Divergent coordination mode of magnesium and zinc alkyls supported by the bifunctional pyrrolylaldiminato ligand

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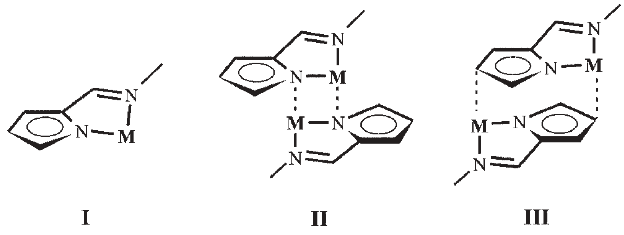
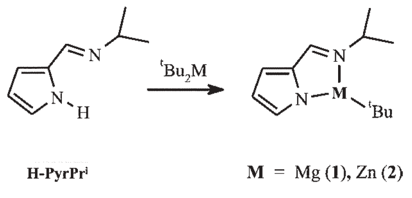
The first magnesium and zinc alkyls derived from *N*-(iso-propyl)-pyrrolylaldimine have been synthesised and structurally characterised: both ^{t}BuM(*N*,*N*′)-type compounds exist as three-coordinate monomers in benzene solution, but in the solid state the magnesium complex is a centrosymmetric dimer with Mg$_2$(μ-N)$_2$ bridges, whereas the zinc complex is a Zn···π bonded dimer with a π-coordinated pyrrole unit.

Over recent years the exploitation of magnesium and zinc complexes supported by β-diketiminato,[1,2] and troponiminato[3] ligand systems has provided a number of spectacular results. For example, it allowed for the isolation and structural characterization of a number of low-coordinate metal alkyl complexes RM(*N*,*N*) and their adducts with donor ligands, and the four-coordinate magnesium alkyl-bridged dimers (*N*,*N*)Mg(μ-R)$_2$Mg(*N*,*N*). This group of complexes has also been used successfully in the oxygenation reaction providing the first examples of structurally authenticated magnesium and zinc alkylperoxides.[1c,4] Moreover, the corresponding alkoxides and carboxylates have found application in the ring-opening polymerization of cyclic esters[2d,5] and in the copolymerization of epoxides and carbon dioxide.[6] Surprisingly, the coordination chemistry of magnesium and zinc with other types of monoanionic nitrogen–nitrogen chelate systems remains relatively poorly explored.[7]

As part of ongoing structure/reactivity studies involving the RZn(*X*,*Y*) chelate complexes,[8] we have started to examine the solid state and solution structures of alkylzinc and alkylmagnesium *N*,*N*′-chelate complexes based on pyrrolyl ligands. We turned our attention to the bifunctional pyrrolylaldiminato ligands, anticipating that a combination of pyrrole and Schiff base type ligands may provide spectacular results. Additionally, the choice of our target complexes was dictated by the fact that the chemistry of main group metal complexes with bidentate pyrrolylaldiminato ligands remains relatively poorly explored. For instance, the first attempts to prepare low-alkyl zinc complexes incorporating pyrrolylaldiminato ligands were unsuccessful and resulted in the formation of bis(pyrrolylaldiminato) compounds with the ligand η^2-coordination mode **I** (Scheme 1).[9] It is also pertinent to note that pyrrolyl-2-yl Schiff bases in combination with Zn(II) ions have appeared an interesting building block for supramolecular architecture through self-assembly.[10] On the other hand, the anionic chelating pyrrolylaldiminato ligands have widely been employed in transition metal chemistry. A search of the Cambridge Structural Database[11] reveals over a hundred published crystal structures, in which pyrrolylaldiminato ligands act as bidentate four-electron donors through the formation of two metal–nitrogen σ-bonds. The observed η^2-coordination for this type of ligand is in strong contrast to the versatile coordination modes exhibited by monofunctional pyrroles.[12] We report here the first structurally authenticated magnesium and zinc alkyls based on a bifunctional pyrrolylaldiminato ligand which exhibits novel diversity of bonding modes of type **II** and **III** in the solid state (Scheme 1).



