DOI: 10.1002/chem.200902425

### β-Diketiminate-Stabilized Magnesium(I) Dimers and Magnesium(II) Hydride Complexes: Synthesis, Characterization, Adduct Formation, and Reactivity Studies

### Simon J. Bonyhady,<sup>[a]</sup> Cameron Jones,<sup>\*[a]</sup> Sharanappa Nembenna,<sup>[a]</sup> Andreas Stasch,<sup>\*[a]</sup> Alison J. Edwards,<sup>[b]</sup> and Garry J. McIntyre<sup>[c]</sup>

Abstract: The preparation and characterization of a series of magnesium(II) iodide complexes incorporating β-diketiminate ligands of varying steric bulk denticity, namely, [(ArNCand  $Me_{2}CH^{-}$  (Ar = phenyl, (<sup>Ph</sup>Nacnac), mesityl (MesNacnac), or 2,6-diisopropylphenyl (Dipp, DippNacnac)), [(DippNCtBu)<sub>2</sub>CH]<sup>-</sup> (<sup>tBu</sup>Nacnac), and [(DippNC-Me)(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCMe)CH]<sup>-</sup> (DmedaNacnac) are reported. The com-[(<sup>Ph</sup>Nacnac)MgI(OEt<sub>2</sub>)], plexes [(<sup>Mes</sup>Nacnac)MgI(OEt<sub>2</sub>)], [(<sup>Dmeda</sup>Nac-[(MesNacnac)MgInac)MgI(OEt<sub>2</sub>)], (thf)], [(<sup>Dipp</sup>Nacnac)MgI(thf)], [(<sup>tBu</sup>Nacnac)MgI], and [(<sup>tBu</sup>Nacnac)MgI-(DMAP)] (DMAP=4-dimethylaminopyridine) were shown to be monomeric by X-ray crystallography. In addition, the related β-diketiminato beryllium and calcium iodide complexes, [(<sup>Mes</sup>Nacnac)BeI] and [{(<sup>Dipp</sup>Nacnac)- $CaI(OEt_2)$ ]<sub>2</sub>] were prepared and crystallographically characterized. The reductions of all metal(II) iodide complexes by using various reagents were attempted. In two cases these reactions

led to the magnesium(I) dimers. [(<sup>Mes</sup>Nacnac)MgMg(<sup>Mes</sup>Nacnac)] and [(<sup>tBu</sup>Nacnac)MgMg(<sup>tBu</sup>Nacnac)]. The remixture duction of a 1:1 of [(<sup>Dipp</sup>Nacnac)MgI(OEt<sub>2</sub>)] and [(<sup>Mes</sup>Nacnac)MgI(OEt<sub>2</sub>)] with potassium gave a low yield of the crystallographically characterized complex [(<sup>Dipp</sup>Nacnac)Mg(µ-H)(µ-I)Mg(<sup>Mes</sup>Nacnac)]. All attempts to form beryllium(I) or calcium(I) dimers by reduc-[(<sup>Mes</sup>Nacnac)BeI], tions of [{(<sup>Dipp</sup>Nacnac)CaI(OEt<sub>2</sub>)}<sub>2</sub>], or  $[{(^{tBu}Nacnac)CaI(thf)}_2]$  have so far been unsuccessful. The further reactivity of the magnesium(I) complexes [(<sup>Mes</sup>Nacnac)MgMg(<sup>Mes</sup>Nacnac)] and [(<sup>*t*Bu</sup>Nacnac)MgMg(<sup>*t*Bu</sup>Nacnac)] towards a variety of Lewis bases and unsaturated organic substrates was explored. These studies led to the complexes

**Keywords:** low oxidation state • magnesium hydrides • magnesium • metal-metal interactions • X-ray diffraction  $[(^{Mes}Nacnac)Mg(L)Mg(L)(^{Mes}Nacnac)]$ (L=THF or DMAP), [(MesNacnac)Mg- $(\mu - AdN_6Ad)Mg(^{Mes}Nacnac)]$  (Ad = 1-[(<sup>tBu</sup>Nacnac)Mg(µ-Adadamantyl),  $N_6Ad)Mg(^{tBu}Nacnac)],$ and  $[(^{\text{Mes}}\text{Nacnac})Mg(\mu - tBu_2N_2C_2O_2)Mg$ (MesNacnac)] and revealed that, in general, the reactivity of the magnesium(I) dimers is inversely proportional to their steric bulk. The preparation and characterization of [("BuNacnac)Mg(µ-H)<sub>2</sub>Mg(<sup>tBu</sup>Nacnac)] has shown the compound to have different structural and physical properties to [("Nacnac)-MgMg(<sup>tBu</sup>Nacnac)]. Treatment of the former with DMAP has given  $[(^{tBu}Nacnac)Mg(H)(DMAP)],$  the Xray crystal structure of which disclosed it to be the first structurally authenticated terminal magnesium hydride complex. Although attempts to prepare  $[(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)]$ were not successful, a neutron diffraction study of the corresponding magnesium(I) complex, [(MesNacnac)Mg-Mg(MesNacnac)] confirmed that the compound is devoid of hydride ligands.

 [a] S. J. Bonyhady, Prof. C. Jones, Dr. S. Nembenna, Dr. A. Stasch School of Chemistry, Monash University PO Box 23, Melbourne, VIC, 3800 (Australia) Fax: (+61)3-9905-4597 E-mail: cameron.jones@sci.monash.edu.au andreas.stasch@sci.monash.edu.au

- [b] Dr. A. J. Edwards Bragg Institute Australian Nuclear Science and Technology Organisation PMB1, Menai, N.S.W. 2234 (Australia)
- [c] Dr. G. J. McIntyre
   Institut Laue-Langevin, 6 rue Jules Horowitz
   BP 156, 38042 Grenoble Cedex 9 (France)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902425.





### Introduction

The chemistry of the Group 2 elements is dominated by the +2 oxidation state so much so that until late 2007 no structurally characterized examples of molecular compounds of these elements were known to exist under normal laboratory conditions with the metal in the +1 oxidation state. This is perhaps surprising considering the rapid expansion of the chemistry of compounds containing p-block elements in very low oxidation states in recent decades.<sup>[1]</sup> That is not to say that low-oxidation-state Group 2 complexes were not known to be capable of existence under extreme conditions. In the case of magnesium, this has been proven by the spectroscopic characterization of monomeric magnesium(I) compounds such as Mg<sup>I</sup>(NC) in deep space.<sup>[2]</sup> In addition, a number of monomeric and dimeric magnesium(I) compounds such as XMgMgX and MgX (X=H or Cl) have been prepared and spectroscopically studied under matrix isolation conditions,<sup>[3,4]</sup> whereas the existence of cluster compounds that have the general formula  $RMg_4X$  (X= halide) has been suggested by mass spectrometry experiments.<sup>[5]</sup> Moreover, a variety of theoretical investigations of compounds of the type RMMR (M=Be, Mg or Ca; R= alkyl, aryl, amide etc.,)<sup>[6]</sup> have concluded that the strength of their M-M bonds is not insignificant, and that examples that are stable under ambient conditions might be accessible if sufficiently bulky ligands (R) are employed.

In 2004, Carmona et al. prepared the first structurally characterized example of a dimeric zinc(I) compound, Cp\*ZnZnCp\* ( $Cp*=C_5Me_5$ ).<sup>[7,8]</sup> Since this initial report, more than half a dozen other examples have been prepared and their chemistry has begun to be developed.<sup>[8,9]</sup> Mindful of the chemical similarities between zinc and magnesium, and the calculated stability of Mg-Mg bonded dimers, we investigated the preparation of such compounds by the potassium metal reductions of the guanidinate or  $\beta$ -diketiminate chelated magnesium(II) precursor complexes [(Priso)Mg(µ-I)<sub>2</sub>Mg(OEt<sub>2</sub>)(Priso)] and [(<sup>Dipp</sup>Nacnac)MgI- $(OEt_2)$ ]  $(Priso = [(DippN)_2CNiPr_2]^-, ^{Dipp}Nacnac = [(DippNC Me_{2}CH^{-}$ ,  $Dipp = C_{6}H_{3}iPr_{2}-2,6)$ , respectively. These afforded the remarkably thermally stable magnesium(I) dimer complexes [(Priso)MgMg(Priso)] (1, decomposes > 170 °C) and [(<sup>Dipp</sup>Nacnac)MgMg(<sup>Dipp</sup>Nacnac)] (2, decomposes > 300 °C).<sup>[10,11]</sup> X-ray crystallographic studies of both compounds revealed them to have Mg-Mg distances of approximately 2.85 Å, that is, slightly longer than the sum of two divalent magnesium covalent radii (2.82 Å).<sup>[12]</sup> Calculations on models of these compounds suggest that they contain covalently bonded  $Mg_2^{2+}$  cores (with bond dissociation energies of approximately 45 kcalmol<sup>-1</sup>) that have largely ionic interactions with their ligands.<sup>[3a,10,13]</sup> The Mg–Mg bonds of the cores are associated with the HOMOs of the models and have high s character, which had been previously calculated for other Mg-Mg bonded dimers.<sup>[6]</sup> The lowest two metalbased unoccupied orbitals of the models are close to degenerate and have what is essentially  $\pi$ -bonding character. To definitively prove the absence of hydride ligands that bridge the metal centers of **2**, the magnesium(II) hydride complex  $[(^{Dipp}Nacnac)Mg(\mu-H)_2Mg(^{Dipp}Nacnac)]$  (**3**) was prepared and was shown to have very different physical and chemical properties.<sup>[13]</sup>

