Pyrrolylaldiminato Complexes of Zn, Mg and Al

Haijun Hao,[a] Sonali Bhandari,[a] Yuqiang Ding,[a] Herbert W. Roesky,*[a] Jörg Magull,[a] Hans-Georg Schmidt,[a] Mathias Noltemeyer,[a] and Chunming Cui[a]

Dedicated to Professor Rüdiger Mews on the occasion of his 60th birthday

Keywords: Zinc / Magnesium / Aluminum / N ligands

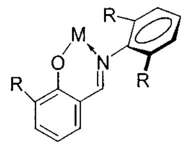
The reaction of 2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-5-R-C$_4$H$_2$NH (R = H, L^{1}H; R = tBu, L^{2}H) with one equivalent of ZnMe$_2$ or MgnBu$_2$ in toluene or n-hexane afforded the bis(pyrrolylaldiminato) complexes ZnL$^1_2$ (**1**), ZnL$^2_2$ (**2**) and MgL$^2_2$ (**3**). Crystalline MgL$^1_2$·THF (**4**·THF) was formed by treatment of LiL^1 with MeMgCl in THF followed by recrystallization from n-hexane. L^{1}AlMe$_2$ (**6**) and L^{2}AlMe$_2$ (**7**) were readily prepared by refluxing L^{1}H and L^{2}H with AlMe$_3$ in toluene or n-hexane for several hours. However, the reaction of LiL^1 with AlCl$_3$ in a 1:1 molar ratio provided L$^1_2$AlCl (**8**), while the reaction of KL^2 with AlCl$_3$ afforded L^{2}AlCl$_2$ (**9**). Compounds **2**, **3**, **5**, and **8** were characterized by a single-crystal X-ray structural analysis. Compounds **2**, **3**, and **5** all have a tetrahedral geometry around the metal atom, while the five-coordinate aluminum in **8** has a trigonal bipyramidal geometry.

Introduction

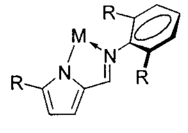
There are only a few reports on pyrrolylaldiminato complexes.[1,2] Bischelating pyrrolylaldiminato ligands with bulky substituents have not drawn as much attention as salicylaldiminato ligands, which have been shown to be excellent ligands for zirconium and nickel complexes that act as olefin polymerization catalysts.[3,4] Very recently, salicylaldiminato zinc compounds have been reported to be active for the copolymerization of CO$_2$ and epoxides.[5]

Both pyrrolylaldiminato and salicylaldiminato ligands are easily prepared and have similar steric demands; their steric and electronic properties may be varied by simply changing the substituents. The chelating pyrrolylaldiminato ligand forms five-membered ring systems with metal ions, whereas salicylaldiminato complexes tend to form six-membered rings (Scheme 1).

Here we present the synthesis and structures of divalent Zn, Mg and trivalent Al compounds ligated by the pyrrolylaldiminato ligands [2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-C$_4$H$_3$N]$^-$ (L^1) and [2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-5-tBu-C$_4$H$_2$N]$^-$ (L^2).



Salicylaldiminato complex



Pyrrolylaldiminato complex

Scheme 1

Results and Discussion

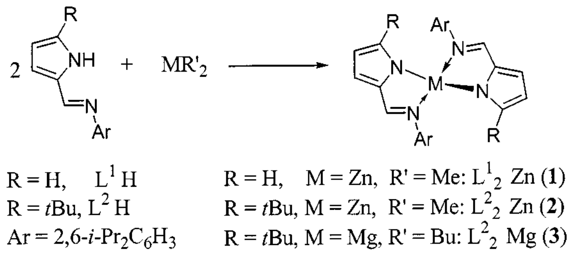
Synthesis and Spectroscopic Characterization of Compounds 1−9

Initially we attempted to prepare monoalkyl zinc and magnesium compounds, since there are plenty of monoalkyl zinc or magnesium compounds known that contain much less bulky amide groups,[6] and which are important precursors for various transformations.[5,7] However, the reaction of L^{1}H or L^{2}H with one equivalent of ZnMe$_2$ or MgnBu$_2$ in toluene or n-hexane resulted in the formation of the bis(pyrrolylaldiminato) compounds **1**−**3** (Scheme 2).

