A New μ_4-Oxo Tetranuclear Magnesium Compound: Coordination Effects of the Azolato Ligands

Nadia C. Mösch-Zanetti,*[a] Marilena Ferbinteanu,[b] and Jörg Magull[a]

Keywords: N ligands / Magnesium / Coordination modes

The μ_4-oxo tetranuclear magnesium compound $[Mg_4(\mu_4\text{-oxo})(\mu\text{-tz})_6]$ **1** (tz = 3,5-*i*Pr_2-1,2,4-triazolato) with six η^1-η^1-bridging triazolato ligands was prepared in a one-step reaction between $MgBr_2$ and tzK. The solid state structure was determined by X-ray diffraction analysis showing the tetrahedral arrangement of the Mg_4O core. The reaction of $MgBr_2$ with pzK and pzH gave $[Mg(pz)_2(pzH)_2]$ **2** (pz = 3,5-*t*Bu_2-pyrazolato), which contains hydrogen bonds between two different ligands, as established by X-ray crystal structure analysis. In solution, compound **2** shows a dynamic behavior involving two different processes. Line shape analysis of variable temperature NMR experiments suggests that the interconversion occurs via an η^2-coordination of the pyrazolato ligand.

Introduction

The structural chemistry of magnesium amido and imido compounds is becoming an increasingly active area of research. The main reason for this recent interest is their use as reagents in numerous organic transformations.[1−7] Stimulated by the desire to elucidate the mechanisms of such reactions, several magnesium bisamido species have been structurally characterized as dimeric units of the type $[R_2NMg(\mu\text{-}NR_2)_2MgNR_2]$;[8−10] monomeric compounds are formed in the presence of sterically demanding amido ligands or additional donors.[11−14] However, polynuclear species with a higher magnesium atom count are still relatively limited. The rather unusual nitrogen-centered hexameric amido species $[Mg_6(\mu_6\text{-}N)(NH\textit{t}Bu)_9]$ was reported as early as 1980.[15] More than 10 years later, hexameric[16] and trimeric arrangements[17,18] were found with bifunctional amido ligands. With imido ligands, hexagonal prismatic structures of the type $[\{(THF)MgNR\}_6]$ (R = Ph, 1-naphthyl) have been reported.[19,20] In addition to these pure magnesium species a nice series[21,22] of mixed alkali metal magnesium compounds including oxide-captured examples such as $[Li_2Mg_2\{N(SiMe_3)_2\}_4(O_2)_x(O)_y]$[23] and $[K_2Mg_2[N(SiMe_3)_2]_4(O_2)\}_8]$[24] has been reported by Mulvey and co-workers. In addition to these amido species, the oxo-centered lithium magnesium cresylate cage $[LiMg_4OR_7\cdot 4THF]$ [R = *o*-$Me(C_6H_4)O^-$] has been reported.[25]

Pyrazolates and triazolates are known to be good bridging ligands for the synthesis of polynuclear complexes[26] and have proven to coordinate to magnesium in a μ_2-bridging mode[27,28] as well as an η^2-fashion[29] forming dimeric units. This prompted us to investigate whether these ligands are suitable for the construction of unusual polynuclear magnesium species. Herein, we present the synthesis and X-ray crystal structure determination of the μ_4-oxo tetranuclear magnesium compound $[Mg_4(\mu_4\text{-oxo})(\mu\text{-tz})_6]$ **1** (tz = 3,5-*i*Pr_2-1,2,4-triazolato) with six η^1-η^1-bridging triazolato ligands. Due to a structural pattern similar to those known for divalent transition metal ions, compound **1** is an appropriate model for the investigation of structural factors that are independent of the *d*-electron configuration. The second compound $[Mg(pz)_2(pzH)_2]$ **2** (pz = 3,5-*t*Bu_2-pyrazolato) employing a more sterically demanding pyrazolato ligand features both protonated and deprotonated ligands allowing an in-depth study of the coordination capabilities of these versatile ligands.

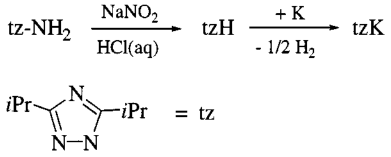
Results and Discussion

The general route for the synthesis of the triazole ligand starts from 4-NH_2-3,5-*i*Pr_2-1,2,4-triazole[30] (4-NH_2-tz) followed by diazotization to produce, after standard workup, tzH in high yield (Scheme 1). Sublimation under reduced pressure at 110 °C gave the analytically pure ligand. The analogous triazole ligand with *tert*-butyl substituents was not accessible since its higher steric demand prevents the formation of the heterocycle. The deprotonation of tzH was achieved with stoichiometric amounts of elemental potas-