An experimental charge density study of 2 has recently confirmed the covalent nature of the metal-metal interaction in that compound,<sup>[14]</sup> but the study indicated that the electron density between the magnesium centers is rather diffuse. It is thought that this diffuseness is the major cause behind the exceptional elongation (by > 0.2 Å) of its Mg-Mg bond upon formation of the Lewis base adducts  $[(^{Dipp}Nacnac)Mg(L)Mg(L)(^{Dipp}Nacnac)]$  (4; L=THF, diox-4-tert-butylpyridine or 4-dimethylaminopyridine ane. (DMAP)). This is despite the apparent weakness of the  $L \rightarrow$ Mg bonds, at least in the case of the ether adducts, which readily and rapidly lose their coordinated ether molecules when placed in vacuo. Note that a related adduct of the magnesium(II) hydride complex 3, namely, [(<sup>Dipp</sup>Nacnac)Mg-(thf)(µ-H)<sub>2</sub>Mg(thf)(<sup>Dipp</sup>Nacnac)], has been reported and shown to have distinctly different properties to those of 4 (L=THF).<sup>[13]</sup> Comparisons of the reactivity of the magnesium(I) dimer, 2, and its magnesium(II) hydride counterpart, 3, towards N-functionalized unsaturated substrates have also been carried out.<sup>[15]</sup> These have revealed 2 to act as a facile two-center/two-electron reductant towards the substrates, whereas 3 generally behaves as a hydromagnesiation reagent. In each case it is thought that the reaction mechanism involves initial coordination of the substrate at the magnesium centers of the reactant prior to its reduction or hydromagnesiation.

Recently, an extension of the chemistry of magnesium(I) dimers that are stable under ambient conditions has been realized with the preparation of the ion-pair complex, [K- $(thf)_{3}_{2}[(DAB)MgMg(DAB)] (DAB = [(DippNCMe)_{2}]^{2-}.^{[16]}$ In this complex, the  $Mg_2^{2+}$  core is coordinated by two dianionic diazabutadiene ligands and its Mg-Mg bond is significantly longer (2.9370(18) Å) than those of 1 or 2. DFT calculations on a model complex revealed this  $\sigma$  bond to have considerable p character (55%) as opposed to the predominantly s-character bonds of 1 and 2. Moreover, whereas 2 readily forms adducts with a range of Lewis bases, the magnesium centers of [K(thf)<sub>3</sub>]<sub>2</sub>[(DAB)MgMg(DAB)] do not coordinate THF. To date there are no known N,N'-chelated beryllium(I) or calcium(I) dimers (such as 1 and 2), but the synthesis of the thermally stable, paramagnetic calcium(I) inverse sandwich complex [(thf)<sub>3</sub>Ca{µ-C<sub>6</sub>H<sub>3</sub>Ph<sub>3</sub>-1,3,5 Ca(thf)<sub>3</sub>] gave hope that this may be achieved.<sup>[17]</sup>

In this paper, we describe efforts to extend the known chemistry of  $\beta$ -diketiminate coordinated magnesium(I) dimers and magnesium(II) hydrides to complexes incorporating a range of ligands of varying steric bulk and denticity. The preparation of precursors to these complexes, the reductions of the precursors, and the further reactivity of the target magnesium(I) complexes towards Lewis bases and/or unsaturated substrates, for example, will be discussed. In addition, although not successful, attempts to prepare Be–Be and Ca–Ca bonded complexes will be discussed.

### **Results and Discussion**

Preparation and characterization of Group 2 metal(II) iodide precursor complexes: The high thermal stability of compound 2 is no doubt derived from the kinetic protection provided by its bulky DippNacnac ligands. To evaluate the importance of this protection, a series of related magnesium(I) compounds that contain chelating  $\beta$ -diketiminate ligands of lesser or greater steric bulk than DippNacnac were targeted. In addition, considering that the Lewis base adducts of 2 (i.e., the four-coordinate complexes 4) are stable up to 250°C (for L=4-tert-butylpyridine),<sup>[13]</sup> the preparation of a four-coordinate, intramolecularly base-stabilized analogue of 2 incorporating a functionalized  $\beta$ -diketiminate was an objective of this study. The ligands that were chosen for these purposes were  $[(ArNCR)_2CH]^-$  R=Me, Ar=phenyl (<sup>Ph</sup>Nacnac) or mesityl (<sup>Mes</sup>Nacnac); R = tBu, Ar = Dipp(<sup>Bu</sup>Nacnac); and [(DippNCMe)(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NCMe)CH]<sup>-</sup> (<sup>Dmeda</sup>Nacnac).

Considering that compound **2** is prepared in over 50% yield through the reduction of the corresponding magnesium(II) iodide complex  $[(^{Dipp}Nacnac)MgI(OEt_2)],^{[10]}$  related complexes involving the above-mentioned ligands were seen as appropriate precursors to the target magnesium(I) dimers. Although  $[(^{Dipp}Nacnac)MgI(OEt_2)]$  was previously prepared by the treatment of  $[Li(^{Dipp}Nacnac)]$  with commercially available MgI<sub>2</sub>,<sup>[18]</sup> more convenient routes to this and related compounds have been developed in our laboratory. Good isolated yields of  $[(^{Dipp}Nacnac)MgI(OEt_2)]$  (**5**),  $[(^{Ph}Nacnac)MgI(OEt_2)]$  (**6**),  $[(^{Mes}Nacnac)MgI(OEt_2)]$  (**7**), and  $[(^{Dmeda}Nacnac)MgI(OEt_2)]$  (**8**) have been obtained through deprotonation of the appropriate  $\beta$ -diketimine with MeMgI in diethyl ether as described in [Eq. (1)]. This

$$LH + MeMgI \xrightarrow{Et_2O} [LMgI(OEt_2)]$$
(1)

L= <sup>Dipp</sup>Nacnac (5), <sup>Ph</sup>Nacnac (6), <sup>Mes</sup>Nacnac (7), <sup>Dmeda</sup>Nacnac (8)

method is not appropriate for <sup>*Bu*</sup>NacnacH, which does not react with the Grignard reagent in boiling diethyl ether over extended periods. Alternatively, <sup>*Bu*</sup>NacnacH can be deprotonated when it is heated at 100 °C with dibutylmagnesium in toluene for 16 h. The complex that was generated in situ,  $[(^{$ *Bu* $}Nacnac)MgnBu]$ , was then allowed to react with one equivalent of I<sub>2</sub>, to give a good yield of  $[(^{$ *Bu* $}Nacnac)MgI]$  (9) after work-up [Eq. (2)]. We have generally found that the ether ligands of 5–8 are readily replaced by THF by dissolving the complexes in that solvent. In the cases of the reactions with 5 and 7, the products  $[(^{$ *Dip* $PNacnac})MgI(thf)]$  (10) and  $[(^{Mes}Nacnac)MgI(thf)]$  (11), respectively, have been fully

$$LH + MgnBu_{2} \xrightarrow{PhMe, 100 \ ^{\circ}C} [LMgnBu] \qquad (2)$$

$$L = {}^{rBu}Nacnac \qquad \downarrow \qquad I_{2} \qquad \downarrow -nBul$$

$$L = (LMgl] \qquad 9$$

characterized [Eq. (3)]. Moreover, the ability of the monomeric compound **9** to accept coordination from Lewis bases was demonstrated by its treatment with DMAP, which gave the complex [( $^{Bu}$ Nacnac)MgI(DMAP)] (**12**) [Eq. (3)].