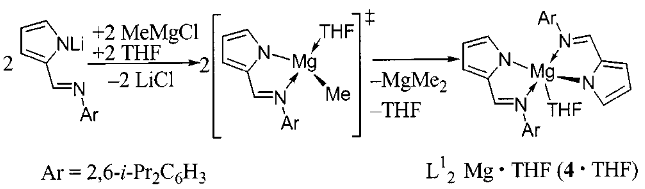
---

[a] Institut für Anorganische Chemie der Universität Göttingen,
Tammannstrasse 4, 37077 Göttingen, Germany
Fax: (internat.) + 49-(0)551/393-373
E-mail: hroesky@gwdg.de

Darensbourg et al. have reported the preparation of mono(salicylaldiminato)methyl zinc compounds;[5] under similar conditions we were not able to isolate any mono(pyrrolylaldiminato) species. We attributed this failure to prepare methylzinc or -magnesium species to the stronger acidity of the pyrrole proton relative to that of the amine hydrogen, and the enhanced basicity of methyl in the monoalkyl intermediate relative to that in MR_2.[8−10] Attempts to prepare the methylmagnesium compounds from the reaction of LiL^1 with MeMgCl afforded the compound MgL^1_2·THF (**4**·THF), which is presumably derived from the dismutation of transient $[L^1MgMe]^{\ddagger}$ to **4**·THF and $MgMe_2$ (Scheme 3), even though we were not able to isolate $MgMe_2$ from this reaction. Furthermore, compounds **1−4** do not react with $ZnMe_2$ or $MgMe_2$ in conventional solvents such as toluene or diethyl ether.



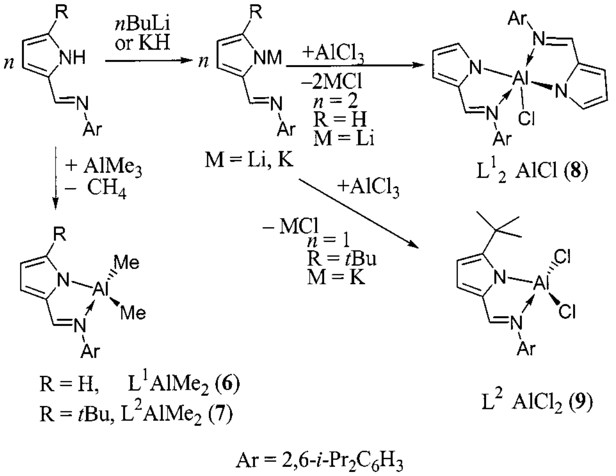
Scheme 2



Scheme 3

The reaction of KL^2 with MeMgCl, after workup and keeping the solution at room temperature for 24 h, provided a small amount of fine colorless crystals. Although the amount of product isolated was too low to calculate the yield, it was sufficient for microanalysis. The EI-MS, ^1H NMR spectrum and X-ray structural analysis revealed that this compound is the methoxy-bridged dimer $(L^2Mg)_2(\mu\text{-}OMe)_2$ (**5**). The reaction was repeated twice. In the ^1H NMR spectrum, the hydrogen resonance of the methoxy group appears at $\delta = 3.58$ as a singlet. The elemental analysis is also in good agreement with this formula. Since we were not able to detect any mono(pyrrolylaldiminato)methylmagnesium in the products, we suppose that this compound is derived from the inadvertent presence of MeOMgCl in the Grignard reagent, or perhaps from small amounts of water present in the solvents. Exposure of **5** to air resulted in an unidentifiable amorphous powder. Due to the potential uses of mono(alkyloxy)magnesium species as catalysts for the ring-opening polymerization of lactides,[11] we tried to prepare **5** in high yield from the reaction of $MgMe_2$ with one equivalent of methanol, followed by reaction with L^2H. This led to a mixture containing L^2H, **3**, and **5** as indicated by EI-MS. Attempts to synthesize **5** from a one-pot reaction of MeMgCl with one equivalent of methanol followed by reaction with LiL^2, or from the metathesis reaction of **3** with $Mg(OMe)_2$, were also unsuccessful.

The reaction of L^1H and L^2H with $AlMe_3$ provided the corresponding dimethylaluminum complexes **6** and **7**, which apparently have a four-coordinate tetrahedral geometry around the Al atoms (Scheme 4), while the reaction of LiL^1 with one equivalent of $AlCl_3$ in THF provided the five-coordinate L^1_2AlCl (**8**) instead of the expected mono(pyrrolylaldiminato) aluminum dichloride L^1AlCl_2. However, treatment of KL^2 with $AlCl_3$ in diethyl ether followed by evaporation resulted in a brown-purple product. After extraction with toluene and recrystallization from diethyl ether, pale yellowish microcrystals were isolated in relatively low yield; they were subsequently characterized as L^2AlCl_2 (**9**). The reaction of **6** or **7** with bromine or iodine led to unidentifiable products.