---

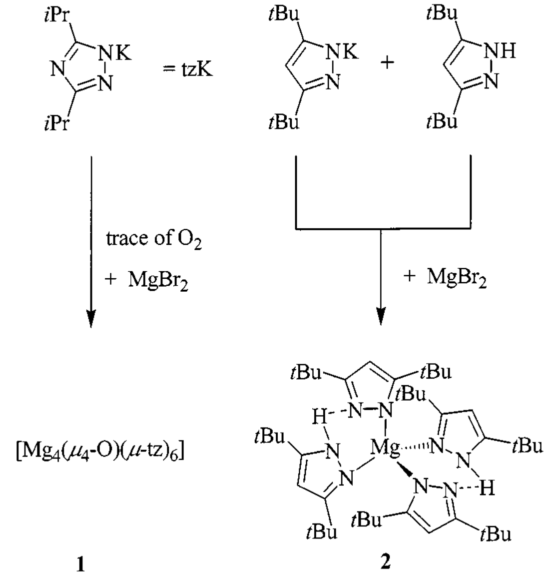
[a] Institut für Anorganische Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 4, 37077 Göttingen, Germany
Fax: (internat.) +49-0551/393-373
E-mail: nmoesch@gwdg.de
[b] University of Bucharest, Faculty of Chemistry, Inorg. Chem. Dept.,
Dumbrava Rosie 23, 70254 Bucharest, Romania

sium in refluxing THF. The white powders of tzK thus obtained were analytically pure and used without further purification. The potassium salt is slightly soluble in THF, readily soluble in acetonitrile and insoluble in hydrocarbon solvents. The ^{1}H NMR spectrum of the dried compound in CD_3CN shows no coordinated THF molecules.



Scheme 1

The reaction of magnesium bromide with two equivalents of tzK in THF at room temperature for 48 h afforded **1** in moderate yield (Scheme 2). The compound is only soluble in polar solvents such as THF, and can be separated from the finely dispersed KBr precipitate by centrifugation. Recrystallization from cold THF gave **1** as large colorless crystals. The NMR spectroscopic data in CD_3CN show signals for one kind of ligand coordinated in a symmetric fashion.



Scheme 2

The source of the oxygen anion cannot be unambiguously identified although several experiments along this line have been carried out. Repeated syntheses under more rigorous anhydrous conditions always led to the isolation of **1** arguing against the source being adventitious water. To avoid contamination with water due to residual $MgBr_2 \cdot H_2O$, the magnesium bromide was prepared from the elements according to literature procedures.[31] The incorporation of oxygen due to a reaction with the employed grease could be ruled out by using commercially available non-silicon grease (Lithelen, Leybold Vakuum GmbH). Such a reaction is not unprecedented, although entire $O{-}SiMe_3$ or $O{-}SiMe_2$ units are usually transferred.[32−34] The cleavage of THF, which cannot be replaced due to insolubility in hydrocarbon solvents, seems unlikely. Cleavage of alkyl aryl ethers by Grignard reagents has been reported but usually requires drastic conditions,[35,36] except for certain crown ethers, where cleavage of an O−Me bond was found within 1 h at room temperature.[37] In addition, an NMR experiment in [D$_8$]THF ($MgBr_2$, 2 equiv. tzK and 10 equiv. THF) did not show any by-products of the cleavage. Replacement of the ethereal solvent by acetonitrile led to unidentified reaction mixtures, from which no uniform product crystallized. Incorporation of KOH remains a possibility, since the parent triazole is deprotonated by the reaction with elemental potassium. However, the yield of **1** argues against it since the potassium metal was freshly cut inside a well-maintained glove box prior to use. Finally, molecular oxygen might be a possible source as its complete exclusion is difficult to accomplish by routine Schlenk techniques. Reactions of organomagnesium compounds with oxygen are known to give peroxide[23,24] and oxide species.[38] Although this is a hint for a reaction with O_2, the oxygen source cannot be pinned down conclusively to one of the above reasons.