$$[LMgI(OEt_2)] \xrightarrow{L'} [LMgI(L')]$$
(3)  

$$L' = THF; L = {}^{Dipp}Nacnac (10), {}^{Ph}Nacnac (11)$$

$$L' = DMAP; L = {}^{rBu}Nacnac (12)$$

To explore the possibility of preparing Be–Be and Ca–Ca bonded complexes, potential precursors to examples of such compounds,  $[(^{Mes}Nacnac)BeI]$  (13) and  $[\{(^{Dipp}Nacnac)CaI-(OEt_2)\}_2]$  (14), were synthesized by treatment of the potassium salt of the  $\beta$ -diketiminate with MI<sub>2</sub> (M=Be or Ca) in a diethyl ether/toluene mixture or neat diethyl ether, respectively, as shown in [Eq. (4)] and [Eq. (5)]. In line with the

$$KL + Bel_2 \xrightarrow{PhMe, Et_2O} [LBel] 13$$
(4)  
$$L = {}^{Mes}Nacnac$$

$$KL + Cal_{2} \xrightarrow{Et_{2}O} [\{LCal(OEt_{2})\}_{2}]$$
 14 (5)  
$$L = ^{Dipp}Nacnac$$

difference in the covalent radii of the Group 2 metals (Be = 0.96 Å, Mg = 1.41 Å, Ca = 1.76 Å),<sup>[12,19]</sup> the beryllium complex is an unsolvated three-coordinate monomer, whereas the calcium complex is a solvated five-coordinate iodidebridged dimer. This is despite the greater steric bulk of the  $\beta$ -diketiminate ligand in **14**. Both can be compared to the related monomeric, four-coordinate, ether solvated magnesium complexes **5–8**.

The spectroscopic data for complexes 6-14 are consistent with their proposed formulations. In all cases, X-ray crystallographic studies were used to authenticate the structures of the complexes. ORTEP diagrams for compounds 7-9, 13, and 14 are depicted in Figure 1 and selected metrical parameters for all compounds are collected in Table 1. Compounds 6 and 7 possess distorted tetrahedral magnesium geometries, and have very similar structures to that previously reported for 5.<sup>[18]</sup> Compound 8 is monomeric and its magnesium center has a distorted square-pyramidal geometry with the ether ligand in the apical position. Not surprisingly, the dimethylamino nitrogen center is significantly more distant from the Mg atom than either nitrogen center of the  $\beta$ -diketiminate fragment of the ligand. In contrast, the magnesium center of monomeric 9 has a distorted trigonal-planar geometry with shorter N-Mg and Mg-I distances than in any of the other complexes. The presence of tert-butyl substituents on the backbone of the ligand has the effect of pushing its Dipp substituents towards the magnesium atom, thus preventing dimerization of the molecule (such as in the dimeric

940



Figure 1. Thermal ellipsoid (25%) drawings of 7–9, 13, and 14. Hydrogen atoms are omitted for clarity. Only one of the two crystallographically independent molecules of 7 is shown. Selected metrical parameters for these compounds, as well as for 6 and 10–12 are given in Table 1. Symmetry transformations (') for 13: -x, y, -z+1/2; 14: 1-x, -y, -z.

Table 1. Selected interatomic distances [Å] and angles [°] for 6-14.

	6	7	8	9	10	11	12	13	14
M–N	2.022(2)	2.031(2)	2.118(2)	1.990(2)	2.038(3)	2.026(2)	2.038(3)	1.600(2)	2.347(2)
	2.023(2)	2.036(2)	2.095(16)	1.991(2)	2.041(3)	2.036(2)	2.049(4)	_	2.367(2)
	-	-	$2.270(2)^{[b]}$	-	-	-	$2.112(4)^{[b]}$	-	-
М-О	2.004(2)	2.019(2)	2.064(2)	-	2.039(3)	2.024(2)	-	-	2.378(2)
M–I	2.670(1)	2.6915(9)	2.827(1)	2.597(1)	2.651(1)	2.662(1)	2.672(1)	2.296(2)	3.1224(8)
						-	-	-	3.090(1)
N-M-N <sup>[a]</sup>	94.19(6)	92.80(7)	87.84(6)	97.11(6)	95.3(1)	92.97(9)	98.1(1)	111.8(2)	81.34(8)

[a] Angle associated with both  $\beta$ -diketiminate nitrogen centers. [b] Distance associated with the -NMe<sub>2</sub> or DMAP nitrogen center.

complex [(<sup>Dipp</sup>Nacnac)Mg( $\mu$ -X)<sub>2</sub>Mg(<sup>Dipp</sup>Nacnac)], X=Cl or Br<sup>[20]</sup>). This distortion is manifested by short Mg···C<sub>*ipso*</sub> interactions in the molecule (2.830 Å mean) compared with those in [(<sup>Dipp</sup>Nacnac)MgI(OEt<sub>2</sub>)] **5** (3.119 Å mean), for example.<sup>[18]</sup>

The molecular structure of the beryllium complex 13 is related to that of 9 in that it is monomeric with a distorted

trigonal-planar metal center. Both Be–N distances of the compound (1.600(2) Å) are at the short end of the reported range (1.502–1.943 Å),<sup>[21]</sup> whereas the Be–I distance (2.296(2) Å) is significantly shorter than those in the only other structurally characterized compound that contains a Be–I bond, [BeI<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>] (2.412 Å mean).<sup>[22]</sup> In contrast, compound **14** is dimeric in the solid state with iodide ligands

bridging the heavily distorted trigonal bipyramidal calcium centers (such as in the dimeric structures of  $[{(^{Dipp}Nacnac)Ca(thf)(\mu-X)}_2] X = F^{[23]}$  or  $Cl^{[24]}$ ).

Reductions of Group 2 metal(II) iodide precursor complexes: Previously we have shown that the reduction of 5 with an excess of potassium metal in toluene over 24 h gives a moderate yield of the yellow magnesium dimer 2.<sup>[10]</sup> When the reaction was carried out by using sodium metal as the reducing agent, a similar yield (ca. 50%) of 2 could be recovered after 5-7 days. Reduction of the closely related THF adduct 10 with sodium in toluene does give 2, but in reduced yields. Note that when an approximately 1:40 mixture of diethyl ether/toluene is used as the solvent, these reductions proceed more rapidly and with similar yields. It is thought that the presence of small amounts of the ether helps to dissolve the precursor. To test the facility of other reducing reagents, 5 was allowed to react with KC8 (1.2 equivalents) in toluene, or with an excess of freshly filed calcium metal in toluene. The former reaction led to low isolated yields of unreacted 5 and [K(<sup>Dipp</sup>Nacnac)], a moderate yield of 2, and a mixture of other products. This suggests that KC88 is a less controllable reducing reagent than potassium metal (at least in the reduction of 5), and that it can lead to over reduction of the magnesium(II) precursor. In contrast, no reaction was observed between 5 and the milder reducing agent, calcium metal.

Armed with the knowledge gained from the various reactions that gave 2, the development of synthetic protocols to access magnesium(I) compounds derived from the precursor complexes 6-9 was initiated. The only product that was isolated, in low yield, from the reductions of 6 with either potassium or sodium metal in toluene was the homoleptic complex [Mg(<sup>Ph</sup>Nacnac)<sub>2</sub>] (15), which was spectroscopically and crystallographically characterized. It is possible that the intermediate in this reaction was the target dimer [(<sup>Ph</sup>Nacnac)MgMg(<sup>Ph</sup>Nacnac)], but because of the sterically unhindered nature of its β-diketiminate ligand it disproportionates to 15 and magnesium metal under the reaction conditions employed. More success was achieved with the bulkier precursor 7, the sodium reduction of which, after five days, reproducibly gave the pale-yellow magnesium(I) compound 16 in yields greater than 50% [Eq. (6)]. Interestingly,

$$[LMgI(OEt_2)] \xrightarrow{\text{Na, PhMe}} [LMgMgL] \quad 16 \tag{6}$$
$$L = {}^{\text{Mes}} \text{Nachac}$$

reduction of this precursor with potassium metal also affords **16**, but only in very low isolated yields (ca. 2–5%). In contrast, reaction of the much bulkier precursor **9** with an excess of potassium in toluene gave a good yield of the orange magnesium(I) dimer, [(<sup>rBu</sup>Nacnac)MgMg(<sup>rBu</sup>Nacnac)] (**17**) after crystallization from toluene [Eq. (7)]. A different outcome resulted from the treatment of **12** with potassium in toluene, namely, the formation of an intractable mixture

of products. Both **16** (m.p. 201–203 °C) and **17** (m.p. 278–280 °C) are very thermally stable in the solid state, and toluene solutions of the compounds can be stored for weeks at 25 °C without showing signs of decomposition. Although the sodium or potassium reductions of the five-coordinate precursor **8** led to red-orange solutions (such as for the red-orange magnesium(I) adduct complexes **4**),<sup>[13]</sup> no identifiable magnesium-containing products were isolated from the reaction mixtures. Instead, the only product that was isolated from the reaction with potassium, and in very low yield, was [{K(<sup>Dmeda</sup>Nacnac)}<sub>6</sub>], which a poor-quality X-ray crystal structure revealed to be hexameric in the solid state. No further efforts were made to reduce compound **8**.