Scheme 4

Compounds **1−9** were fully characterized by EI-MS, ^1H NMR spectroscopy and elemental analysis. The EI-MS showed the molecular ion peaks in all cases. In the ^1H NMR spectra, the resonances for the methyl groups of the isopropyl substituents in **2**, **3**, and **8** appeared as four distinguishable doublets, while for the remaining compounds only two doublets were observed. These observations indicate that in **2**, **3**, and **8** the metals have more congested environments than the others in the series due to the *t*Bu substituents in **2** and **3** and the higher coordination number in **8**. Similar to the salicylaldiminato zinc complexes,[12] compounds **1−3** are chiral complexes with only C_2 symmetry; the other enantiomer is also formed in the product. Since the molecules have only C_2 symmetry, the isopropyl methyl groups of **1** display two sets of doublets even when rotation about the $N-C_{(phenyl)}$ bond is rapid at room temperature. In compounds **2** and **3**, the methyl groups of the isopropyl substituents display four sets of doublets due to the steric influence of the *t*Bu group causing a slow rotation about the $\mathrm{N-C_{(phenyl)}}$ bond on the NMR timescale. The ^{1}H NMR spectrum of the ligand in **4** resembles that of **1**, indicating that the coordinated THF has no observable influence on the rotation about the $\mathrm{N-C_{(phenyl)}}$ bond at room temperature.

X-ray Single Crystal Analysis for 2, 3, 5, and 8

Compounds **2** and **3** crystallize in a triclinic system, space group $P\bar{1}$. Their structures exhibit a distorted tetrahedral geometry around the metal center with four nitrogen atoms arranged at the vertices (Figure 1 and 2, respectively). In compound **2** the $\mathrm{Zn-N_{(pyrrole)}}$ (av. 2.00 Å) and $\mathrm{Zn-N_{(imine)}}$ (av. 2.06 Å) bonds are shorter than the Mg−N bonds in **3** (av. 2.05 Å and 2.11 Å, respectively) leading to a slightly wider angle formed by the bischelating nitrogens and the metal atom (av. 85.56° in **2** vs. av. 84.72° in **3**). The $\mathrm{Zn-N_{(imine)}}$ bond lengths are similar to those in bis(salicylaldiminato) zinc complexes (range 1.99−2.00 Å), while the $\mathrm{Zn-N_{(pyrrole)}}$ bond lengths (av. 2.00 Å) are slightly longer than the Zn−O bond lengths (range 1.91−1.95 Å) in bis(salicylaldiminato) zinc complexes.[5]

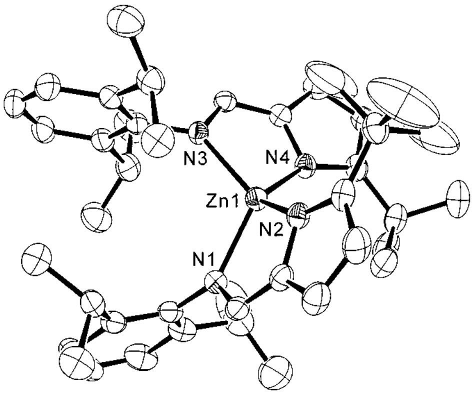


Figure 1. Molecular structure of **2** (hydrogen atoms are omitted for clarity)

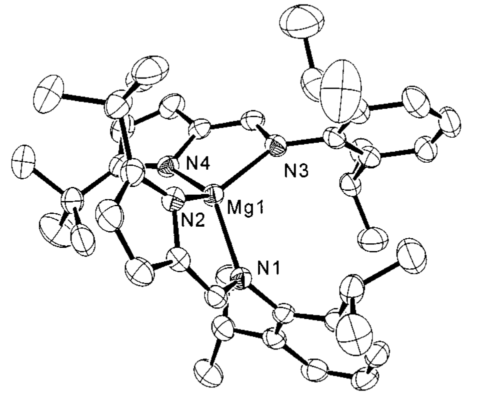


Figure 2. Molecular structure of **3** (hydrogen atoms are omitted for clarity)

Compound **5** is a centrosymmetric dimer with each magnesium atom having a tetrahedral geometry (Figure 3). The magnesium and oxygen atoms form a four-membered coplanar ring and there is a C_2 axis passing through the two Me−O bonds. The Mg−O−Mg−O ring is perpendicular to the Mg1−N1−N2 plane. The Mg−N bond lengths [Mg1−N2: 2.043(2) Å; Mg1−N1: 2.100(2) Å] are similar to those in **3**. The Mg−O bond lengths (av. 1.94 Å) are nearly the same as those in $[\mathrm{Mg(\mu\text{-}OMe)\{\eta^{2}\text{-}(\mathit{i}Pr_{2})ATI\}}]_2$ (av. 1.94 Å, ATI = *N*,*N′*-diisopropylaminotroponiminate).[13]

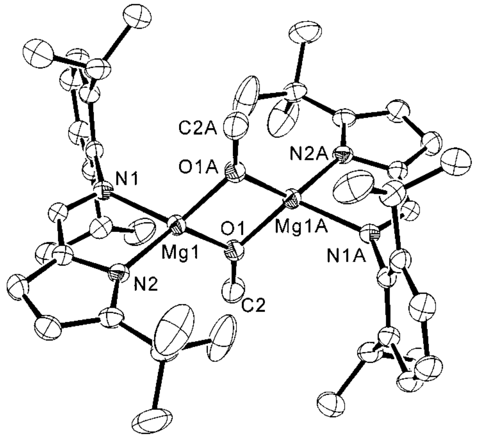


Figure 3. Molecular structure of **5** (hydrogen atoms are omitted for clarity)