A structural analysis of **1** reveals a slightly distorted tetrahedral oxo-centered arrangement of four Mg atoms bridged by six η^1-η^1-triazolato ligands. Figure 1 shows an ORTEP view of **1**, crystallographic data are given in Table 1 and selected bond lengths and angles in Table 2. The Mg_4O unit is embedded in a matrix of 10 disordered molecules of THF, none of which is coordinated to a metal atom. This is consistent with the NMR spectroscopic data of the isolated and dried material in CD_3CN, where no THF signals are detectable. This is similar to the situation with the structures of proteins surrounded by disordered water molecules. Therefore, the structural parameters of the THF molecules were only approximately refined. The geometry at the four-coordinate Mg atoms is distorted tetrahedral, unlike the trigonal-bipyramidal geometry in the inorganic species $[Mg_4(\mu_4\text{-}O)(\mu\text{-}Br)_6 \cdot 4Et_2O]$ published in 1964 by Stucky and Rundle,[38] where each Mg atom is additionally coordinated by an Et_2O molecule. The smaller coordination number in **1** apparently does not influence the Mg−O bond lengths {1.937(2)−1.950(2) Å in **1**; 1.95 Å in $[Mg_4(\mu_4\text{-}O)(\mu\text{-}Br)_6 \cdot 4Et_2O]$[38]}. Similar structural features are exhibited by complexes of beryllium in the basic acetates $[Be_4(\mu_4\text{-}O)(RCO_2)_6]$,[39] for example, and even in well-known transition metal systems such as $[Co_4(\mu_4\text{-}O)(\mu\text{-}pz)_6]$,[40,41] suggesting that the formation of **1** arises from geometrical packing and ionic effects rather than from the electronic configuration of the metal. The structure of **1** should also be compared with that of the cresylate species $[LiMg_4(\mu_5\text{-}O)R_7 \cdot 4THF]$ ($R = o\text{-}Me(C_6H_4)O^-$),[25] where a $Mg_4(\mu_4\text{-}O)$ core is additionally coordinated by a lithium cresylate. This leads to an oxo-centered, trigonal bipyramidal $LiMg_4(\mu_5\text{-}O)$ core. Unlike in **1**, all the Mg atoms are coordinated by one molecule of THF. The Mg−O(central) bonds are slightly longer [2.002(4) to 2.041(2) Å], presumably due to the higher coordination number.

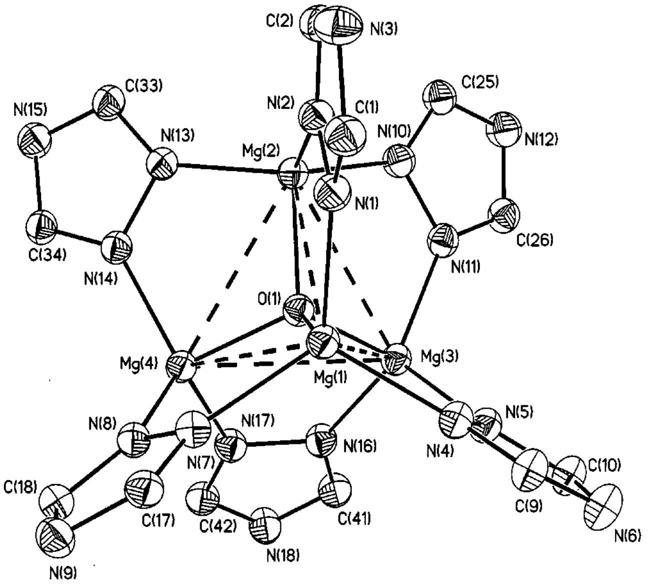


Figure 1. Molecular view of [$Mg_4(\mu_4\text{-oxo})(\mu\text{-tz})_6$] (**1**); *iso*-propyl groups have been omitted for clarity

The $MgON_3$ tetrahedra show a pronounced trigonal distortion with the Mg atom lying almost within the N_3 plane [O(1)−Mg(1)−N(1) = 100.71°]. This structure ensures a perfect alignment of the lone pairs of the N atoms toward the metal and, in addition, obeys Bent's rules:[42,43] the hybrid orbitals pointing towards the less electronegative atom acquire a higher *s* character and therefore increased angles [N(1)−Mg(1)−N(4) = 117.16°]. The $MgON_3$ tetrahedron can be modeled with $s^{1+x/3}p^{3-x/3}$ hybrid orbitals in the Mg−N directions and with $s^{1-x}p^{3+x}$ orbitals for the Mg−O axis. From this, the N−Mg−N bond angles are $\arccos[-(1 + x/3)/(3 - x/3)]$. Thus, the experimental angles yield an estimation of $x = 0.73$, showing a distinct redistribution of *s* vs. *p* character compared to the sp^3 reference.

Compound **2** may be prepared by two different routes. The more straightforward method involves the addition of two equiv. of pzH[44] and pzK[45] each to $MgBr_2$ in THF (Scheme 2). The product is soluble in most organic solvents, including hexane and toluene. Compound **2** may also be prepared by the addition of water to a hexane solution containing [$\{Mgpz_2\}_2$], a species recently reported by Winter.[29] During the reaction with water, a white precipitate is formed and **2** is found exclusively in solution. Evaporation of the solvent gave pure **2** in 40% yield (based on the amount of pzK). The ^1H NMR spectrum in C_6D_6 of the precipitate shows six different signals in the *t*Bu region pointing to a mixture of compounds. At this point it is unclear whether one of these species is the compound [$Mg_4(\mu_4\text{-O})(\mu\text{-pz})_6$], similar to **1**, although mass spectrometry points to its existence.[46] An interesting experiment would be a similar reaction with the triazolato ligand to find out whether water is the oxo anion source; however tzK and $MgBr_2$ do not react at all in toluene or hexane due to their insolubility in these solvents.