To shed light on the mechanisms and kinetics of the reactions that gave the magnesium(I) dimers 2, 16, and 17, two co-reduction experiments were carried out. In the first, an equimolar mixture of 9 and 5 was treated with an excess of potassium in toluene at 25 °C. After stirring for one day, a <sup>1</sup>H NMR spectrum of an aliquot of the mixture was obtained. This revealed the consumption of both starting materials and the predominant formation of 2 and 17. Resonances for several other products were observed in the spectrum, although none of these could be confidently identified or isolated from the reaction mixture. Accordingly, another co-reduction reaction of equimolar amounts of 5 and 7 was carried out by treatment of the mixture with an excess of potassium in toluene. The reaction was stopped after 24 h and work-up of the reaction mixture gave a low isolated yield of the unusual mixed-ligand hydride/iodide-bridged product  $[(^{Dipp}Nacnac)Mg(\mu-H)(\mu-I)Mg(^{Mes}Nacnac)]$  (18) as shown in [Eq. (8)]. At this stage it is not known what the

$$[LMgI(OEt_2)] \xrightarrow{K, PhMe} LMg \xrightarrow{H} MgL' 18$$

$$[L'MgI(OEt_2)] \xrightarrow{L= Mes}Nacnac$$

$$L' = ^{Dipp}Nacnac$$
(8)

other products of the reaction are, although the absence of significant amounts of **2** and **16** in the mixture possibly indicates that the reductions of **5** and **7** proceed at similar rates. What is of most interest, however, is the presence of a hydride ligand in **18**. This most likely results from hydrogen abstraction from the toluene solvent or magnesium-coordinated diethyl ether. Such processes are commonly observed in alkali-metal reductions of main group element halide complexes.<sup>[25]</sup>

The formation of compound **18** raised the question as to whether magnesium hydride complexes are by-products in the formation of **2**, **16**, and **17**. To probe this, aliquots were taken just prior to work-up from standard reduction reaction mixtures that gave these compounds. After removal of volatiles from the aliquots and dissolution of the residues in [D<sub>6</sub>]benzene, analyses were carried out by <sup>1</sup>H NMR spectroscopy. The reaction mixture that gave 17 contained no obvious magnesium hydride compounds or any other significant by-product. In contrast, the mixture that afforded the less kinetically protected complex 16 comprised an approximately 75:25 mixture of 16 and the homoleptic complex, [Mg(<sup>Mes</sup>Nacnac)<sub>2</sub>] (19). Other than small amounts of unidentified products in the reaction mixture that gave 2, the magnesium hydride complex 3 was also found to be present in significant amounts (ca. 15%) as determined by integration of its characteristic hydride resonance at  $\delta = 4.03$  ppm. Of further note is the presence of another hydride resonance in the spectrum at  $\delta = 4.00$  ppm, the integration of which is approximately half the value of the former. It is possible that this originates from a mixed hydride/iodide complex, [(<sup>Dipp</sup>Nacnac)Mg(µ-H)(µ-I)Mg(<sup>Dipp</sup>Nacnac)] (also see complex 18), although the product could not be isolated. The fact that significant amounts of hydride by-products are formed in this reaction and apparently not the other two is unusual. We cannot be sure why this is but it is noteworthy that the precursor to 17 (i.e., 9) does not incorporate coordinated ether, whereas the precursor to 2, [(DippNacnac)MgI- $(OEt_2)$ ], does. If the reduction that gave 2 is accompanied by hydrogen abstraction from diethyl ether (to give 3) but not from toluene, this might explain why the reaction mixture that generates 17 is free of magnesium hydride by-products. It could then be argued that the reduction that gives 16 from an ether-coordinated precursor does generate magnesium hydride by-products, but that these by-products are unstable with respect to redistribution to give the observed complex 19 and insoluble magnesium hydride materials such as MgH<sub>2</sub> or MgHI. It is unlikely that 19 forms through the disproportionation of 16 because the latter compound is thermally robust and its toluene solutions show no signs of decomposition for at least several weeks at room temperature.

In attempts to extend the above-mentioned chemistry to the formation of a Be-Be bonded dimer, the beryllium(II) iodide complex 13 was reduced with either lithium in diethyl ether, sodium in toluene, or potassium in a diethyl ether/toluene (1:40) mixture. In all cases, the <sup>1</sup>H NMR spectra of the reaction mixtures revealed that numerous products had been formed, none of which could be identified. It is possible that because of the smaller size of beryllium relative to magnesium, the reduction of 13 initially yields the radical [(<sup>Mes</sup>Nacnac)Be<sup>•</sup>], which undergoes intramolecular reactions (e.g., C-H activations) more rapidly than it can dimerize to give [(MesNacnac)BeBe(MesNacnac)].<sup>[26]</sup> It is of note that in the first minute of the lithium reduction, the reaction solution took on a deep-blue color, which rapidly faded thereafter. This is perhaps indicative of the presence of a reactive intermediate radical species, similar to that proposed. Given the greater electronegativity of magnesium over beryllium, the reduction of 13 with half an equivalent of [(<sup>Mes</sup>Nacnac)MgMg(<sup>Mes</sup>Nacnac)] **16** in [D<sub>6</sub>]benzene was also

## **FULL PAPER**

attempted. However, even when this mixture was heated in a sealed tube at 100 °C for several hours, more than 95% of each complex remained unreacted. That said, a very low yield (i.e., several crystals) of the magnesium(II) iodide complex [(<sup>Mes</sup>Nacnac)Mg( $\mu$ -I)<sub>2</sub>(<sup>Mes</sup>Nacnac)] deposited in the tube upon cooling, although there was no spectroscopic or other evidence for the corresponding generation of [(<sup>Mes</sup>Nacnac)BeBe(<sup>Mes</sup>Nacnac)]. The complex [(<sup>Mes</sup>Nacnac)Mg( $\mu$ -I)<sub>2</sub>(<sup>Mes</sup>Nacnac)] was crystallographically characterized although no spectroscopic data were obtained.<sup>[27]</sup>

Similarly, attempts were made reduce to  $[{(^{Dipp}Nacnac)CaI(OEt_2)}_2]$  14 or the previously reported complex [{(<sup>'Bu</sup>Nacnac)CaI(thf)}2]<sup>[28a]</sup> with sodium or potassium in toluene. No evidence for the formation of calcium(I) compounds was obtained, and the only product isolated from the reductions of 14 was the known homoleptic complex [Ca(<sup>Dipp</sup>Nacnac)<sub>2</sub>],<sup>[28b,c]</sup> whereas the sodium reduction of  $[{(^{Hu}Nacnac)CaI(thf)}_2]$  afforded a moderate yield (ca. 50%) of the crystallographically and spectroscopically characterized complex [{Na(<sup>tBu</sup>Nacnac)}<sub>2</sub>] (20). These results suggest that because of the larger size of calcium relative to magnesium,  $\beta$ -diketiminate coordinated calcium(I) dimers may not be stable towards disproportionation and/or other decomposition processes at room temperature.<sup>[29]</sup>

All of the compounds 15-20 were spectroscopically characterized, although comment will be passed here only on the data for 16–18. The <sup>1</sup>H NMR spectrum of 16 is indicative of this compound possessing high symmetry in solution in that it displays three sharp methyl resonances (two associated with the mesityl groups and one arising from the backbone methyl substituents). This implies unrestricted partial or full rotation of its mesityl groups about the exocyclic N-C bonds and/or rotation of the two magnesium heterocycles about the Mg-Mg bond of the compound. Similarly, the spectrum of 17 exhibits only two isopropyl methyl doublet resonances and one methine septet resonance. However, at 298 K these are broad, which indicates restricted rotation of its 2,6-diisopropylphenyl groups and/or the two sterically bulky magnesium heterocycles. Heating solutions of 17 in [D<sub>6</sub>]benzene to 340 K leads to a sharpening of all resonances in the spectrum. This implies that at this temperature the previously restricted rotations become rapid with respect to the NMR timescale. No signals were observed in the <sup>25</sup>Mg{<sup>1</sup>H} NMR spectra of nearly saturated [D<sub>6</sub>]benzene solutions of either 2, 16, or 17, presumably because of the quadrupolar nature and low natural abundance (I=5/2,10% abundant) of that nucleus. The <sup>1</sup>H NMR spectrum of 18 highlights sets of resonances for both its <sup>Dipp</sup>Nacnac and <sup>Mes</sup>Nacnac ligands in addition to a singlet at  $\delta = 3.92$  ppm, which corresponds to the bridging hydride ligand.

