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Peculiar Binding Modes of a Ligand with Two Adjacent β-Diiminato Binding Sites in Alkali and Alkaline-Earth Metal Chemistry

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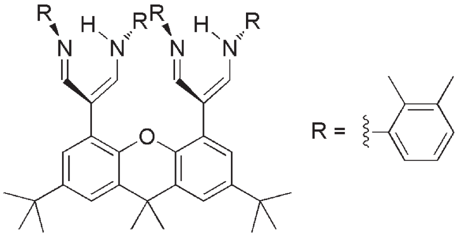
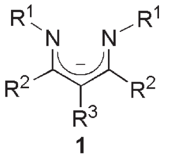
Reaction of the diprotic ligand [Xanthdim]H_2 (a ligand system where two adjacent β-dialdimine units are linked by a xanthyl backbone) with 2 equiv of potassium hydride or benzylcesium gave access to bimetallic alkali metal complexes. These complexes were structurally characterized by X-ray diffraction, which showed that the β-diiminato units are orientated in a W-conformation. Treatment with 2 equiv of $Mg[N(SiMe_3)_2]_2(THF)_2$ led to the formation of the heteroleptic complex [Xanthdim]$[MgN(SiMe_3)_2(THF)]_2$, that crystallized as a highly strained monomer. The heteroleptic Mg complex is remarkably stable against ligand exchange but is not active in CO_2/cyclohexene oxide copolymerization. Reaction with $Ca[N(SiMe_3)_2]_2(THF)_2$ gave the homoleptic complex [Xanthdim][Ca(THF)]. Both alkaline-earth metal complexes display considerable distortions in their solid state structure.

Introduction

β-Diketiminates (**1**) are versatile ligand systems which, both in the main group and transition metal chemistry, can stabilize high as well as low metal oxidation states. The "usual" coordination mode **A** in Scheme 1 allows for the preparation of coordinatively unsaturated complexes.[1] However, apart from **A** many other binding modes have been observed (**B**−**H**).[1] We have recently reported on a ligand precursor where two β-diiminato units are oriented parallel to each other: [Xanthdim]H_2.[2]



[Xanthdim]H_2



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In its deprotonated form, it has been employed successfully as a ligand for the syntheses of (i) zinc complexes that were investigated as epoxide/CO_2 copolymerization catalysts,[3] (ii) iron(II) complexes, which react with O_2 to give $Fe^{III}-O-Fe^{III}$ compounds,[4] and (iii) copper(I) complexes[5] that activate O_2 for the coupling of phenols. In these complexes, the β-diiminato units of $[\text{Xanthdim}]^{2-}$ were found to bind the transition metal ions in mode **A**.

These studies have now been extended to alkali and alkaline-earth metal chemistry for three reasons. Alkali metal complexes represent valuable starting materials in the synthesis of transition metal complexes via salt metathesis. As hitherto only the Li complex has been studied, we were interested, whether any structural differences occur on going from lithium, which is chelated via mode **A**,[2] to the higher homologues. Second, bearing in mind the known β-diketiminato alkaline-earth chemistry,[6] the question arose whether heteroleptic bimetallic complexes, [Xanthdim]-$(MR)_2$, are stable against ligand exchange through the Schlenk equilibrium. Third, the potential of alkaline-earth metal compounds as polymerization catalysts is one of our interests and seemed worth evaluating for complexes of Xanthdim.[7]

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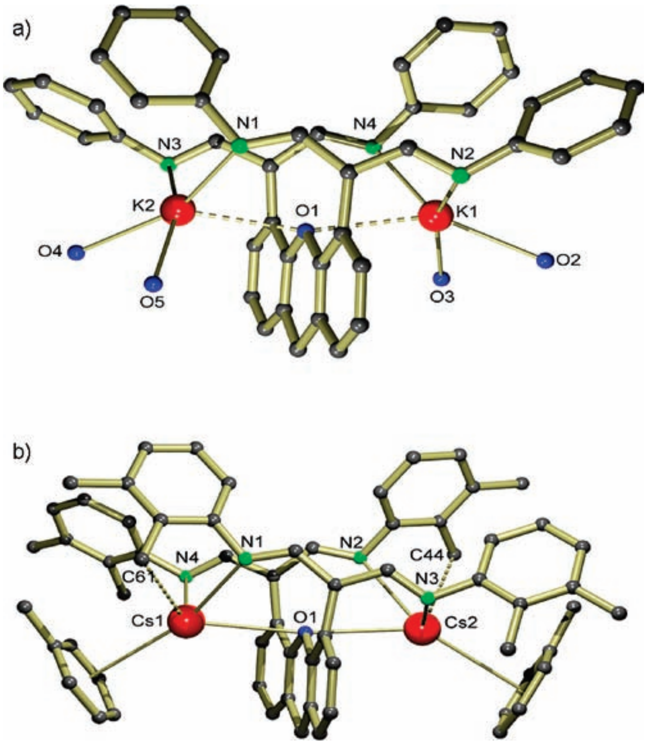