The solid state structure of **2** determined by X-ray crystallography shows the magnesium atom tetrahedrally surrounded by two η^1-coordinated pyrazole and two pyrazolato ligands. Figure 2 shows an ORTEP view of **2**, crystallographic data are given in Table 1 and selected bond lengths and angles in Table 2. A particular feature are the intramolecular hydrogen bonds between two pairs of different ligands [N(4)−H(4)···N(2) 2.7448(17) Å, 153(3)°] preventing the possibility of η^2-coordination [Mg(1)−N(1) 2.038(1) Å vs. Mg(1)−N(2) 2.737(1) Å] although a preference for such a coordination even in a sterically congested six-coordinate species has been previously found.[29]

Table 1. Experimental crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{48}H_{84}MgN_{18}O\cdot 10THF$	$C_{44}H_{78}MgN_8$
Mol. wt.	1747.61	743.45
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	24.9166(9)	23.4784(17)
b (Å)	16.6528(6)	11.0558(9)
c (Å)	25.7123(9)	19.2892(15)
β (deg)	106.737(3)	112.149(6)
V (Å^3)	10216.9(6)	4637.5(6)
Z	4	4
T (K)	133(2) K	133(2)
Density $\rho_{calcd.}$ (Mg/m^3)	1.136	1.065
Absorption coefficient (mm^{-1})	0.097	0.076
F(000)	3816	1640
Reflections collected	167504	11682
Reflection unique	17573 (R_{int} = 0.0828)	3884 (R_{int} = 0.0731)
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0727 $wR2$ = 0.2048	$R1$ = 0.0471 $wR2$ = 0.1256
Goodness-of-fit on F^2 [b]	1.037	1.039

[a] $R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$; $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$. [b] $S = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma(n - p)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2**

Complex **1**			
Mg(1)−O(1)	1.950(2)	Mg(2)−O(1)	1.941(2)
Mg(3)−O(1)	1.937(2)	Mg(4)−O(1)	1.944(2)
Mg(1)−N(1)	2.065(3)	Mg(1)−N(4)	2.058(3)
Mg(1)−N(7)	2.062(3)	Mg(1)−Mg(2)	3.167(2)
Mg(1)−O(1)−Mg(2)	108.97(10)	Mg(1)−O(1)−Mg(2)	108.62(10)
O(1)−Mg(1)−N(1)	100.71(11)	O(1)−Mg(1)−N(4)	98.90(10)
O(1)−Mg(1)−N(7)	100.42(10)	N(1)−Mg(1)−N(4)	117.16(12)
Complex **2**			
Mg(1)−N(1)	2.038(1)	Mg(1)−N(2)	2.737(1)
Mg(1)−N(3)	2.202(1)	Mg(1)−N(4)	2.957(1)
N(2)···H(4)−N(4)	2.7448(17)	N(2)···H(4)−N(4)	154(3)
N(1)−Mg(1)−N(3)	105.77(5)	N(1)−Mg(1)−N(1A)[a]	118.24(8)
N(1)−Mg(1)−N(3A)[a]	103.39(5)		

[a] Equivalent atoms "A" generated with: $-x$, y, $-z + 1/2$.