Molecular ion peak envelopes having the expected isotopic mass distributions were observed in the electron ionization mass spectra (EIMS) of **16** and **17** (as was the case for **2**), whereas the only identifiable fragments in the EIMS of **18** were derived from the free  $\beta$ -diketiminate ligands. The infra-red (IR) spectra of **16** and **17** appear to show only ligand vibrational modes, and no Mg–H stretching bands could be assigned in the IR spectrum of **18**. It is believed that the latter are masked by ligand modes in the fingerprint region of the spectrum. A number of low-wavenumber absorptions were observed in the Raman spectra of **16** and **17**, which could not be confidently assigned as arising from Mg–Mg stretching modes. It is noteworthy, however, that the most intense of these (**16**:  $\tilde{\nu} = 151 \text{ cm}^{-1}$ ; **17**:  $\tilde{\nu} = 154 \text{ cm}^{-1}$ ) occur close to that for **2** ( $\tilde{\nu} = 148 \text{ cm}^{-1}$ ),<sup>[10]</sup> and all are at lower wavenumbers than that experimentally detected for the Mg–Mg vibration mode of the two-coordinate compound ClMgMgCl ( $\tilde{\nu} = 176 \text{ cm}^{-1}$ ).<sup>[3a]</sup>

Complexes 15-20 were crystallographically authenticated,<sup>[27]</sup> although only the molecular structures of 16-18 are depicted in Figure 2 (see Table 2 for the relevant metrical parameters). Both 16 and 17 are Mg-Mg bonded dimers but there are significant differences between them. First, the Mg-Mg distance for the less-hindered compound 16 (2.808(1) Å) is markedly shorter than that for the very-hindered compound 17 (2.847(2) Å). Interestingly, the Mg–Mg bond length in one polymorph of the previously reported compound 2 (2.8457(8) Å)<sup>[10]</sup> is not significantly different to that of 17, and in another polymorph it is slightly longer  $(2.8624(15)\ \text{\AA})^{[14]}$  despite the lesser steric buttressing of the magnesium heterocycles of that compound. Although the nitrogen substituents of both complexes are the same, the steric differences between the two compounds arise from the variation in size of the backbone methyl (in 2) versus tert-butyl substituents (in 17) of the compounds. This disparity can be quantified to some extent by an examination of their C-N-C angles, which for 2 (mean = 118.6°) are considerably less than those for 17 (mean =  $123.5^{\circ}$ ).<sup>[30]</sup> Differences in ligand sterics can also be used to explain the fact that the magnesium heterocycles of 16 are essentially planar, whereas those of both 2 and 17 are somewhat distorted from planar (mean distance of Mg atoms from the NCCCN leastsquares planes: 16 = 0.129 Å, 2 = 0.529 Å, 17 = 0.624 Å).<sup>[31]</sup> Also of note is the fact that the dihedral angles between the least-squares planes of the bulkier heterocycles of 2 and 17 (80.2° and 76.5°, respectively) are much larger than that of 16 (43.9°). The more obtuse angles of the former pair probably aid a minimization of the intramolecular interactions of the bulky Dipp substituents of those compounds. It might be expected that close to orthogonal heterocycles would also be favored for 16. The fact that this does not occur may be a result of crystal-packing effects overriding the intracyclic interactions between the mesityl groups in the compound and/or the likely weak barrier to rotation about its Mg-Mg bond. Whatever the case, it is worthy to mention that the corresponding zinc(I) dimer [(<sup>Mes</sup>Nacnac)ZnZn(<sup>Mes</sup>Nacnac)] (dihedral angle between least squares heterocycle planes = 44.6°; Zn–Zn distance = 2.3813(8) Å) is isostructural to 16.<sup>[9d]</sup>

Although the absence of hydride ligands bridging the Mg centers of 2 has been proven by the preparation of the magnesium(II) hydride complex 3 (see above), this is not yet the case for 16 (see below). Accordingly, a neutron diffraction



Figure 2. Thermal ellipsoid (25%) drawings of **16–18**. Hydrogen atoms (except H(1) in the structure of **18**) are omitted for clarity. Selected metrical parameters for these compounds are given in Table 2. Symmetry transformations (') for **16**: -x+1/2, y, -z+1/2; **17**: -x+1, y, -z+1/2.

study was undertaken on **16**, full details of which can be found in the Supporting Information.<sup>[27]</sup> All hydrogen and non-hydrogen atoms of the molecule were included in the refinement. The observed metrical parameters for the compound are essentially the same as those obtained from the

944 -

Table 2. Selected interatomic distances [Å] and angles [°] for 16-18.

16		17				18			
Mg1-N1	2.039(1)	Mg1-N1	2.077(2)	Mg1-N1	2.036(4)	Mg1-N2	2.037(5)	Mg1–I1	2.865(2)
Mg1-N2	2.037(2)	Mg1-N2	2.069(2)	Mg1-H1	1.88(8)	N1-C2	1.316(7)	N2-C4	1.345(7)
Mg1-Mg1	2.808(1)	Mg1-Mg1'	2.847(2)	C2-C3	1.410(8)	C3-C4	1.400(8)	Mg2-N4	2.024(5)
N1-C2	1.329(2)	N1-C2	1.324(3)	Mg2–N3	2.028(5)	Mg2-H1	1.98(8)	Mg2–I1	2.758(2)
N2-C4	1.331(2)	N2-C4	1.350(3)	N3-C31	1.326(8)	N4-C33	1.325(8)	C31-C32	1.401(9)
C2-C3	1.407(2)	C2-C3	1.429(3)	C32-C33	1.411(9)	Mg1…Mg2	3.101(2)		
C3-C4	1.405(2)	C3-C4	1.401(3)						
N2-Mg1-N1	91.99(6)	N2-Mg1-N1	93.90(9)	N1-Mg1-N2	93.6(2)	N4-Mg2-N3	94.6(2)		
N2-Mg1-Mg1'	135.08(5)	N2-Mg1-Mg1'	133.35(7)	Mg2-I1-Mg1	66.92(6)	Mg2-H1-Mg1	107(1)		
N1-Mg1-Mg1'	132.86(5)	N1-Mg1-Mg1'	132.12(7)						

X-ray crystal structure. Importantly, no significant residual nuclear density was located near the Mg–Mg vector of the compound. Therefore, the possibility of hydride ligands between the magnesium centers of the compound can be eliminated.

The molecular structure of **18** reveals it to possess two essentially co-planar magnesium heterocycles, which are bridged by one hydride and one iodide ligand. The hydride (H1) was located from difference maps and its positional parameters were freely refined. This allowed the observation that the hydride and iodide ligands do not symmetrically bridge the two magnesium centers, because the iodide has a significantly closer interaction with the [Mg(<sup>Mes</sup>Nacnac)] heterocycle than the [Mg(<sup>Dipp</sup>Nacnac)] heterocycle than the [Mg(<sup>Dipp</sup>Nacnac)] heterocycle than the [Mg(<sup>Dipp</sup>Nacnac)] heterocycle than the Mg…Mg separation (3.101(2) Å) is significantly longer than in the magnesium(II) compounds **2**, **16**, or **17** and in the magnesium(II) hydride dimer **3** (2.890(2) Å).