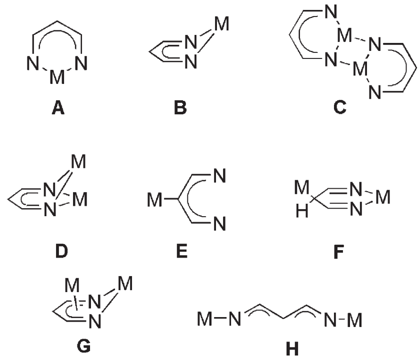
Figure 1. Crystal structure of (a) [Xanthdim][K(THF)$_2$]$_2$. For clarity, hydrogen atoms and all alkyl groups on the Xanthdim ligand and on the aryl rings have been omitted. Only the O atoms of the THF ligands are shown. (b) [Xanthdim][Cs(toluene)]$_2$. For clarity, hydrogen atoms and all alkyl groups on the xanthyl backbone have been omitted. Agostic interactions are shown by dashed lines. Selected bond distances and angles are given in Table 1.

Results and Discussion

Addition of a KH/THF suspension to a clear yellow solution of [Xanthdim]H$_2$ in THF leads to the evolution of gas (H$_2$) and a color change to orange, both indicative of a successful deprotonation. After workup, an orange solid could be isolated in 77% yield. A ^{1}H NMR spectrum recorded in C$_6$D$_6$ showed characteristics that confirmed the formation of [Xanthdim]$^{2-}$: disappearance of the signal corresponding to the acidic NH protons in [Xanthdim]H$_2$ at around 12 ppm and a concomitant transformation of a pseudo-doublet at 8.09 ppm into a singlet corresponding to the four protons of the β-diiminato units. Spectroscopic and analytical data are in agreement with the formation of the complex [Xanthdim][K(THF)$_2$]$_2$ (**2**) (Scheme 2). It is noteworthy that the integrals of the multiplet signals belonging to the protons of coordinated THF molecules decrease on continued drying of product **2** under vacuum. Crystals of **2** suitable for single crystal X-ray diffraction could be obtained by slow diffusion of hexane into a concentrated THF solution. The molecular structure is shown in Figure 1a.

The potassium ions bind in a completely different coordination mode to the β-diketiminato binding pockets than the lithium ions in [Xanthdim][Li(OEt$_2$)$_2$]$_2$.[2] Bonding in [Xanthdim][K(THF)$_2$]$_2$ can be described by type **H** (Scheme 1), in which the β-diiminato units have a W-conformation. Apparently the significant size of the K$^+$ ions makes this mode more favorable as it allows for interaction of the metal cation with the xanthyl framework. Bonding of type **H** has been observed already previously in case of a β-diketiminato potassium salt,[8] which forms a polymer structure containing infinite chains. In the case of **2**, however, the coordinative saturation of the potassium cations proceeds intramolecularly, so that both β-diiminato units are involved in the binding of each cation. The coordination spheres are completed by two coordinated THF molecules as well as by the O atom of the xanthene moiety and can be described as distorted trigonal bipyramids. Each K$^+$ ion binds to the β-diiminato units with one short and one long contact. The bond distances K1$-$N4 (2.802(2) Å) and K2$-$N1 (2.747(2) Å) are typical for K$-$N bonds, while the K1$-$N2 (2.977(2) Å) and K2$-$N3 (2.982(2) Å) distances approximately correspond to the sum of the van der Waals radii for N and K (r_K (2.270 Å) + r_N (0.700 Å) = 2.970 Å). The K1$\cdots$K2 distance amounts to 5.762(1) Å, and the K1$-$O1$-$K2 unit is almost linear (161.8(1)°). The two C$-$C and the two N$-$C distances within each of the β-diiminato entities are very similar. This indicates that the effective charge delocalization within these units is similar.

Scheme 1. Typical Binding Modes for β-Diiminato Ligands[a]



[a] For the sake of clarity, only the ligand framework without substituents is shown.