Scheme 1



Scheme 2

The reaction of the corresponding ^{t}Bu$_2$M reagent with 1 eq. of *N*-(iso-propyl)-pyrrolylaldimine (H-PyrPr^i) in toluene solution allows for the isolation of the target alkyl complexes ^{t}BuMg(PyrPr^i) (**1**) and ^{t}BuZn(PyrPr^i) (**2**) almost quantitatively (Scheme 2).† The ^{1}H NMR spectra of **1** and **2** in a d$_6$-benzene solution are very similar and exhibit single sharp resonances of the M–^{t}Bu protons and the imine proton, and multiplets of the pyrrole protons. Cryoscopic molecular weight determinations showed that both compounds are monomeric in benzene solution. While this observation is not surprising for the zinc complex, to our knowledge **1** represents the first example of a monomeric three-coordinate alkylmagnesium compound supported by a bidentate ligand deprived of steric hindrances. Up to now, the reported low-coordinate RMg(*N*,*N*) complexes were only observed for the mentioned sterically demanding β-diketiminate derivatives.[1b,d–e] Thus, for **1** the solvation provided by benzene is strong enough to

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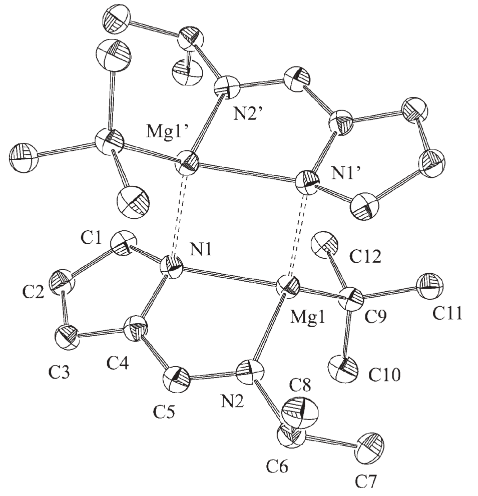

Fig. 1 ORTEP diagram of [^{t}BuMg(PyrPr^i)]$_2$ (**1**) with thermal ellipsoids drawn at the 40% probability level. Atoms labelled with a prime belong to the centrosymmetric counterparts of the dimeric unit ($-x$, $-y$, $1 - z$).

override the σ-N donor interaction observed in the solid state (*vide infra*).[13]

In the solid state, the molecular structures of **1** and **2** were determined by X-ray diffraction techniques.‡ The X-ray studies were carried out in order to determine the degree of aggregation, the presence or absence of intermolecular non-covalent interactions, and other pertinent structural details. The crystal structure of **1** comprises individual four-coordinate dimeric molecules with no unusually short intermolecular contacts (Fig. 1).

Compound **1** is a centrosymmetric dimer with $Mg_2(\mu\text{-}N)_2$ bridges formed by the pyrrole nitrogen and with each magnesium having a distorted tetrahedral geometry. The bridging mode of the pyrrolide anion leads to slight pyramidalization of the nitrogen atom and the formation of unsymmetrical Mg–N–Mg bridges with bond lengths Mg(1)–N(1) of 2.156(2) Å and Mg(1)′–N(1) of 2.204(2) Å. The shortest Mg–N bond is to the imine nitrogen atom (2.140(2) Å). The pyrrole-imine chelation results in the formation of a five-membered ring with the Mg atom displaced 0.414(1) Å out from the almost flat chelate plane. The fused chelate and pyrrole ring systems are not coplanar, with the imine arm slightly twisted away along the C(4)–C(5) vector from the pyrrole ring. Pyrrole nitrogen–carbon bond lengths are equal to 1.376(3) Å and 1.401(3) Å, and the C–C bond lengths within the pyrrole ring fall in the narrow range 1.366–1.399 Å, while the C(4)–C(5) bond is slightly longer (1.420(3) Å). This is consistent with the delocalization of the pyrrole π system and a weak conjugation with the imine group. The imine nitrogen–carbon bond length is observed to be 1.297(3) Å. The Mg–C bond length is 2.129(2) Å. Thus, the revealed molecular structure for **1** represents the first example of μ,η^2-coordination exhibited by a bifunctional pyrrolylaldiminato ligand.