The molecular structure of **8** (Figure 4) is best described as a distorted trigonal bipyramidal geometry around the aluminum atom with the N2 and N2A atoms located at the top of the vertex [N2−Al1−N2A: 165.16(8)°], and the chlorine atom, N1 and N1A atoms arranged at the equatorial positions (the Al1, Cl1, N1 and N1A atoms are essentially coplanar). There is a C_2 axis passing through the Al−Cl bond. The average $\mathrm{Al-N_{(imino)}}$ bond length is 1.993 Å, slightly longer than those found in salicylaldiminato aluminum complexes (range 1.94−1.98 Å).[14,15] The $\mathrm{Al-N_{(pyrrole)}}$ bond length (av. 1.96 Å) is slightly longer than that (av. 1.90 Å) in the recently reported compound $\mathrm{AlCl_2\{C_4H_3N(CH_2NMe_2)\text{-}2\}}$ (**A**),[16] while the Al−Cl bond length [2.1582(8) Å] is slightly shorter than that in **A**. This can be attributed to a partial conjugation between the imine C and N atoms and the aromatic pyrrole ring.

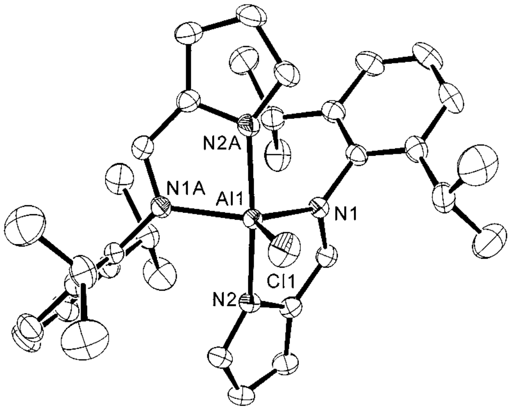


Figure 4. Molecular structure of **8** (hydrogen atoms are omitted for clarity)

The N−M−N angles associated with the bite of the pyrrolylaldiminato ligand in **2**, **5** and **8** (range 84−86° for Zn, 81.57(5)° for Al), are evidently more acute than the corresponding O−M−N angles in salicylaldiminato zinc[12] and aluminum[14,15] compounds (range 95−100° for Zn and 93−98° for Al). The M−N bond lengths (av. 2.00 Å for Zn in **2**, av. 1.96 Å for Al in **8**) are longer than the M−O distances (range 1.87−1.96 Å for Zn,[5,12] and 1.75−1.78 Å for Al[14,15] in salicylaldiminato complexes).

Conclusion

In summary, we have synthesized a series of pyrrolylaldiminato compounds of Zn, Mg, and Al. The structural investigations illustrate that the substituents at the 5-position of the pyrrole significantly enhance the steric demand. The variability of the steric properties of pyrrolylaldiminato ligands enhances the potential of these systems for catalytic processes.

Experimental Section

General Remarks: All experiments were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. Aluminum trichloride, trimethyl aluminum, di-*n*-butylmagnesium, methylmagnesium chloride and bromide, and dimethylzinc were purchased commercially. LiL^1 and LiL^2 were prepared according to the literature method.[1] KL^2 was prepared by the reaction of L^2H with KH in THF followed by filtration, evaporation in vacuo, and washing with *n*-hexane, and was used without further characterization. ^1H NMR spectra were recorded on Bruker AS-250 or Bruker AM-200 spectrometers. IR spectra were recorded on a Bio-Rad FTS-7 spectrometer as nujol mulls between KBr plates. EI-mass spectra were obtained on a Finnigan MAT8230 or a Varian MAT CH5 spectrometer.

ZnL^1_2 (1): A solution of L^1H (0.50 g, 2.0 mmol) in *n*-hexane (20 mL) was added to a solution of $ZnMe_2$ (1.0 mL of a 2.0 M solution in toluene, 2.0 mmol) diluted with *n*-hexane (20 mL) at −78 °C. After the addition the mixture was warmed slowly to ambient temperature and was then stirred at room temperature for 36 h. The volatiles were removed in vacuo and the residue was recrystallized from a mixed solvent of toluene and *n*-hexane (10:1) at −32 °C to afford a white solid. Yield: 0.45 g (20% based on L^1H). M.p. 221−224 °C. ^1H NMR (200.131 MHz, C_6D_6): δ = 0.6 (d, *J* = 6.8 Hz, 12 H, $CHMe_2$), 1.06 (d, *J* = 6.8 Hz, 12 H, $CHMe_2$), 3.13 (sept, *J* = 6.8 Hz, 4 H, $CHMe_2$), 6.54 (dd, *J* = 3.6, 1.7 Hz, 2 H, pyrrole), 6.83 (dd, *J* = 3.6, 1.0 Hz, 2 H, pyrrole), 6.85−7.10 (m, 8 H, aryl and pyrrole), 7.12 (d, *J* = 1.0 Hz, 2 H, pyrrole), 7.49 (d, *J* = 1.0 Hz, 2 H, N=C*H*). EI-MS: *m*/*z* (%) = 570 (100) [M^+]. $C_{34}H_{42}N_4Zn$ (572.11): calcd. C 71.38, H 7.44, N 9.79; found C 71.20, H 7.44, N 9.94.