We further set out to prepare the cesium analogue by a direct deprotonation of [Xanthdim]H$_2$ with an excess of benzylcesium. Addition of benzylcesium to the ligand precursor in benzene at room temperature resulted in an immediate color change from yellow to orange. After removal of excessive benzylcesium by centrifugation and of all volatiles under vacuum, the desired product was isolated in quantitative yield as an orange powder (Scheme 2). Crystallization from a hot toluene solution led to the formation of [Xanthdim][Cs(toluene)]$_2$ (**3**). Complex **3** crystallizes as a monomer of approximate, noncrystallographic, C_2 symmetry (Figure 1b). As in **2**, the bridging pockets display a W-conformation (type **H**). Each Cs$^+$ ion bridges both β-diiminato units and is bound to an O atom of the xanthene moiety and a toluene ligand. The coordination sphere is further filled with an agostic interaction between Cs1 and C61 (3.599(6) Å) and Cs2 and C44 (3.594(6) Å). Aside from the Cs1$-$N1 distance (3.145(4) Å), the Cs$-$N bonds are in the narrow range of 3.003(4)$-$3.061(4) Å. The average value of the distance between the cesium ions and the oxygen atom of the xanthene backbone amounts to 3.215(4) Å. Hence, the observed Cs$-$O interaction occurs at a quite long distance in comparison to reported cesium/THF contacts in a methandiide complex (average value: 3.099(16) Å)[9] or in an

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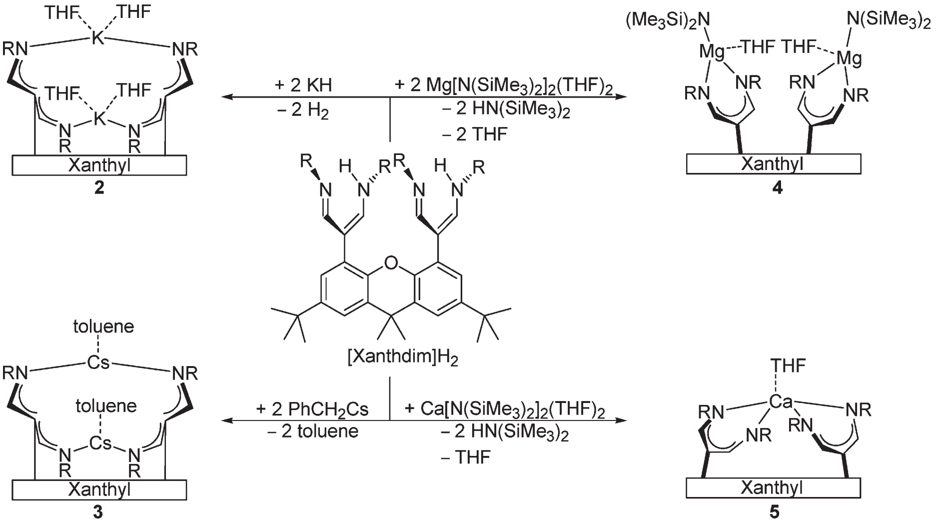
Scheme 2. Syntheses of the Alkali and Alkaline-Earth Metal Complexes (R = 2,3-Dimethylphenyl)



allyl complex (average value: 2.93(5) Å).[10] The Cs1−O1−Cs2 angle of 171.7(1)° is more expanded than the K1−O1−K2 angle in **2** (161.8(1)°). Within the β-diiminato unit, the two C−C and the two N−C distances are very similar to those in the potassium complex. This indicates a similar charge distribution. The Cs1···Cs2 distance is measured at 6.284(2) Å.

The reaction of [Xanthdim]H_2 with 2 equiv of Mg[N$(SiMe_3)_2]_2(THF)_2$ needs considerably more forcing conditions. Double deprotonation could only be achieved after 16 h at 70 °C in benzene. The product [Xanthdim][MgN$(SiMe_3)_2(THF)]_2$ (**4**) could be isolated in 64% crystalline yield (Scheme 2). The complex is stable toward ligand exchange in benzene solution (also at higher temperatures), and the Schlenk equilibrium is fully at the heteroleptic side. Recrystallization from hot benzene gave the analytically pure product in the form of yellow rodlike crystals. The crystal structure shows a nonsymmetric monomeric complex (Figure 2a, Table 1). Whereas the comparable mononuclear (DIPP-nacnac)MgN$(SiMe_3)_2$ (DIPP-nacnac = CH{(CMe)-(2,6-iPr$_2$C$_6$H$_3$N)}$_2$) has been prepared as a THF-free complex,[11] in the bimetallic complex **4** each Mg^{2+} ion is bound to a β-diiminato unit, a $(Me_3Si)_2N^-$ ligand, and a THF ligand. The coordination sphere around the tetracoordinate Mg^{2+} can be described as distorted tetrahedral, and there are no obvious agostic interactions. Bond distances to Mg compare well to those in a similar THF adduct: (DIPP-nacnac)MgN-(iPr)$_2$(THF).[12] The β-diiminato units are bound to magnesium in their typical U-conformation (mode **A**). The significant bulk of the MgN$(SiMe_3)_2$(THF) moieties causes considerable distortions (Figure 3). For example, the C3−C2−C24 angle is remarkably small (118.2(1)°) whereas the C1−C2−C24 angle is significantly enlarged (124.5(2)°). The second β-diiminato moiety is even more distorted, and angles of 116.6(1)° and 126.6(1)° are observed. Thus, the distance C24···C27 (4.940(3) Å) is larger than that between the xanthyl ipso atoms C2···C12 (4.704(5) Å). Further