Reactivity of magnesium(I) dimers: The availability of a series of magnesium(I) dimers of varying steric bulk, namely, 17 > 2 > 16, presented the opportunity of comparing the further reactivity of these compounds. In the first instance, two magnesium heterocycle scrambling reactions were attempted by dissolving approximately equimolar mixtures of 2 and 16 or 2 and 17 in  $[D_6]$  benzene and monitoring the solutions by <sup>1</sup>H NMR spectroscopy. In each case no reaction occurred at 25 °C or when the solutions were heated at 100 °C for one hour. This strongly suggests that there is no appreciable dimer/monomer equilibrium in solution for all of the compounds, despite the aforementioned experimental evidence for the deformability of the Mg-Mg bond of 2. This result is, however, consistent with the relatively high Mg-Mg bond-dissociation energies that have been calculated for magnesium(I) dimers.<sup>[3a,6,13]</sup>

Compound **2** has been shown to readily form adducts **4** with several ether or pyridine Lewis bases (such as THF, dioxane, 4-*tert*-butylpyridine, or DMAP).<sup>[13]</sup> X-ray crystallography revealed the two magnesium heterocycles of all of these complexes to be effectively parallel, as opposed to the nearly orthogonal heterocycles in **2**. This change in the orientation of the heterocycles likely occurs to sterically accommodate coordination of the Lewis bases. For comparison, the less bulky magnesium(I) dimer **16** was treated with

either THF or DMAP, which led to moderate isolated yields of the adduct complexes  $[(^{Mes}Nacnac)Mg(L)-Mg(L)(^{Mes}Nacnac)]$ , in which L=THF (21) or DMAP (22) as described in [Eq. (9)]. In contrast, the more bulky magnesium(I) dimer 17 does not react when dissolved in neat THF



and is recovered in good yield after its treatment with DMAP in toluene or  $[D_6]$ benzene.<sup>[32]</sup> Presumably, the low reactivity of **17** towards Lewis base coordination is derived from its sterically well-shielded Mg centers. It is interesting that, although compound **21** readily loses its THF of coordination (at >85 °C under N<sub>2</sub>), it is more resistant to this process than is **4** (L=THF. THF loss occurs at >70 °C under N<sub>2</sub>).<sup>[13]</sup> It is thought that this higher stability results from the lesser steric bulk of the  $\beta$ -diketiminate ligands of **21**, which leads to stronger THF coordination than in **4** (in which L=THF).

Compounds 21 and 22 were spectroscopically characterized. As was the case for 4, the NMR spectra of 21 and 22 that were recorded in  $[D_6]$ benzene display fewer resonances than would be expected if their THF or DMAP ligands remained strongly coordinated in solution. It seems, therefore, that a fluxional ligand dissociation/coordination process is occurring for the complexes, which is rapid compared with the NMR timescale, and leads to time-averaged structures for the complexes that are more symmetrical than the solidstate structures. The low solubility of complexes 21 and 22 in  $[D_8]$ toluene at temperatures below 0°C precluded lowtemperature NMR spectroscopic studies on the compounds.

Although X-ray crystal structures of both **21** and **22** were obtained, only that of **22** was of sufficient quality for inclusion here (Figure 4, Table 3).<sup>[33]</sup> The two Mg centers of the compound possess flattened tetrahedral geometries with Mg–N<sub>DMAP</sub> bonds that are significantly longer than the Mg–N<sub>Nacnac</sub> interactions. Note that the former are somewhat

www.chemeurj.org

Table 3.	Selected	interatomic	distances	[Å]	and angles	[°]	for 22	2 and	27-2	29.

22		27		28		29	
Mg1–Mg2	2.937(1)	Mg1-N1	2.041(2)	Mg1-N1	2.020(3)	Mg1-N1	2.060(1)
Mg1-N1	2.120(2)	Mg1-N2	2.072(2)	Mg1-N2	2.030(2)	Mg1-N2	2.051(1)
Mg1-N2	2.126(2)	Mg1-N3	2.078(2)	Mg1-N3	2.051(2)	Mg1-N3	2.062(1)
Mg1-N5	2.202(2)	Mg1-N5'	2.042(2)	Mg1-N5'	2.044(2)	Mg1–N4	2.101(1)
Mg2–N3	2.131(2)	N3-N4	1.304(3)	N3-N4	1.303(3)	Mg2–N5	2.011(1)
Mg2–N4	2.122(2)	N4-N5	1.312(3)	N4-N5	1.309(3)	Mg2–N6	2.017(1)
Mg2–N7	2.209(2)	N5-N5′	1.419(4)	N5-N5′	1.423(4)	Mg2-O1	1.952(1)
N2-Mg1-N1	87.96(7)	N2-Mg1-N1	97.95(8)	N2-Mg1-N1	94.4(1)	Mg2-O2	1.963(1)
N5-Mg1-Mg2	111.49(5)	Mg1-N3-N4	116.6(1)	Mg1-N3-N4	117.3(2)	C24-N3	1.302(2)
N3-Mg2-N4	88.60(6)	N3-N4-N5	118.0(2)	N3-N4-N5	117.3(2)	C25-N4	1.300(2)
N7-Mg2-Mg1	111.84(5)	N4-N5-N5'	114.9(2)	N4-N5-N5'	114.4(2)	C24-O1	1.282(2)
						C25-O2	1.287(2)
						C24-C25	1.548(2)
						N1-Mg1-N2	92.27(5)
						N5-Mg2-N6	94.19(5)

shorter than the related bonds in 4 (L=DMAP; Mg- $N_{DMAP} = 2.235(2) \text{ Å})^{[13]}$  which is consistent with the less-hindered magnesium centers of 22. There are a number of other notable differences between the geometries of the two compounds. These include the dihedral angle between their Mg heterocycle least-squares planes, which is much more obtuse in 22 (72.2° as compared with 43.9° in 16) than in 4 (L=DMAP; 3.4° as compared with 80.2° in 2). In addition, the Mg-Mg distance in 22 (2.9369(12) Å) is shorter than that recorded for 4 (L=DMAP, 3.1962(14) Å). However, it should be pointed out that the latter compound co-crystallized with approximately 8% of the corresponding magnesium(II) hydroxide complex [{(<sup>Dipp</sup>Nacnac)Mg(DMAP)(µ-OH)]2],<sup>[34]</sup> and therefore its Mg–Mg distance cannot be considered as completely accurate. No similar co-crystallization occurred for 22, and accordingly the magnitude of the significant increase (by ca. 0.13 Å) in the Mg-Mg distance of 16 upon coordination with DMAP (to give 22) is reliable. It is very likely that the steric differences between the  $\beta$ -diketiminate ligands MesNacnac and DippNacnac are the origin of the contrasting geometries of 22 and 4 (L = DMAP).

It has been demonstrated that the magnesium(I) dimer 2 acts as a facile two-center/two-electron reducing agent towards a variety of N- or O-functionalized unsaturated organic substrates. For example, its reactions with CyN=C= NCy (Cy=cyclohexyl), PhN=NPh,  $AdN_3$  (Ad=1-adamantyl), or tBuN=C=O gave good yields of the complexes 23-26, respectively (Figure 3).<sup>[15]</sup> The mechanisms of these reactions are thought to involve coordination of each substrate at the magnesium centers of 2 prior to their reduction.<sup>[35,36]</sup> Evidence for this includes the fact that compound 4 (L =THF) is unreactive towards CyN=C=NCy in neat THF, most likely because its magnesium centers are coordinatively saturated. If this proposal is correct, it was believed that the more accessible Mg centers of 16 would lead to it being a more effective reducing agent than 2, whereas the hindered system 17 would be a less effective reductant.