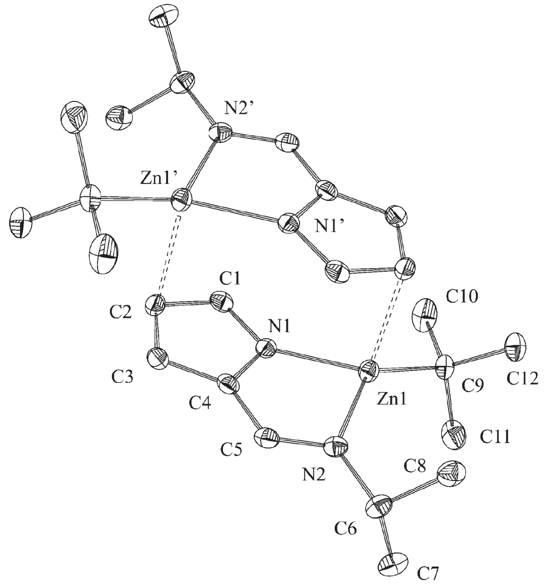

Fig. 2 ORTEP diagram of [^{t}BuZn(PyrPr^i)]$_2$ (**2**) with thermal ellipsoids drawn at the 40% probability level. Atoms labelled with a prime belong to the centrosymmetric counterparts of dimeric unit ($1 - x$, $-y$, $1 - z$).

The molecular structure of compound **2** is shown in Fig. 2. The monomeric species consists of the three-coordinate zinc atom chelated by the pyrrole-imine ligand. Unlike for **1**, the five-membered ring formed by the pyrrolylaldiminato ligand with the metal centre and the pyrrole ring is coplanar. The Zn-bonded *tert*-butyl substituent is placed above this plane with the dihedral C(9)–Zn(1)–N(1)–N(2) angle being 157.65°. In this case the $Zn\text{–}N_{pyrrole}$ bond (1.996(2) Å) is slightly shorter than the $Zn\text{–}N_{imine}$ bond (2.089(2) Å). A markedly distorted tetrahedral geometry around the zinc centre with associated the intermolecular Zn–C distances of 2.715(3) Å between the coordinatively unsaturated metal centres and the C(2) carbon atoms of the pyrrole ring from the adjacent monomeric molecule clearly reflects the formation of the Zn···π bonded dimer. The intermolecular Zn–C distances involving the C(3) and C(1) carbon atoms are significantly longer, 3.070(3) Å and 3.149(4) Å, respectively. Thus, the zinc atoms interact with the adjacent molecule mainly by the aromatic π orbital at the C(2) carbons, indicating in this case a certain tendency of the pyrrole ligand towards an intermolecular η^1-bonding mode. Therefore, the coordination mode of pyrrole ligand in **2** may be described as an η^2-σ-N donor to one zinc atom and a η^1-π-donor to the other zinc atom. The pyrrole N–C bond lengths are equal to 1.356(4) Å and 1.370(4) Å, the C–C bond lengths between carbons 1 and 2 as well as 3 and 4 are slightly longer, 1.394(4) Å and 1.386(4) Å, while the C–C bond between carbons 2 and 3 is the longest, 1.400(4) Å. The imine group is attached to the C(4) carbon with a C(4)–C(5) bond length of 1.434(3) Å and the imine nitrogen–carbon bond length of 1.286(4) Å. The Zn–C bond length is 1.990(3) Å. Furthermore, when one looks at the molecular structure of **1** and **2** presented in Fig. 1 and 2, an association is imposed such that both compounds may be regarded as slided isomers in the solid state where the metal centres in the monomeric three-coordinate species slide over the pyrrole π system; the relatively soft low-coordinate zinc centre favours a bonding interaction to the pyrrole π system, while the analogous magnesium centre prefers σ-N bonding to the pyrrole ring.

In conclusion, the observed tendency of magnesium and zinc alkyl derivatives of *N*-(iso-propyl)-pyrrolylaldimine to form three-coordinate RM(*N*,*N*′) chelate complexes in solution indicates that pyrrolyl-2-yl Schiff bases act as relatively strongly coordinating chelate ligands. The results also demonstrate that the bifunctional pyrrolylaldiminato type ligands exhibit diversity of bonding in the solid state which could provide useful tools in the field of molecular design. Further studies on the identification and characterization of weak interactions as well as factors controlling structure and reactivity of main group metal complexes supported by multifunctional pyrrolylaldiminato ligands are in progress.