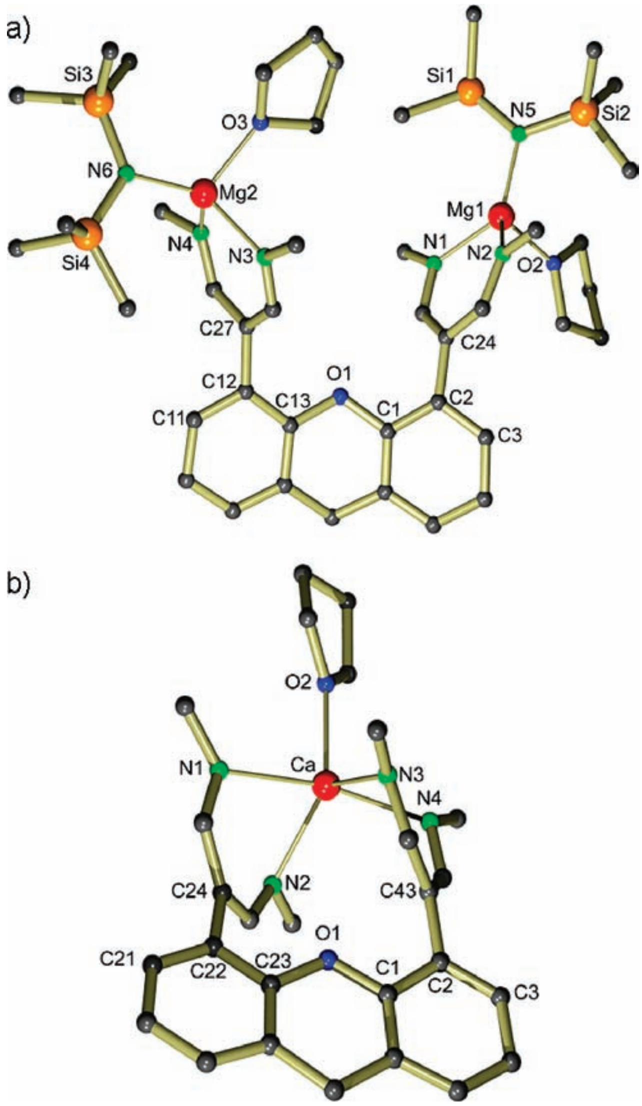


Figure 2. Crystal structure of (a) [Xanthdim][MgN$(SiMe_3)_2(THF)]_2$ and (b) [Xanthdim][Ca(THF)]. For clarity, hydrogen atoms and all alkyl groups on the Xanthdim ligand have been omitted. Only the C_{ipso} atoms of the *N*-aryl groups are shown. Selected bond distances and angles are given in Table 1.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for All Crystal Structures

		[Xanthdim][K(THF)$_2$]$_2$			
K1−N2	2.977(2)	K2−N1	2.747(2)	K1−O1−K2	161.8(1)
K1−N4	2.802(2)	K2−N3	2.982(2)		
K1···O1	2.936(2)	K2···O1	2.900(2)		
K1−O2	2.696(2)	K2−O4	2.669(2)		
K1−O3	2.725(2)	K2−O5	2.681(2)		
K1···K2	5.762(1)				
		[Xanthdim][Cs(toluene)]$_2$			
Cs1−N1	3.145(4)	Cs2−N2	3.041(4)	Cs1−O1−Cs2	171.7(1)
Cs1−N4	3.003(4)	Cs2−N3	3.061(4)		
Cs1−O1	3.300(4)	Cs2−O1	3.129(3)		
Cs1···Ar$_{\text{center}}$	3.308(3)	Cs2···Ar$_{\text{center}}$	3.325(3)		
Cs1···C61	3.599(6)	Cs2···C44	3.594(6)		
Cs1···Cs2	6.284(2)				
		[Xanthdim][MgN(SiMe$_3$)$_2$(THF)]$_2$			
Mg1−N1	2.081(3)	Mg2−N3	2.086(3)	C1−C2−C24	124.5(2)
Mg1−N2	2.071(3)	Mg2−N4	2.072(3)	C3−C2−C24	118.2(1)
Mg1−N5	1.992(3)	Mg2−N6	2.011(3)	C11−C12−C27	116.6(1)
Mg1−O2	2.072(3)	Mg2−O3	2.058(3)	C13−C12−C27	126.6(1)
Mg1···Mg2	8.003(3)				
		[Xanthdim][Ca(THF)]			
Ca1−N1	2.427(2)	C1−C2−C43	117.6(2)	N1−Ca−N2	76.8(2)
Ca1−N2	2.385(2)	C3−C2−C43	125.1(2)	N3−Ca−N4	78.0(2)
Ca1−N3	2.365(2)	C21−C22−C24	125.7(2)		
Ca1−N4	2.424(2)	C23−C22−C24	117.4(2)		
Ca1−O2	2.366(2)				