This proved to be the case because the more hindered of the four substrates, CyN=C=NCy and PhN=NPh, did not react with **17** in toluene at ambient temperature. There was



Figure 3. Previously reported reduction products from reactions of **2** with unsaturated substrates.

a reaction between **17** and the less-hindered substrate tBuN=C=O at room temperature although an inseparable mixture of products resulted from this. Compound **17** behaved similarly to **2** with regard to its reaction with AdN<sub>3</sub>, which proceeded at -78 °C and afforded a moderate yield of the azide coupled product **27** as described by [Eq. (10)]. Reactions of less-hindered **16** with all four substrates took place rapidly in toluene at -78 °C, but tractable products from those with the carbodiimide or azobenzene could not



946

be isolated upon work-up.<sup>[37]</sup> The reaction with the azide yielded a product analogous to **25** and **27** (namely, complex **28**), whereas that with tBuN = C=O afforded a moderate isolated yield of the reductively coupled product **29** as described by [Eq. (11)]. The structural similarities between the



azide-coupled products 25, 27, and 28 are obvious, and all are isostructural to the only other known alkyl azide-coupled complexes  $[(L)Fe^{II}(\mu-AdN_6Ad)Fe^{II}(L)]$   $(L=^{Dipp}Nacnac$ or <sup>tBu</sup>Nacnac) reported by Holland and co-workers to be formed in reactions of  $AdN_3$  with  $\beta$ -diketiminato iron(I) complexes.<sup>[38]</sup> Like the iron complexes, compounds 25, 27, and 28 do not appear to be shock or thermally sensitive to detonation, despite containing covalently bonded N<sub>6</sub> chains within their dianionic bridging ligands. This contrasts to some related hexaazadienes, RNNN(R)N(R)NNR (R= alkyl, aryl etc.,), which are high-energy materials that can be susceptible to explosion.<sup>[39]</sup> Metal-induced isocyanate reductive-coupling reactions have been previously reported, but their products normally incorporate a bridging N.O-chelating ligand, for example,  $[L_nM{ON(R)C_2N(R)O}ML_n]$ , with two delocalized OCN fragments.<sup>[40]</sup> Conversely, the coupled ligand in 26 was reported to be largely localized and exhibited an unprecedented N,O/O,O'-ligation of its two Mg centers. In 29, the same bridging ligand exhibits delocalization over its NCO units, but coordinates the two {Mg(MesNacnac)} fragments in a N,N'/O,O'-mode. To the best of our knowledge this has not been previously observed in an isocyanate coupled complex. The differences between the ligating mode of  $[O_2C_2N_2tBu_2]^{2-}$  in **26** and **29** are again thought to be of a steric origin. That is, N,N'-chelation of the {Mg(<sup>Dipp</sup>Nacnac)} fragment by two bulky NtBu units is expected to be disfavored, as compared with a similar chelation of the smaller {Mg(MesNacnac)} moiety.

The spectroscopic data for **27–29** are consistent with them retaining their solid-state structures in solution and will not be commented on here. Each compound was crystallographically authenticated and their molecular structures are shown in Figure 4 (see Table 3). The structures of **27** and **28** are closely related to each other and that of **25** in that they possess distorted tetrahedral Mg centers that are chelated by close to planar  $[AdN_6Ad]^{2-}$  ligands. The bond lengths of the N<sub>6</sub> fragment of each compound are suggestive of delocalization over the outer N<sub>3</sub> units, whereas the central N–N distance is reminiscent of a single bond. In **29**, the MgO<sub>2</sub>C<sub>2</sub>N<sub>2</sub>Mg bicyclic unit is effectively planar and its C–O and C–N distances are normal for delocalized double bonds, whereas the central C–C separation is indicative of a single bond.

## **FULL PAPER**

It would be expected that the addition of dihydrogen to the Mg-Mg bonds of magnesium(I) dimers to give compounds of the type [LMg(µ-H)<sub>2</sub>MgL] would be an exothermic process. Indeed, for a range of complexes in which L is an N,N'-chelating guanidinate ligand (such as 1), calculations have shown the magnitude of this exothermicity to be approximately 24 kcal mol<sup>-1.[41]</sup> This can be compared with the enthalpy of hydrogenation of magnesium metal to give MgH<sub>2(s)</sub>, which is  $-17.9 \text{ kcal mol}^{-1}$ .<sup>[42]</sup> Despite this, high temperatures (>250 °C) and/or H<sub>2</sub> pressures are generally required to overcome the kinetic barrier to this reaction. Similarly, compounds 1 and 2 have been found to be unreactive towards H<sub>2</sub> at one atmosphere pressure and 80 °C in arene solvents.<sup>[10]</sup> In the current study we have extended this prior work to the treatment of the less-hindered dimer 16 with dihydrogen. Under one atmosphere of H<sub>2</sub> in toluene, the compound showed no signs of hydrogenation after 4 h at 80°C. When higher hydrogen pressures were employed in reaction vessels containing toluene solutions of either 16 or 2 (ca. 5 atm.), and the mixtures were heated at 80°C for four hours, still no hydrogenation reactions occurred and the starting materials were recovered. When the pressures in these reaction vessels were increased to approximately 70 atmospheres and the mixtures were heated at 80 °C for four hours, NMR spectroscopic analyses showed that the reactions yielded numerous products, which are believed to be β-diketiminate cleavage and/or hydrogenation products. On no occasion was there any convincing evidence for the presence of the target magnesium hydride complexes in the reaction mixtures.

Preparation and characterization of magnesium(II) hydride complexes: As already mentioned, definitive proof of the absence of hydride ligands bridging the metal centers of 2 came with the synthesis of 3. This compound was prepared in moderate yield by heating a hexane solution of [(<sup>Dipp</sup>Nacnac)MgnBu] and PhSiH<sub>3</sub> at reflux for two days.<sup>[13,43]</sup> Its subsequent treatment with THF led to the adduct  $[(^{\text{Dipp}}\text{Nacnac})Mg(thf)(\mu-H)_2Mg(thf)(^{\text{Dipp}}\text{Nacnac})].^{[13]}$ Compound 3 represented the first example of a structurally characterized complex of the general type, [LMg(µ-H)<sub>2</sub>MgL],<sup>[44,45]</sup> and it was shown to act as an effective hydromagnesiation reagent towards a range of unsaturated substrates.<sup>[15]</sup> To extend the chemistry of well-defined, neutral magnesium hydride complexes, and to draw comparisons with the magnesium(I) dimers 16 and 17, the preparation of magnesium hydride complexes incorporating the MesNacnac and <sup>tBu</sup>Nacnac ligands was explored.

In an attempt to access the magnesium hydride complex  $[(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)]$ ,  $^{Mes}NacnacH$  was heated with one equivalent of  $MgnBu_2$  in toluene for two hours at 60 °C and the volatiles were removed in vacuo to yield a solid residue. This was dissolved in hexane, treated with PhSiH<sub>3</sub>, and the solution was heated at reflux for three days. The only identifiable product obtained from the reaction mixture was a low isolated yield of the homoleptic compound **19**. This result could indicate that  $[(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)Mg(\mu-H)_2Mg(^{Mes}Nacnac)$ 



Figure 4. Thermal ellipsoid (25%) drawings of 22 and 27–29. Hydrogen atoms from all structures and isopropyl groups from the structure of 27 are omitted for clarity. Only one of the two crystallographically independent molecules of 28 is shown. Selected metrical parameters for these compounds are given in Table 3. Symmetry transformations (') for 27: -x, -y+2, -z; 28: -x+1, -y, -z.

H)<sub>2</sub>Mg(<sup>Mes</sup>Nacnac)] was generated in the reaction, but the compound is unstable with respect to redistribution under the reaction conditions employed. Compound **19** was subsequently intentionally synthesized in good yield (68%) by the reaction of two equivalents of <sup>Mes</sup>NacnacH with MgnBu<sub>2</sub>.<sup>[46]</sup> All other attempts to prepare [(<sup>Mes</sup>Nacnac)Mg-( $\mu$ -H)<sub>2</sub>Mg(<sup>Mes</sup>Nacnac)] such as by the treatment of [(<sup>Mes</sup>Nacnac)MgCH<sub>2</sub>Ph] with PhSiH<sub>3</sub> have so far proved to be fruitless.

It seemed reasonable that magnesium hydride complexes incorporating the bulkier <sup>*i*Bu</sup>Nacnac ligand would be more accessible than [(<sup>Mes</sup>Nacnac)Mg( $\mu$ -H)<sub>2</sub>Mg(<sup>Mes</sup>Nacnac)]. An example of such a complex was ultimately prepared by deprotonating <sup>*i*Bu</sup>NacnacH with MgnBu<sub>2</sub> to yield in situ generated [(<sup>*i*Bu</sup>Nacnac)MgnBu], which was subsequently treated with PhSiH<sub>3</sub> and heated at reflux in toluene for two days. Upon work-up of the reaction mixture, the complex [(<sup>*i*Bu</sup>Nacnac)Mg( $\mu$ -H)<sub>2</sub>Mg(<sup>*i*Bu</sup>Nacnac)] (**30**) was isolated as a colorless crystalline material in moderate yield as described in [Eq. (12)]. It is of note that a higher reaction temperature is required for the synthesis of **30** than for the preparation of **3**, probably because of the greater steric bulk of the  $\beta$ -di-



ketiminate ligand in the former. Unlike **3**, compound **30** does not appear to form an isolable complex with THF, but when treated with the stronger Lewis base, DMAP, a good yield of the monomeric magnesium hydride complex  $[(^{IBu}Nacnac)Mg(H)(DMAP)]$  (**31**) resulted as shown in [Eq. (13)]. This represents the first example of a complex that is structurally authenticated as possessing a terminal