ZnL^2_2 (2): A solution of L^2H (1.0 g, 3.2 mmol) in toluene (20 mL) was added to an excess of $ZnMe_2$ (2 mL of a 2.0 M solution in toluene, 4.0 mmol) diluted with toluene (20 mL) at −78 °C with stirring. The solution was warmed slowly to ambient temperature and stirred at room temperature for 16 h. After removal of all volatiles the residue was extracted with 10 mL of hot *n*-hexane. Colorless crystals formed while cooling the hot extract slowly to ambient temperature. Yield: 0.73 g (33% based on L^2H). M.p. 228−250 °C. ^1H NMR (200.13 MHz, C_6D_6): δ = 0.25 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 0.97 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.05 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.12 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.33 (s, 18 H, *t*Bu), 2.78 (sept, 2 H, *J* = 6.8 Hz, $CHMe_2$), 3.76 (sept, 2 H, *J* = 6.8 Hz, $CHMe_2$), 6.50 (d, *J* = 3.8 Hz, 2 H, pyrrole), 7.00−7.18 (m, 8 H, aryl, pyrrole), 7.47 (s, 2 H, N=C*H*). EI-MS: *m*/*z* (%) = 682 (100) [M^+]. $C_{42}H_{58}N_4Zn$ (684.29): calcd. C 73.72, H 8.54, N 8.19; found C 73.76, H 8.43, N 8.21.

MgL^2_2 (3): A solution of L^2H (0.93 g, 3.0 mmol) in *n*-hexane (30 mL) was added to an excess of $MgnBu_2$ (3.0 mL of a 1.0 M solution in toluene, 3.0 mmol) diluted with *n*-hexane (20 mL) at −78 °C whilst stirring. The solution was warmed slowly to ambient temperature and stirred at room temperature for 16 h. After filtration and washing the precipitate with *n*-hexane (20 mL), the combined filtrate was concentrated and stored at 0 °C in the refrigerator for 24 h to afford colorless crystals suitable for X-ray structural analysis. Yield: 0.58 g (30% based on L^2H). M.p. 240−242 °C. ^1H NMR (200.13 MHz, C_6D_6): δ = 0.28 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.01 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.08 (d, *J* = 6.9 Hz, 6 H, $CHMe_2$), 1.18 (d, *J* = 6.8 Hz, 6 H, $CHMe_2$), 1.33 (s, 18 H, *t*Bu), 2.81 (sept, 2 H, *J* = 6.8 Hz, $CHMe_2$), 3.57 (sept, 2 H, *J* = 6.9 Hz, $CHMe_2$), 6.45 (d, *J* = 3.6 Hz, 2 H, pyrrole), 6.88 (d, *J* = 3.6 Hz, 2 H, pyrrole), 6.90−7.00 (m, 8 H, aryl, pyrrole), 7.53 (s, 2 H, N=C*H*). EI-MS: *m*/*z* (%) = 642 (100) [M^+], 627 (50) [M^+ − Me]. $C_{42}H_{58}MgN_4$ (643.23): calcd. C 78.42, H 9.09, N 8.71; found C 78.34, H 9.11, N 8.69.

MgL^1_2·THF (4·THF): MeMgCl (0.67 mL of a 1.0 M solution in THF, 2.0 mmol) was added dropwise to a suspension of LiL^1 (0.50 g, 2.0 mmol) in THF (30 mL) at −78 °C. After the addition the mixture was warmed slowly to ambient temperature and stirred at room temperature for 16 h. The mixture was stripped of all volatiles and the residue was extracted with *n*-hexane (20 mL). The *n*-hexane extract was stored at 0 °C to afford colorless crystals. Yield: 0.35 g (29%). M.p. 208−210 °C. ^1H NMR (200.131 MHz, C_6D_6): δ = 1.03 (br, 4 H, THF), 1.15 (d, *J* = 6.9 H, $CHMe_2$), 1.18 (d, *J* = 6.9 Hz, 12 H, $CHMe_2$), 3.17 (sept, *J* = 6.9 Hz, 4 H, $CHMe_2$), 3.37 (br, 4 H, THF), 6.23 (d, *J* = 1.6 Hz, 2 H, pyrrole), 6.33 (dd, *J* = 3.4, 1.6 Hz, 2 H, pyrrole), 6.80 (dd, *J* = 3.4, 1.6 Hz, 2 H, pyrrole), 7.08−7.20 (m, 6 H, Aryl), 7.76 (d, *J* = 1.1 Hz, 2 H, C*H*=N). EI-MS: 530.2 (95) [M^+], 464.2 (100) [M^+ − 2Pr]. $C_{38}H_{50}MgN_4O$ (602.14, including one molecule of THF): calcd. C 75.67, H 8.66, N 9.29; found C 75.11, H 8.65, N 9.22.