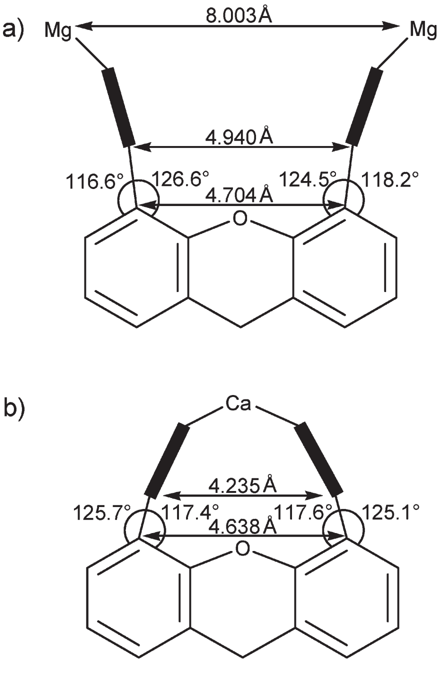

Figure 3. Typical distortion of the Xanthdim ligand in (a) [Xanthdim][MgN(SiMe$_3$)$_2$(THF)]$_2$ and (b) [Xanthdim][Ca(THF)].

distortion becomes apparent by the fact that the NCCCN units are bending away from each other. The angle between the C3−C24 vector and the NCCCN least-squares plane is 11.9(2)° (for the C12−C27 vector, a value of 13.1(2)° is observed). Consistent with the steric bulk of the (Me$_3$Si)$_2$N$^-$ ligand, Mg1 and Mg2 are lying 0.600(1) Å and 0.502(1) Å out of the corresponding NCCCN planes, respectively. Thus, although the C$_{\text{ipso}}$ atoms in the xanthyl bridge are only separated by 4.704(5) Å, the final Mg1···Mg2 distance of 8.003(3) Å measures nearly double this value. This is likely caused by steric bulk and demonstrates the enormous flexibility of this ligand system.

The attempted preparation of the analogous Ca complex, however, failed. Heating a solution of [Xanthdim]H$_2$ and 2 equiv of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ in benzene to 70 °C overnight resulted in a 2-fold deprotonation of the ligand and the exclusive formation of the homoleptic complex [Xanthdim][Ca(THF)] (**5**) was observed. ^{1}H NMR solution studies also show that the Schlenk equilibrium for [Xanthdim][CaN(SiMe$_3$)$_2$(THF)]$_2$ is completely at the homoleptic side. Heating a solution of [Xanthdim]H$_2$ and Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ in a 1:1 stoichiometry and subsequent crystallization from hot hexane gave **5** in high crystalline yields (Scheme 2). The molecular structure is shown in Figure 2b and relevant bond lengths and angles are summarized in Table 1.

[Xanthdim][Ca(THF)] crystallizes as a monomer with approximate, noncrystallographic, C_2 symmetry. The β-diiminato units coordinate face-on to Ca^{2+}. The coordination sphere of Ca^{2+} is completed by an additional THF ligand. The average Ca···N distances of 2.400(2) Å are somewhat longer than in the homoleptic (DIPP-nacnac)$_2$Ca complex (2.379(1) Å).[6b] This might be on account of an additional THF ligand in [Xanthdim][Ca(THF)]. Furthermore there is no evident contact to the oxygen atom O1 of the xanthene backbone: the distance Ca···O1 measures 4.125(4) Å. The observed face-on coordination of the β-diiminato units to Ca^{2+} is rather unusual. As a result of this coordination geometry, the angles between the xanthene backbone and the NCCCN units are highly distorted (Figures 2 and 3). In contrast to **4**, the inner angle (for example, C1−C2−C43: 117.6(2)°) is reduced from 120°, while the outer angle is highly extended (C3−C2−C43: 125.1(2)°). The NCCCN units are bending toward each other. The angle between the C2−C43 vector and the NCCCN least-squares plane is 2.8(2)° (for the C22−C24 vector, a value of 8.7(2)° is observed). The Ca distance to the NCCCN least-squares planes are 1.576 and 1.668 Å, respectively.

