218	1.232
T [°C]	+20	–70	–70
θ (max.)	25.0	26.1	25.5
Reflections total, unique	46522, 6746	47563, 11555	53094, 7411
R_{int}	0.045	0.156	0.056
Obsd. reflections [$I > 2\sigma(I)$]	4327	8075	4934
Parameters	333	728	411
R_1	0.0530	0.0906	0.0429
$wR2$	0.1663	0.2078	0.1189
GOF	1.02	1.10	1.02
Min./max. residual e$^-$ density [e Å^{-3}]	–0.27/0.45	–0.34/0.34	–0.38/0.47

[a] Density corrected for the additional 2.5 toluene molecules which have been treated with SQUEEZE.

and treated with the SQUEEZE procedure incorporated in the program PLATON.[18]

(**2**-NN)[CaN(SiMe$_3$)$_2$·(thf)$_2$]$_2$ cocrystallized with two molecules of benzene which were disordered over two positions and have been refined as regular hexagons.

[(**2**-NN)Ca]$_2$ crystallized in the chiral space group $P2_12_12_1$ and has been checked for the correct absolute structure [Flack parameter 0.049(54)]. The complex has no crystallographic symmetry but approximate D_2 symmetry. No higher crystal symmetry could be found. The somewhat poor crystal quality led to weak diffraction and subsequently somewhat higher R values ($wR2$ = 0.2078, $R1$ = 0.0906).

CCDC-729095 {for (**1**-NN)[MgN(SiMe$_3$)$_2$·thf]$_2$}, -729096 {for [(**1**-NN)Zn]$_3$}, -729097 {for (**2**-NN)[CaN(SiMe$_3$)$_2$·thf]$_2$}, -729098 {for (**2**-NN)[ZnEt]$_2$}, -729099 {for [(**2**-NN)Ca]$_2$}, -729100 [for (**2**-NN)H$_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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