$(L^2Mg)_2(\mu\text{-}OMe)_2$ (5): A solution of KL^2 (0.68 g, 2.0 mmol) in THF (20 mL) was added dropwise to a solution of MeMgCl (0.68 mL of a 3 M solution in THF, 2.0 mmol) in THF (20 mL) at −78 °C. After the addition it was warmed slowly to ambient temperature and stirred at room temperature for 16 h. After the removal of all volatiles, the residue was washed with *n*-hexane (20 mL) and extracted with toluene (40 mL). Colorless crystals of **5** formed on allowing the toluene solution to stand. The amount of **5** was small but sufficient for microanalysis. The reaction was repeated twice. M.p. 295−297 °C. ^1H NMR (200.131 MHz, C_6D_6): δ = 1.04 (d, *J* = 6.8 Hz, 12 H, $CHMe_2$), 1.18 (s, 18 H, *t*Bu), 1.20 (d, *J* = 6.8 Hz, 12 H, $CHMe_2$), 3.10 (sept, 4 H, $CHMe_2$), 3.58 (s, 6 H, OCH_3), 6.42 (d, *J* = 3.6 Hz, 2 H, pyrrole), 6.85 (d, *J* = 3.6 Hz, 2 H, pyrrole), 7.00−7.20 (m, 6 H, aryl), 7.63 (s, 2 H, N=C*H*). EI-MS: *m*/*z* (%) = 728 (100) [M^+]. $C_{44}H_{64}Mg_2N_4O_2$ (729.61): calcd. C 72.43, H 8.84, N 7.68; found C 71.97, H 8.79, N 7.53.

L^1AlMe_2 (6): A solution of L^1H (2.54 g, 10 mmol) and $AlMe_3$ (5.3 g of a 16% solution in *n*-hexane, 11 mmol) in toluene (40 mL) was refluxed for 4 h. The solution was then cooled to ambient temperature. Subsequently, all volatiles were removed in vacuo. The residue was recrystallized from *n*-hexane at −32 °C to afford colorless crystals. Yield: 1.77 g (57%). M.p. 83−85 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ = −0.77 (s, 6 H, Al*Me*$_2$), 1.01 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.11 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 3.01 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 6.39 (d, *J* = 3.6 Hz, 1 H, pyrrole), 6.92 (dd, *J* = 3.6 Hz, 1 H, pyrrole), 7.05−7.20 (m, 4 H, Aryl), 7.26 (m, 1 H, pyrrole-*H*), 7.76 (d, *J* = 1.1 Hz, 1 H, N=C*H*). EI-MS: *m*/*z* (%) = 310 (0.1) [M$^+$], 295 (100) [M$^+$ − Me].

L^{2}AlMe$_2$ (7): A solution of L^{2}H (6.2 g, 20 mmol) in *n*-hexane (50 mL) was added dropwise to a solution of AlMe$_3$ (12 g of a 15% solution in *n*-hexane, 25 mmol) in *n*-hexane (50 mL). After the addition the resulting solution was warmed slowly to ambient temperature and stirred at room temperature for 16 h. After the removal of all volatiles the residue was extracted with *n*-hexane (20 mL). Cooling the extract to −32 °C for 16 h afforded colorless crystals. Yield: 6.3 g (86%). M.p. 117−119 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ = −0.23 (s, 6 H, Al*Me*$_2$), 0.92 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.15 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.35 (s, 9 H, *t*Bu), 3.20 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 6.34 (d, *J* = 3.8 Hz, 1 H, pyrrole), 6.78 (d, *J* = 3.8 Hz, 1 H, pyrrole), 7.00−7.18 (m, 4 H, aryl, pyrrole), 7.44 (s, 1 H, N=C*H*). EI-MS: *m*/*z* (%) = 366 (20) [M$^+$], 351 (100) [M$^+$ − Me]. $C_{23}H_{35}AlN_2$ (366.52): calcd. C 75.37, H 9.62, N 7.64; found C 75.38, H 9.67, N 7.56.