Ding et al. reported in 2006 the discovery of a bimetallic Mg complex that has been shown to be highly active in the CO_2/cyclohexene oxide copolymerization already at the remarkably low CO_2 pressure of 1 bar.[13] Hence, we were interested in exploring the potential of the heteroleptic complex $[Xanthdim][MgN(SiMe_3)_2(THF)]_2$ (**4**) in the CO_2/cyclohexene oxide copolymerization. However, at the higher CO_2 pressure of 10 bar, the bimetallic complex **4** was not active within the temperature range of 60−100 °C. Apparently, the parallel arrangement of the β-diiminato units results in a structural orientation of the Mg atoms that does not allow for an effective CO_2/cyclohexene oxide copolymerization, or the latter is prohibited by the steric bulk within the reaction pocket.

Conclusions

A series of *bis*(β-diiminato) alkali (K, Cs) and alkaline-earth (Mg, Ca) metal complexes is easily accessible by deprotonation reactions of $[Xanthdim]H_2$. All compounds were structurally characterized by NMR and X-ray diffraction. Within the dinuclear potassium and cesium complexes **2** and **3** the *bis*(β-diiminato) units exhibit the binding mode **H**, coordinating in a W-conformation to the metal ions. For larger metals, this conformation is likely favored on account of possible metal···xanthyl interactions.

2-Fold deprotonation with $Mg[N(SiMe_3)_2]_2(THF)_2$ gave access to the heteroleptic magnesium amide complex $[Xanthdim][MgN(SiMe_3)_2(THF)]_2$ (**4**). On account of the bulk of the $MgN(SiMe_3)_2(THF)$ fragment, the Xanthdim ligand suffers considerable strain. The metal···metal distance of 8.003(3) Å, the highest observed so far for Xanthdim complexes, proves the significant flexibility of this particular ligand system. Complex **4** was found to be inactive in the CO_2/cyclohexene oxide copolymerization. Treatment with $Ca[N(SiMe_3)_2]_2(THF)_2$ gave exclusively the mononuclear calcium complex [Xanthdim][Ca(THF)] (**5**). In this case, the ligand is distorted in order to enable binding of a single metal center via both β-diiminato functions. This unusual coordination mode leaves one side of the metal completely free for neutral ligands. The potential of complex **5** as a Lewis-acidic catalyst is currently under investigation.

Experimental Section

General Methods. Solvents were dried by standard methods and distilled prior to use. All moisture and air sensitive reactions were carried out under an inert argon atmosphere using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. NMR spectra were recorded on a Bruker DPX300 spectrometer. The compounds benzylcesium,[9] $Mg[N(SiMe_3)_2]_2(THF)_2$,[14] and $Ca[N(SiMe_3)_2]_2(THF)_2$[14] were prepared according to the literature.

Synthesis of $[Xanthdim][K(THF)_2]_2$ (2). Addition of a solution of $[Xanthdim]H_2$ (200 mg, 229 μmol) in 3 mL of THF to KH (35.0 mg, 876 μmol) suspended in 4 mL of THF led to a yellow suspension, which was stirred for 18 h at room temperature. After removal of excessive KH by filtration, the clear orange solution was concentrated to a volume of 1 mL. The addition of 4 mL of hexane and storage at −30 °C (for 4 days) led to the precipitation of a microcrystalline solid. Filtration and drying of the orange solid in vacuum yielded 174 mg of $[Xanthdim][K(THF)_{0.25}]_2$ (176 μmol, 77%). Crystals of **2** suitable for single crystal X-ray analysis were grown by slow diffusion of hexane into a concentrated THF solution. Drying of the crystals in vacuum again resulted in the partial loss of coordinated THF. ^1H NMR (300 MHz, C_6D_6): δ 1.34 (m, 8H, THF), 1.39 (s, 18H, $C(CH_3)_3$), 1.72 (s, 6H, $C(CH_3)_2$), 2.06 (s, 12H, CH_3), 2.16 (s, 12H, CH_3), 3.39 (m, 8H, THF), 6.57 (d, $^3J = 7.3$ Hz, 4H, C*H*), 6.83 (d, $^3J = 7.7$ Hz, 4H, aryl), 7.11 (ps-t, 4H, aryl), 7.51 (d, $^4J = 2.4$ Hz, 2H, aryl), 7.82 (d, $^4J = 2.4$ Hz, 2H, aryl), 8.09 (s, 4H, NC*H*). ^{13}C NMR (75 MHz, C_6D_6): δ 14.1 (CH_3), 20.6 (CH_3), 25.7 (THF), 31.8 ($C(CH_3)_3$), 32.1 ($C(CH_3)_2$), 34.7 ($C(CH_3)_3$), 35.3 ($C(CH_3)_2$), 67.6 (THF), 106.1 (C_q), 116.6 (Ar), 119.4 (Ar), 123.1 (Ar), 127.2 (Ar), 128.9 (Ar), 129.4 (Ar), 130.5 (Ar), 132.6 (Ar), 136.9 (Ar), 146.3 (Ar), 146.6 (Ar), 154.9 (Ar), 163.3 (N*C*H). Anal. calcd for $C_{77}H_{100}K_2N_4O_5$: C, 74.59; H, 8.13. Found: C, 74.33; H, 8.25.