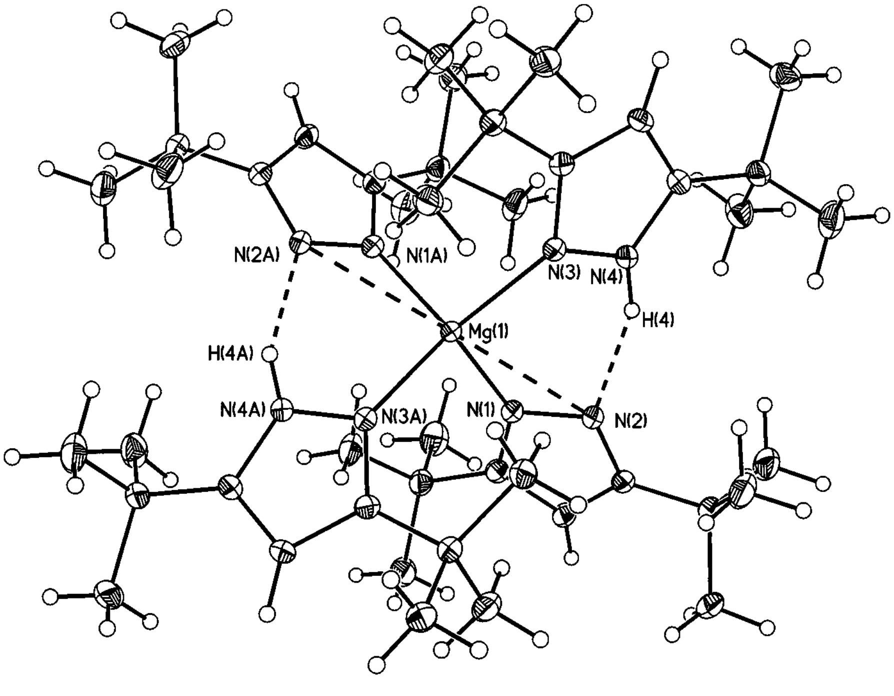


Figure 2. Molecular view of [Mg(pz)$_2$(pzH)$_2$] (**2**)

The ^{1}H NMR spectrum of **2** at room temperature shows broad resonances for one kind of ligand, indicating a dynamic process. As the sample was cooled to 183 K the individual resonances of the four *t*Bu, two CH and one NH protons appeared, consistent with the structure in the solid state at 133 K (Figure 3). The temperature dependent behavior of the *t*Bu region can be modeled with two separate exchanges $A_1 \rightleftarrows B_1$ with rate constant k_{τ} (coalescence temperature ≈243 K) as well as $A_1(B_1) \rightleftarrows A_2(B_2)$ with rate constant k_{H} (coalescence temperature ≈290 K) (Figure 3). This is consistent with a rapid interchange of the A_1 and B_1 signals of the deprotonated ligand. The process coalescing at higher temperatures corresponds to the exchange of the bridging proton between different ligands interchanging A_1 in A_2 and parallel B_1 in B_2 (with equal rate constant k_{H}).

The rates were measured by line shape analysis by solving the following matrix:[47−49]

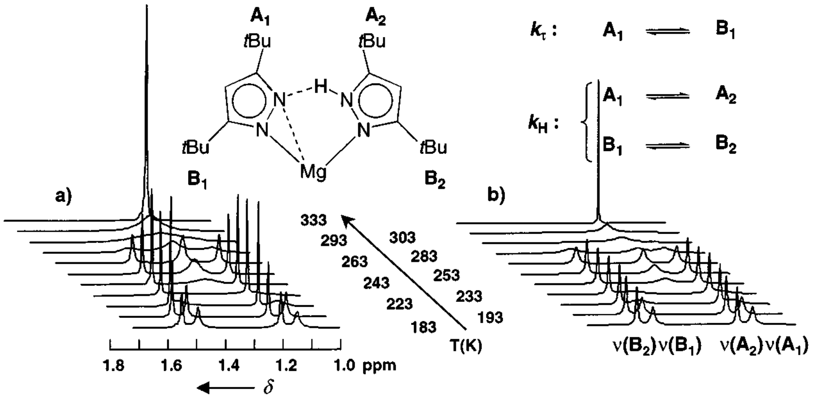


Figure 3. a) Variable temperature ^1H NMR spectra (500 MHz, [D$_8$]toluene) of **2** showing the *t*Bu resonances; b) computer simulated spectra and proposed kinetic processes

$$\begin{pmatrix} \nu(\mathrm{A}_1)+\alpha T+ik_\tau(T)+ik_\mathrm{H}(T) & 0 & -ik_\tau(T) & 0 \\ -ik_\mathrm{H}(T) & \nu(\mathrm{A}_2)+\alpha T+ik_\mathrm{H}(T) & 0 & 0 \\ -ik_\tau(T) & 0 & \nu(\mathrm{B}_1)+\alpha T+ik_\tau(T)+ik_\mathrm{H}(T) & -ik_\mathrm{H}(T) \\ 0 & 0 & -ik_\mathrm{H}(T) & \nu(\mathrm{B}_2)+\alpha T+ik_\mathrm{H}(T) \end{pmatrix}$$

where ν denotes the chemical shift of the four types of protons.

The real part of the eigenvalues corresponds to the position of the peaks, while the imaginary part corresponds to their bandwidths. The solutions of this matrix were used to form the spectrum as the sum of four Lorentzian peaks. In addition, a slight shift of the barycenter of the experimental signals with temperature required a linear adjustment αT, which was added to each diagonal element. This is probably due to a general modification of the average Mg−N bond lengths with temperature. Targeting only a qualitative simulation, kinetic terms corresponding to spin-lattice relaxation were not ascribed. Both the chemical shift ν and the rate constant *k* have the common meaning of a frequency and therefore, in this case, *k* is defined in units of the chemical shifts. The coalescence appears when the frequency of the chemical exchange becomes similar to those of the magnetic resonance.