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Notes and references

† General experimental procedure: All operations were carried out under dry nitrogen using standard Schlenk techniques. $^{t}Bu_2Mg$[12] and $^{t}Bu_2Zn$[14] were synthesized according to the literature method. A representative synthesis of **1**: a solution of *N*-(iso-propyl)-pyrrolylaldimine (0.45 g, 3.31 mmol) in toluene (10 mL) was cooled to −78 °C, and $^{t}Bu_2Mg$ (3.0 mL of a 1.1 M solution in toluene, 3.31 mmol) was added dropwise. Then the reaction mixture was warmed to room temperature and stirred for 4 h. Compound **1** was obtained as yellow crystals after a recrystallization from toluene solution at −25 °C, yield 70%. Cryoscopic molecular weight (benzene solution): formula weight calcd for $C_{12}H_{20}N_2Mg$ 216.62, found 220. Anal. calcd for $C_{12}H_{20}N_2Mg$: C, 66.54; H, 9.31; N, 12.93. Found: C, 66.38; H, 9.63; N, 12.98. ^1H NMR (C_6D_6, 400 MHz): δ 0.93 (s, 9H, Mg–^{t}Bu), 1.28 (d, 6H, CH(CH_3)$_2$), 3.19 (br, 1H, C*H*(CH_3)$_2$), 6.61, 6.80, 7.36 (br, 3H, pyrrole), 7.54 (s, 1H, C*H*=N). The preparation of **2** (colorless crystals, yield 75%) was carried out in the same manner as described for **1**, using H-PyrPr^i (0.35, 2.57 mmol) and $^{t}Bu_2Zn$ (1.84 mL of a 1.4 M solution in toluene, 2.57 mmol). Cryoscopic molecular weight (benzene solution): formula weight calcd for $C_{12}H_{20}N_2Zn$ 257.68, found 253. Anal. calcd for $C_{12}H_{20}N_2Zn$: C, 55.94; H, 7.82; N, 10.87. Found: C, 55.63; H, 7.83; N, 10.92. ^1H NMR (C_6D_6, 400 MHz): δ 0.81 (s, 9H, Zn–^{t}Bu), 1.26 (d, 6H, CH(CH_3)$_2$, 3.08 (sept, 1H, C*H*(CH_3)$_2$), 6.62 (dd, 1H, pyrrole), 6.86 (d, 1H, pyrrole), 7.1 (d, 1H, pyrrole), 7.44 (s, 1H, C*H*=N).

‡ *Crystal data:* for **1**. $C_{24}H_{40}Mg_2N_4$, $M = 433.22$, triclinic, $a = 8.5297(7)$ Å, $b = 8.9152(8)$ Å, $c = 9.5123(9)$ Å, $\alpha = 88.853(5)°$, $\beta = 82.971(7)°$, $\gamma = 64.670(6)°$, $U = 648.47(10)$ Å^3, $Z = 1$, $F(000) = 236$, $D_c = 1.109$ g m^{-3}, $T = 100(2)$ K, space group $P\bar{1}$ (no. 2), μ(Mo-Kα) = 0.109 mm^{-1}, 3049 reflections measured, 1566 unique ($R_{int} = 0.036$) which were used in all calculations. The final w$R(F^2)$ was 0.1116. For **2**. $C_{12}H_{20}N_2Zn$, $M = 257.69$, monoclinic, $a = 12.8805(7)$ Å, $b = 8.8359(5)$ Å, $c = 11.8961(6)$ Å, $\beta = 107.715(3)°$, $U = 1289.71(12)$ Å^3, $Z = 4$, $F(000) = 544$, $D_c = 1.327$ g m^{-3}, $T = 100(2\ )$K, space group $P2_1/c$ (no. 14), μ(Mo-Kα) = 1.876 mm^{-1}, 3732 reflections measured, 2007 unique ($R_{int} = 0.026$) which were used in all calculations. The final w$R(F^2)$ was 0.0786. CCDC 277419 and 277420. See http://dx.doi.org/10.1039/b509669c for crystallographic data in CIF or other electronic format.

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