L$^1_2$AlCl (8): A solution of LiL^1 (1.3 g, 5.0 mmol) in THF (20 mL) was added dropwise to a solution of AlCl$_3$ (0.67 g, 5.0 mmol) in THF (20 mL) at −78 °C. After complete addition the resulting solution was warmed slowly to ambient temperature and stirred at room temperature for 16 h. After removal of all volatiles the residue was extracted with toluene (20 mL). Cooling the extract to −32 °C for 20 h afforded yellow crystals. Yield: 2.36 g (83% based on the ligand). M.p. 190−213 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.72 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 0.96 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.01 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.42 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 2.89 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 3.67 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 6.01 (dd, *J* = 3.7 Hz, 2 H, pyrrole), 6.16 (m, 2 H, pyrrole), 6.57 (dd, *J* = 3.7 Hz, 2 H, pyrrole), 6.85−7.10 (m, 12 H, Ar−*H*), 7.53 (d, *J* = 1.16 Hz, 2 H, N=C*H*). MS: *m*/*z* (%) = 568 (100) [M$^+$]. $C_{34}H_{42}AlClN_4$ (569.15): calcd. C 71.75, H 7.74, N 9.84; found C 72.05, H 7.63, N 9.90.

L^{2}AlCl$_2$ (9): A suspension of KL^2 (5.70 g, 16.0 mmol) in THF (20 mL) was added to a solution of AlCl$_3$ (2.13 g, 16.0 mmol) in THF (20 mL) at −90 °C whilst stirring. The resulting solution was warmed slowly to ambient temperature and was stirred at room temperature for 16 h. After the removal of all volatiles the residue was extracted with diethyl ether and the extract was stored at −32 °C to afford pale white microcrystals. Yield: 2.54 g (39%). M.p. 187−190 °C. ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.89 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.27 (d, *J* = 6.8 Hz, 6 H, CH*Me*$_2$), 1.35 (s, 9 H, *t*Bu), 3.40 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 6.19 (d, *J* = 3.9 Hz, 1 H, pyrrole), 6.61 (d, *J* = 3.9 Hz, 1 H, pyrrole), 6.95−7.15 (m, 6 H, Ar−H), 7.27 (s, 1 H, N=C*H*). MS: *m*/*z* (%) = 406 (100) [M$^+$]. $C_{21}H_{29}AlCl_2N_2$ (407.36): calcd. C 61.92, H 7.18, N 6.88; found C 61.20, H 7.21, N 6.41.

X-ray Crystallographic Study: Single crystals of **2**, **3**, **5**, and **8** were taken from the flask under nitrogen gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether.[17] Diffraction data for **2**, **3**, and **8** were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K while those for **5** were collected on a Stoe two-circle diffractometer at 133(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-96 for **2**, **3**, and **8**; SHELXS-97 for **5**)[18] and refined against F^2 using SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically with similarity and rigid-bond restraints. All hydrogen atoms were included in the refinement in their geometrically ideal positions. Crystallographic data for **2**, **3**, **5**, and **8** are given in Table 1 and selected bond lengths and angles in Table 2.

CCDC-171433 (**2**), CCDC-171434 (**3**), CCDC-171435 (**5**) and CCDC-171436 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for compounds **2**, **3**, **5**, and **8**

	2	**3**	**5**	**8**
Empirical formula	$C_{42}H_{58}N_4Zn$	$C_{42}H_{58}MgN_4$	$C_{44}H_{64}Mg_2N_4O_2$	$C_{34}H_{42}AlClN_4$
Molecular weight	684.29	643.23	729.61	569.15
Temperature	200(2) K	200(2) K	133(2) K	203(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	triclinic	triclinic	monoclinic
Z	2	2	1	4
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions	a = 10.295(3) Å	a = 10.335(2) Å	a = 9.0932(10) Å	a = 20.284(4) Å
	b = 10.464(3) Å	b = 10.455(2) Å	b = 10.3835(10) Å	b = 9.8282(11) Å
	c = 19.861(6) Å	c = 20.080(4) Å	c = 12.9191(13) Å	c = 16.174(3) Å
	α= 75.56(3)°	α = 75.27(3)°	α = 109.864(8)°	
	β= 6.700(19)°	β = 86.82(3)°	β = 103.762(8)°	β = 99.89(2)°
	γ = 8.115(12)°	γ = 67.87(3)°	γ = 94.294(9)°	
Volume	1921.1(10) Å^3	1941.9(7) Å^3	1097.99(19) Å^3	3176.4(8) Å^3
Density (calculated)	1.183 Mg/m^3	1.100 Mg/m^3	1.103 Mg/m^3	1.190 Mg/m^3
Absorption coefficient	0.672 mm^{-1}	0.079 mm^{-1}	0.093 mm^{-1}	0.177 mm^{-1}
Final *R* indices	$R1$ = 0.0391	$R1$ = 0.0397	$R1$ = 0.0477	$R1$ = 0.0329
$[I > 2\sigma(I)]$	$wR2$ = 0.0895	$wR2$ = 0.1012	$wR2$ = 0.1365	$wR2$ = 0.0820
R indices	$R1$ = 0.0445	$R1$ = 0.0452	$R1$ = 0.0559	$R1$ = 0.0362
(all data)	$wR2$ = 0.0939	$wR2$ = 0.1059	$wR2$ = 0.1413	$wR2$ = 0.0870