A fit of the chemical rate constants to the Arrhenius equation yielded activation energies of E_τ = 8.3 kcal/mol and E_H = 15.2 kcal/mol; use of the Eyring form gave similar results (E_τ = 8.0 kcal/mol and E_H = 14.7 kcal/mol). The low value of E_τ points to an interchange of the two N atoms of the deprotonated ligand via η^2-coordination. Surprisingly, in previously reported magnesium η^2-pyrazolato complexes dynamic processes were proposed, but seem to be faster than the NMR time scale.[29] The value of E_H is consistent with a facile exchange of the proton between two ligands favored by an N−H···N hydrogen bond established in the low temperature structure. These intramolecular rearrangements are complex processes at the quantum level. However, the employed classical rate laws allow a semi-quantitative statement that, due to the possible η^1- and η^2-coordination modes, the pseudo-rotation of the deprotonated ligand is more rapid than the intramolecular proton exchange.

Conclusion

Here, we present a μ_4-oxo tetranuclear main group metal compound with azolato ligands. Due to the lack of *d*-electrons, compound **1** represents a model for this structural prototype allowing the conclusion that the forces to build this structure pattern are mainly of an ionic nature and that *d*-*d* electron interactions seem not to play a role. In addition, our investigations of **2** offer an illustration for the paradigm used in supramolecular concepts stating that hydrogen bonds and coordination effects compete in the same range of bonding energies.

Experimental Section

General Remarks: All preparations were carried out under an atmosphere of dry nitrogen. All common reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise indicated. Melting points were determined on a Büchi B-540 melting point apparatus in sealed glass tubes and are uncorrected. NMR spectra were recorded on Bruker Avance 200 or Bruker Avance 500 spectrometers. The chemical shifts are referenced to external $SiMe_4$.

tzH: 4-NH_2-3,5-*i*Pr_2-triazole was synthesized according to a published method from *i*PrCOOH and hydrazine hydrate at 180 °C. Subsequently, a solution of 4-NH_2-3,5-*i*Pr_2-triazole (4.28 g, 0.025 mol) in aqueous HCl (6 M, 5.5 mL) was treated with a solution of $NaNO_2$ (2.01 g, 0.029 mol) in 30 mL of water and stirred until evolution of N_2 ceased. The temperature was kept in the range 20−30 °C by occasional cooling with an ice bath. After neutralization, extraction with CH_2Cl_2 and evaporation of the solvent the pure product was obtained as colorless crystals (3.42 g, 88%). m.p. 154 °C. ^1H NMR (C_6D_6, 200.1 MHz):δ = 12.98 (br. s, NH, 1 H), 3.19 [hept, C*H*(CH_3)$_2$, 2 H], 1.35 [d, CH(*CH_3*)$_2$, 12 H]. ^{13}C NMR (C_6D_6, 125.8 MHz):δ = 164.0 (C ring), 27.6 [*C*H(CH_3)$_2$], 21.5

$[CH(CH_3)_2]$. $C_8H_{15}N_3$ (153.2): calcd. C 62.71, H 9.87, N 27.42; found C 62.79, H 9.61, N 27.23.

tzK: A solution of tzH (1.65 g, 10.8 mmol) in 60 mL of THF was treated with one equivalent of potassium metal (0.43 g). The solution was stirred under reflux for 5 h after which all the metal had reacted. The solvent was removed under reduced pressure to give the product as a white powder that was pure enough for further reactions (1.92 g, 93%). m.p. > 300 °C ^1H NMR (CD_3CN, 200.1 MHz):$\delta = 2.84$ [hept, 2 H, $CH(CH_3)_2$], 1.18 [d, 12 H, $CH(CH_3)_2$]. $C_8H_{14}KN_3$ (191.3): calcd. C 50.22, H 7.38, N 20.44; found C 49.88, H 7.29, N 20.42.

$[Mg_4(\mu_4\text{-oxo})(\mu\text{-tz})_6]$ (1): Freshly distilled THF (20 mL) was added to a mixture of $MgBr_2$ (0.21 g, 1.14 mmol) and tzK (0.43 g, 2.25 mmol). The resulting suspension was stirred for 48 h at room temp. The fine precipitate was then centrifuged and the solution decanted. After evaporation of the solvent to a volume of approximately 10 mL, colorless crystals of **1** formed overnight (0.11 g, 38% based on Mg). ^1H NMR (CD_3CN, 200.1 MHz, room temp.): $\delta = 3.07$ [sept, $^3J_{H,H} = 7$ Hz, 2 H, $CH(CH_3)_2$], 1.16 [d, $^3J_{H,H} = 7$, 12 Hz, $CH(CH_3)_2$]. ^{13}C NMR (CD_3CN, 125.8 MHz, room temp.): $\delta = 171.11$ (C ring), 29.71 $[CH(CH_3)_2]$, 23.13 $[CH(CH_3)_2]$. $C_{48}H_{84}Mg_4N_{18}O$ (1026.5): calcd. C 56.16, H 8.25, N 24.56; found C 55.78, H 8.41, N 24.03.