Synthesis of $[Xanthdim][Cs(toluene)]_2$ (3). $[Xanthdim]H_2$ (23.5 mg, 26.8 μmol) and benzylcesium (14.9 mg, 66.5 μmol) were stirred for one hour in 0.5 mL of benzene. The color of the solution changed immediately from yellow to orange. After centrifugation, the volatile components were removed under vacuum. The yellow-orange residue was additionally dried for one hour at 80 °C to give $[Xanthdim]Cs_2$ in quantitative yield. ^1H NMR (300 MHz, C_6D_6): δ 1.34 (s, 18H, $C(CH_3)_3$), 1.76 (s, 6H, $C(CH_3)_2$), 2.11 (s, 12H, CH_3), 2.15 (s, 12H, CH_3), 6.53 (d, $^3J = 7.8$ Hz, 4H, aryl), 6.84 (d, $^3J = 7.4$ Hz, 4H, aryl), 7.11 (ps-t, 4H, aryl), 7.43 (d, $^4J = 2.5$ Hz, 2H, aryl), 7.93 (d, $^4J = 2.4$ Hz, 2H, aryl), 8.09 (s, 4H, NC*H*); ^{13}C NMR (75 MHz, C_6D_6): δ 14.9 (CH_3), 21.0 (CH_3), 32.1 ($C(CH_3)_3$), 34.9 ($C(CH_3)_2$), 35.0 ($C(CH_3)_3$), 36.6 ($C(CH_3)_2$), 106.8 (C_q), 118.0 (Ar), 121.4 (Ar), 123.3 (Ar), 127.7 (Ar), 127.9 (Ar), 129.3 (Ar), 130.7 (Ar), 134.2 (Ar), 137.3 (Ar), 144.6 (Ar), 146.3 (Ar), 155.5 (Ar), 163.6 (N*C*H). Anal. calcd for $C_{75}H_{84}Cs_2N_4O$: C, 68.07; H, 6.40. Found: C, 67.83; H, 6.44.

Crystals suitable for X-ray structural analysis could be obtained by slowly cooling a hot toluene solution to room temperature.

Synthesis of $[Xanthdim][MgN(SiMe_3)_2(THF)]_2$ (4). $[Xanthdim]H_2$ (435 mg, 518 μmol) and $Mg[N(SiMe_3)_2]_2(THF)_2$ (536 mg, 1.10 mmol) were dissolved in 10 mL of benzene and stirred for 16 h at 70 °C. Concentration of the solution to 5 mL and cooling to 5 °C led to the formation of light yellow rods suitable for X-ray structural analysis. Yield: 462 mg, 333 μmol, 64%. ^1H NMR (300 MHz, C_6D_6): δ 0.25 (s, 36H, $Si(CH_3)_3$), 1.22 (m, 8H, THF), 1.44 (s, 18H, $C(CH_3)_3$), 1.69 (s, 6H, $C(CH_3)_2$), 2.03 (s, 12H, CH_3), 2.40 (s, 12H, CH_3), 3.75 (m, 8H, THF), 6.85 (d, $^3J = 7.4$ Hz, 4H, aryl), 6.94 (ps-t, 4H, aryl), 7.15 (d, $^3J = 7.5$ Hz, 4H, aryl), 7.40 (br, 2H, aryl), 7.46 (d, $^4J = 2.4$ Hz, 2H, aryl), 7.97 (s, 4H, NC*H*). ^{13}C NMR (75 MHz, C_6D_6): δ 6.41 ($Si(CH_3)_3$) 17.0 (CH_3), 21.1 (CH_3), 25.3 (THF), 32.1 ($C(CH_3)_3$), 34.2 ($C(CH_3)_2$), 34.7 ($C(CH_3)_3$), 35.8 ($C(CH_3)_2$), 70.2 (THF), 104.1 (C_q), 121.2 (Ar), 123.0 (Ar), 126.4 (Ar), 126.7 (Ar), 130.0 (Ar), 130.1 (Ar), 131.0 (Ar), 131.1 (Ar), 139.0 (Ar), 145.2 (Ar), 147.0 (Ar), 152.9 (Ar), 165.5 (N*C*H). Anal. calcd for $C_{81}H_{120}Mg_2N_6O_3Si_4$: C, 70.15; H, 8.72. Found: C, 70.72; H, 8.56.