Table 2. Selected bond lengths (Å) and bond angles (deg) for complexes **2**, **3**, **5**, and **8**

Compound **2**			
Zn1−N1	2.0683(18)	N1−Zn1−N4	132.73(7)
Zn1−N2	1.9956(19)	N2−Zn1−N3	129.19(7)
Zn1−N3	2.0548(19)	N2−Zn1−N4	116.62(7)
Zn1−N4	1.9985(19)	N3−Zn1−N1	134.62(14)
N1−Zn1−N2	85.75(8)	N3−Zn1−N4	85.26(7)
Compound **3**			
Mg1−N1	2.1005(13)	N4−Mg1−N1	131.06(5)
Mg1−N2	2.0525(12)	N2−Mg1−N1	84.49(6)
Mg1−N3	2.1154(13)	N4−Mg1−N3	84.95(5)
Mg1−N4	2.0476(13)	N4−Mg1−N2	134.00(5)
N4−Mg1−N2	116.87(5)	N4−Mg1−N3	112.14(5)
Compound **5**			
Mg1−O1A	1.938(1)	O1A−Mg1−N2	129.97(6)
Mg1−O1	1.940(1)	O1−Mg1−N2	125.69(6)
Mg1−N2	2.043(2)	O1A−Mg1−N1	118.15(6)
Mg1−N1	2.100(2)	O1−Mg1−N1	118.11(6)
O1−Mg1−O1A	84.95(5)	N2−Mg1−N1	83.99(6)
Compound **8**			
Al1−N1	1.9931(11)	N2−Al1−N1	81.57(5)
Al1−N2	1.9615(12)	N1A−Al1−N1	127.01(7)
Al1−Cl1	2.1582(8)	N2A−Al1−Cl1	97.42(4)
N2−Al1−N2A	165.16(8)	N2A−Al1−Cl1	97.42(4)
N2A−Al1−N1A	81.57(5)	N1A−Al1−Cl1	116.50(4)
N2−Al1−N1A	91.80(5)	N1−Al1−Cl1	116.50(4)
N2A−Al1−N1	91.80(5)		

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. SB thanks the Alexander von Humboldt Foundation for a fellowship.

---

[1] D. M. Dawson, D. A. Walker, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* **2000**, 459−466.
[2] V. C. Gibson, P. J. Maddox, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 1651−1652.
[3] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847−6856.
[4] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460−462.
[5] D. J. Darensbourg, P. Rainey, J. Yarbrough, *Inorg. Chem.* **2001**, *40*, 986−993.
[6] M. Westerhausen, T. Bollwein, A. Pfizner, T. Nilges, H.-J. Deiseroth, *Inorg. Chim. Acta* **2001**, *312*, 239−244.
[7] M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019.
[8] M. Westerhausen, T. Bollwein, N. Makropoulos, T. M. Rotter, T. Habereder, M. Suter, H. Nöth, *Eur. J. Inorg. Chem.* **2001**, 851−857.
[9] M. M. Olmstead, W. J. Grigsby, D. R. Chacon, T. Hascall, P. P. Power, *Inorg. Chim. Acta* **1996**, *251*, 273−284.
[10] V. R. Magnuson, G. D. Stucky, *Inorg. Chem.* **1969**, *8*, 1427−1433.
[11] M. H. Chisholm, J. C. Huffman, K. Phomphrai, *J. Chem. Soc., Dalton Trans.* **2001**, 222−224.
[12] M. H. Chisholm, J. C. Gallucci, H. Zheng, J. C. Huffman, *Inorg. Chem.* **2001**, *40*, 5051−5054.
[13] P. J. Bailey, C. M. E. Dick, S. Fabre, S. Parsons, *J. Chem. Soc., Dalton Trans.* **2000**, 1655−1661.
[14] M. S. Hill, A. R. Hutchison, T. S. Keizer, S. Parkin, M. A. VanAelstyn, D. A. Atwood, *J. Organomet. Chem.* **2001**, *628*, 71−75.
[15] P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 1472−1476.
[16] J.-H. Huang, H.-J. Chen, J.-C. Chang, C.-C. Zhou, G.-H. Lee, S.-M. Peng, *Organometallics* **2001**, *20*, 2647−2650.
[17] T. Kottke, D. Stalke, *J. Appl. Crystalogr.* **1993**, *26*, 615−619.
[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[19] G. M. Sheldrick, SHELXL 97; University of Göttingen, Göttingen, Germany, **1997**.

Received October 31, 2001
[I01408]