$[Mg(pz)_2(pzH)_2]$ (2): Freshly distilled THF (20 mL) was added to a mixture of $MgBr_2$ (0.16 g, 0.87 mmol), pzK (0.38 g, 1.74 mmol) and pzH (0.31 g, 1.72 mmol). The resulting suspension was stirred for 48 h at room temp. The solvent was then removed under reduced pressure and the resulting white residue was extracted with hexane. After removal of hexane, the powder was recrystallized from toluene at −25 °C to give **2** as colorless crystals (0.21 g, 32%). ^1H NMR (C_6D_6, 500.1 MHz, 193 K): $\delta = 13.22$ (s, 1 H, NH), 6.15 (s, 1 H, CH), 6.05 (s, 1 H, CH), 1.60 [s, 9 H, $C(CH_3)_3$], 1.54 [s, 9 H, $C(CH_3)_3$], 1.22 [s, 9 H, $C(CH_3)_3$], 1.16 [s, 9 H, $C(CH_3)_3$].). ^{13}C NMR (C_6D_6, 125.8 MHz, room temp.): $\delta = 159.57$ (CH ring), 98.72 (C ring), 31.76 $[C(CH_3)_3]$, 30.991 $[C(CH_3)_3]$. $C_{44}H_{78}MgN_8$ (743.5): calcd. C 70.25, H 10.54, N 14.90; found C 70.70, H 10.52, N 14.96.

X-ray Crystal Structure Analysis: The data were collected on a Stoe IPDS II-array detector system instrument with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined against F^2 on all data by full-matrix least-squares procedures with SHELX-97.[50]

1: To verify the complex composition of **1**·10THF and especially the connectivity in the 10 solvent molecules, complete crystal structure determinations were carried out with five different crystals. The best results are presented in this paper. All THF molecules are disordered and refined with restraints. In the Mg_4 unit two *i*Pr groups are disordered.

CCDC-166225 (**1**) and CCDC-166226 (**2**) 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].

Acknowledgments

Generous support from Prof. H. W. Roesky and the Alexander-von-Humboldt-Foundation (M. F.) is gratefully acknowledged.

[1] K. W. Henderson, W. J. Kerr, J. H. Moir, *Chem. Commun.* **2000**, 479−480.

[2] K. W. Henderson, J. F. Allan, A. R. Kennedy, *Chem. Commun.* **1997**, 1149−1150.

[3] D. A. Evans, S. A. Nelson, *J. Am. Chem. Soc.* **1997**, *119*, 6452−6453.

[4] K. Kobayashi, M. Kawakita, H. Akamatsu, O. Morikawa, H. Konishi, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2645−2647.

[5] Y. Kondo, A. Yoshida, T. Sakamoto, *J. Chem. Soc., Perkin Trans. 1* **1996**, 2331−2332.

[6] W. Schlecker, A. Huth, E. Ottow, J. Mulzer, *J. Org. Chem.* **1995**, *60*, 8414−8416.

[7] P. E. Eaton, C.-H. Lee, Y. Xiong, *J. Am. Chem. Soc.* **1989**, *111*, 8016−8018.

[8] M. Westerhausen, W. Schwarz, *Z. Anorg. Allg. Chem.* **1992**, *609*, 39−44.

[9] W. Clegg, K. W. Henderson, R. E. Mulvey, P. A. O'Neil, *J. Chem. Soc., Chem. Commun.* **1994**, 769−770.

[10] M. M. Olmstead, W. J. Grigsby, D. R. Chacon, T. Hascall, P. P. Power, *Inorg. Chim. Acta* **1996**, *251*, 273−284.

[11] D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. A. Malik, M. Motevalli, R. Möseler, H. Powell, J. D. Runnacles, A. C. Sullivan, *Polyhedron* **1990**, *9*, 2959−2964.

[12] L. M. Englehardt, P. C. Junk, W. C. Patalinghug, R. E. Sue, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc., Chem. Commun.* **1991**, 930−932.

[13] R. A. Bartlett, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1994**, *33*, 4800−4803.

[14] J. L. Sebestl, T. T. Nadasdi, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 1289−1294.

[15] G. Dozzi, G. Del Piero, M. Cesari, S. Cucinella, *J. Organomet. Chem.* **1980**, *190*, 229−236.

[16] W. Clegg, M. Frank, R. E. Mulvey, P. A. O′Neil, *J. Chem. Soc., Chem. Commun.* **1994**, 97−98.

[17] W. Clegg, L. Horsburgh, R. E. Mulvey, R. Rowlings, *Chem. Commun.* **1996**, 1739−1740.