Synthesis of [Xanthdim][Ca(THF)] (5). $[Xanthdim]H_2$ (37.9 mg, 43.3 μmol) and $Ca[N(SiMe_3)_2]_2(THF)_2$ (22.7 mg, 44.9 μmol) were dissolved in 400 μL of benzene and heated overnight at 70 °C. The volatile compounds were removed under vacuum.

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Table 2. Crystal Data

compound	[Xanthdim][K(THF)$_2$]$_2$	[Xanthdim][Cs(toluene)]$_2$	[Xanthdim] [MgN(SiMe$_3$)$_2$(THF)]$_2$	[Xanthdim][Ca(THF)]
formula	$C_{77}H_{100}K_2N_4O_3\cdot(C_6H_{14})$	$C_{68}H_{76}Cs_2N_4O\cdot(C_7H_8)_3$	$C_{81}H_{120}Mg_2N_6O_3Si_4\cdot(C_6H_6)_{2.5}$	$C_{65}H_{76}CaN_4O_2$
MW	1325.98	1507.56	1582.09	985.38
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	13.9189(2)	26.3062(10)	18.326(2)	13.414(2)
b (Å)	27.2842(5)	13.9374(5)	27.314(3)	15.571(3)
c (Å)	21.1070(3)	21.3637(7)	21.130(2)	15.920(3)
α	90	90	90	106.18(2)
β	106.6950(10)	91.916(2)	115.644(6)	112.26(2)
γ	90	90	90	91.33(2)
V (Å^3)	7677.8(2)	7826.9(5)	9535.0(18)	2924.3(11)
Z	4	4	4	2
ρ (g·cm^{-3})	1.147	1.279	1.102	1.119
μ(Mo$_{K\alpha}$) (mm^{-1})	0.175	0.979	0.125	0.152
T (°C)	−173	−100	−100	−93
θ(max)	26.8	24.9	24.8	25.3
refl total, unique	79266, 16196	80307, 13457	158975, 16333	19563, 9896
R_{int}	0.060	0.071	0.110	0.044
obsvd refl ($I > 2\sigma(I)$)	12067	9045	10387	6149
parameter	888	797	1029	665
R_1	0.0549	0.0563	0.0658	0.0494
wR_2	0.1404	0.1277	0.1879	0.1314
GOF	1.02	1.02	1.03	1.03
min/max resd (e·Å^{-3})	−0.57/0.78	−0.90/0.95	−0.35/0.65	−0.53/0.52

After addition of 200 μL of hexane, **5** could be obtained as yellow crystals (35.1 mg, 35.6 μmol, 82%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.01 (m, 4H, THF), 1.33 (s, 18H, C(CH_3)$_3$), 1.77 (s, 6H, C(CH_3)$_2$), 2.14 (s, 12H, CH_3), 2.27 (s, 12H, CH_3), 3.16 (m, 4H, THF), 6.36−6.42 (m, 4H, aryl), 6.78−6.82 (m, 8H, aryl), 7.48 (d, $^4J = 2.2$ Hz, 2H, aryl), 7.57 (d, $^4J = 2.4$ Hz, 2H, aryl), 8.01 (s, 4H, NCH). ^{13}C NMR (75 MHz, C_6D_6): δ 14.6 (CH$_3$), 20.8 (CH$_3$), 25.1 (THF), 31.1 (C(CH$_3$)$_3$), 32.1 (C(CH$_3$)$_2$), 34.9 (C(CH$_3$)$_3$), 36.6 (C(CH$_3$)$_2$), 69.0 (THF), 99.7 (C_q), 119.7 (Ar), 120.3 (Ar), 124.8 (Ar), 124.9 (Ar), 126.9 (Ar), 129.0 (Ar), 131.7 (Ar), 132.8 (Ar), 136.9 (Ar), 145.2 (Ar), 149.9 (Ar), 154.2 (Ar), 160.6 (NCH). Anal. calcd for $C_{65}H_{76}CaN_4O_2$: C, 79.23, H 7.77. Found: C, 78.82; H, 7.83.

Crystal Structure Determinations. Single crystals have been measured on Siemens SMART CCD or STOE IPDS II diffractometers. Structures have been solved and refined using the programs SHELXS-97 and SHELXL-97, respectively.[15] In all cases the hydrogen atoms have been placed on calculated positions. All geometry calculations and graphics have been performed with PLATON.[16] Crystal data are shown in Table 2.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 744041 [Xanthdim]-[K(THF)$_2$]$_2$, 744040 [Xanthdim][Cs(toluene)]$_2$, 744042 [Xanthdim][MgN(SiMe$_3$)$_2$(THF)]$_2$, and 744039 [Xanthdim][Ca-(THF)]. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21-EZ, UK (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for all crystal structures as CIF files and ORTEP representations for all crystal structures in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

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