[18] M. Veith, A. Spaniol, J. Pöhlmann, F. Gross, V. Huch, *Chem. Ber.* **1993**, *126*, 2625−2635.

[19] T. Hascall, K. Ruhlandt-Senge, P. P. Power, *Angew. Chem.* **1994**, *106*, 350−351; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 356−357.

[20] W. J. Grigsby, T. Hascall, J. J. Ellison, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1996**, *35*, 3254−3261.

[21] R. E. Mulvey, *Chem. Commun.* **2001**, 1049−1056.

[22] P. C. Andrews, A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts, R. B. Rowlings, *Angew. Chem.* **2000**, *112*, 2036−2038; *Angew. Chem. Int. Ed.* **2000**, *39*, 1960−1962.

[23] A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816−7824.

[24] A. R. Kennedy, R. Mulvey, C. L. Raston, B. A. Roberts, R. B. Rowlings, *Chem. Commun.* **1999**, 353−354.

[25] K. W. Henderson, R. E. Mulvey, F. B. M. Reinhard, *J. Am. Chem. Soc.* **1994**, *116*, 10777−10778.

[26] G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151−238.

[27] D. A. Atwood, A. H. Cowley, R. A. Jones, *Organometallics* **1993**, *12*, 236−238.

[28] C.-C. Chang, T.-Y. Her, F.-Y. Hsieh, C.-Y. Yang, M. Y. Chiang, G.-H. Lee, Y. Wang, S.-M. Peng, *J. Chin. Chem. Soc. (Taipei)* **1994**, *41*, 783−789.

[29] D. Pfeiffer, M. J. Heeg, C. H. Winter, *Angew. Chem.* **1998**, *110*, 2674−2676; *Angew. Chem. Int. Ed.* **1998**, *37*, 2517−2519.

[30] R. M. Herbst, J. A. Garrison, *J. Org. Chem.* **1953**, *18*, 872−877.

[31] *Gmelins Handbuch der anorganischen Chemie, Magnesium, Teil B, die Verbindungen des Magnesiums*; Verlag Chemie: Berlin, 1939.

[32] H. Bock, M. Sievert, C. L. Bogdan, B. O. Kolbesen, A. Wittershagen, *Organometallics* **1999**, *18*, 2387−2389.

[33] T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 2896−2905.

[34] C. N. McMahon, S. G. Bott, L. B. Alemany, H. W. Roesky, A. R. Barron, *Organometallics* **1999**, *18*, 5395−5408.

[35] E. Müller, *Methoden der Organischen Chemie (Houben Weyl)*; 4th Ed.; Thieme Verlag: Stuttgart, **1973**, Vol. XIII/2a.

[36] H. Meerwein, *Methoden der Organischen Chemie (Houben Weyl)*; Thieme Verlag: Stuttgart, **1965**, Vol. VI/3.

[37] G. J. M. Gruter, G. P. M. van Klink, O. S. Akkerman, F. Bickelhaupt, *Organometallics* **1993**, *12*, 1180−1188.

[38] G. Stucky, R. E. Rundle, *J. Am. Chem. Soc.* **1964**, *86*, 4821−4825.

[39] A. Tulinsky, *Acta Crystallogr.* **1959**, *12*, 634−637.

[40] I. G. Dance, *Comprehensive Coordination Chemistry*; (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty) Pergamon Press: Oxford, **1987**, Vol. 1, pp 135.

[41] M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson, J. Trotter, *Acta Crystallogr., Sect. C* **1994**, *50*, 1023−1026.

[42] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275−311.

[43] N. Fröhlich, G. Frenking, *Chem. Rev.* **2000**, *100*, 717−774.

[44] J. Elguero, E. Gonzalez, R. Jacquier, *Bull. Soc. Chim. Fr.* **1968**, 707−713.

[45] C. Yélamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 3892−3894.

[46] We thank the referees for their helpful comments and suggestions.

[47] C. P. Poole, *Theory of Magnetic Resonance*; 2nd ed.; John Wiley & Son: New York, 1987, pp 171.

[48] G. Binsch, *J. Am. Chem. Soc.* **1969**, *91*, 1304−1309.

[49] The formation of the matrix can be intuitively described as follows: i) The real part of the matrix elements corresponds to the spin Hamiltonian; the diagonal elements contain only chemical shifts without coupling between different types of protons. ii) The imaginary part is related to the kinetic equations; nondiagonal elements -*ik*H or -*ik*t are added at intersections between the lines and columns of the corresponding interchange. iii) The sum of the imaginary parts on each diagonal element must contain all the rate constants that affect a given species. iv) The sum of the imaginary terms of each row or column must be zero.

[50] G. M. Sheldrick, Universität Göttingen, **1997**.

Received August 23, 2001
[I01323]