948 -



Mg–H bond and it contrasts with the dimeric structure of the related complex  $[(^{Dipp}Nacnac)Mg(thf)(\mu-H)_2Mg-(thf)(^{Dipp}Nacnac)].^{[13]}$ 

The NMR spectroscopic data for 30 and 31 are compatible with their solid-state structures (see below) and both exhibit singlet hydride resonances (30:  $\delta = 3.83$  ppm, 31:  $\delta =$ 4.65 ppm) in their <sup>1</sup>H NMR spectra that lie close to those reported for **3** ( $\delta = 4.03$  ppm) and [(<sup>Dipp</sup>Nacnac)Mg(thf)( $\mu$ -H)<sub>2</sub>Mg(thf)(<sup>Dipp</sup>Nacnac)] ( $\delta$  = 4.21 ppm). After examinations of the IR spectra (Nujol mulls) of solid samples of both complexes, Mg-H stretching bands could not be confidently assigned. In the case of 30, this is not surprising because stretching bands associated with Mg-H-Mg moieties have been reported to occur in the range 1250–1300 cm<sup>-1</sup>, and thus for 30 these could be masked by ligand vibration modes.<sup>[44]</sup> The terminal Mg-H stretching absorption of 31 would, however, be expected to occur at a significantly higher wavenumber. For amido magnesium hydride complexes,  $[{Mg(NR_2)H}_2]$ , purported to exhibit bridging amide and terminal hydride ligands, Mg-H stretching bands in the range 1580-1630 cm<sup>-1</sup> have been reported.<sup>[44]</sup> The IR spectrum of **31** exhibits an intense band centered at  $1614 \text{ cm}^{-1}$ , which was originally considered to arise from a Mg-H stretching mode. However, an examination of the IR spectrum of the isostructural complex 12 showed it to be almost identical to that of 31, and therefore, this band likely results from a stretching mode associated with an unsaturated N-C bond of the DMAP ligand. Preparation of the deuterated analogues of 30 and 31 would shed light on the positions of the Mg-H stretching bands of these complexes. This would, however, be very difficult to achieve by using the synthetic methods employed to generate the nondeuterated compounds, and thus was not attempted.

Both **30** and **31** were crystallographically characterized and their molecular structures are depicted in Figure 5 (see Table 4). The hydride ligands of both complexes were located from difference maps and their positional parameters freely refined. In the case of **30**, this highlights one magnesium atom of the compound (Mg(1)) to have a distorted square-planar geometry, whereas the other (Mg(2)) has distorted tetrahedral geometry. Unusually, this results in the two magnesium heterocycles of the compound being close to orthogonal (the dihedral angle between least-squares planes = 77.8° in **30** as compared with 76.5° in **17**), which contrasts with the close to parallel magnesium heterocycles in **3**. These differences are almost certainly a result of the differing steric profiles of the β-diketiminate ligands in the complexes. That said, the Mg···Mg separation in **30** 



Figure 5. Thermal ellipsoid (25%) drawings of **30** and **31**. Hydrogen atoms are omitted for clarity. Selected metrical parameters for these compounds are given in Table 4.

Table 4. Selected interatomic distances [Å] and angles [°] for 30 and 31.

30		31				
Mg1…Mg2	2.835(2)	Mg1-N1	2.066(3)			
Mg1-N1	2.053(4)	Mg1-N2	2.077(3)			
Mg1-N2	2.071(4)	Mg1-N3	2.135(3)			
Mg1-H1	1.91(5)	Mg1-H1	1.75(7)			
Mg1-H2	1.80(5)	N2-Mg1-N1	94.4(1)			
Mg2-N3	2.056(4)	N1-Mg1-N3	104.4(1)			
Mg2-N4	2.036(4)	N2-Mg1-N3	105.7(1)			
Mg2-H1	1.82(5)	N1-Mg1-H1	124(2)			
Mg2-H2	1.84(5)	N2-Mg1-H1	121(2)			
N1-Mg1-Mg2	94.5(2)	N3-Mg1-H1	106(2)			
H1-Mg1-H2	78(2)					
N3-Mg2-N4	96.5(2)					
H1-Mg2-H2	80(2)					

(2.835(2) Å) is shorter than that in the less-hindered compound **3** (2.890(2) Å), and intriguingly, is less than the Mg–Mg bond length of the magnesium(I) dimer **17**. Compound

**31** is monomeric and possesses a distorted tetrahedral magnesium center that contains a terminal hydride ligand. The Mg–N<sub>Nacnac</sub> and Mg–N<sub>DMAP</sub> bond lengths are significantly less than those in the magnesium(I) dimer **4** (L=DMAP), but are close to those in the isostructural magnesium(II) iodide complex **12**.

### Conclusion

In summary, the preparation and characterization of a series of magnesium(II) iodide complexes incorporating β-diketiminate ligands of varying steric bulk and denticity has been described. In addition, one example each of a  $\beta$ -diketiminato beryllium iodide and calcium iodide complex has been synthesized and fully characterized. The reductions of all metal(II) iodide complexes by using various reagents were attempted. In two instances, previously unreported dimeric magnesium(I) complexes 16 and 17 resulted from the reduction reactions. It is apparent from the other reactions that the less bulky magnesium(I) dimer [(<sup>Ph</sup>Nacnac)MgMg-(<sup>Ph</sup>Nacnac)] is unstable with respect to disproportionation, and that the potentially tridentate  $\beta$ -diketiminate ligand DmedaNacnac is not effective for the synthesis of isolable magnesium(I) complexes. The attempted reductions of beryllium(II) and calcium(II) iodide precursor complexes have not been successful so far, which indicates that β-diketiminate stabilized beryllium(I) and calcium(I) complexes may be difficult targets to achieve.

A comparison of the reactivity of **16**, **17**, and the previously reported magnesium(I) complex **2** towards a variety of Lewis bases and unsaturated organic substrates has been carried out. The results of these investigations show the complexes to be facile two-center/two-electron reductants, and imply that their steric bulk is inversely proportional to their reactivity towards the substrates studied. The tunable and often selective reducing abilities of these compounds, coupled with their solubility, ease of handling, and straightforward syntheses give them much potential as alternatives to more classical reducing agents such as s-block metals or Sm<sup>II</sup> compounds,<sup>[47]</sup> which are widely employed in organic and organometallic synthetic methodologies.

To definitively disprove the presence of bridging hydride ligands in 16 and 17, attempts were made to prepare their magnesium(II) hydride counterparts [(MesNacnac)Mg(µ-[(<sup>tBu</sup>Nacnac)Mg(µ-H)<sub>2</sub>Mg- $H_2Mg(^{Mes}Nacnac)]$ and (<sup>tBu</sup>Nacnac)], respectively. Only the latter complex could be accessed in this study and it was found to have very different properties to 17, thereby confirming that 17 is not a magnesium hydride complex. Its treatment with the strong Lewis base, DMAP, led to the formation of the monomeric complex,  $[({}^{Bu}Nacnac)Mg(H)(DMAP)]$ , which exhibits the only known example of a structurally characterized terminal Mg-H moiety. Although the other magnesium(II) hydride complex [(MesNacnac)Mg(µ-H)2Mg(MesNacnac)] could not be isolated, the absence of hydride ligands in 16 was alternatively confirmed by a neutron diffraction study of that complex.

#### **Experimental Section**

General methods: All manipulations were carried out by using standard Schlenk and glove-box techniques under an atmosphere of high-purity dinitrogen. Toluene, hexane, THF, and benzene were distilled over molten potassium, whereas diethyl ether was distilled over a Na/K alloy (25:75). <sup>1</sup>H and <sup>13</sup>C<sup>1</sup>H NMR spectra were recorded on either Bruker DPX 300 or DPX 400 spectrometers in deuterated solvents and were referenced to the residual <sup>1</sup>H or <sup>13</sup>C resonances of the solvent used. In data assignments m<sub>c</sub> denotes the chemical shift at the center of a multiplet. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded by using a Perkin-Elmer RXI FTIR spectrometer as Nujol mulls between NaCl plates. Raman spectra were recorded for crystalline samples sealed in glass capillaries under dinitrogen by using a Renishaw RM2000 microRaman spectrometer with 782 nm excitation from a diode laser. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Microanalyses were obtained from Campbell Microanalytical (Ottago, NZ). DippNacnacH, [48] PhNacnacH, [49] MesNacnacH, [48] DmedaNacnacH [50], and <sup>1Bu</sup>NacnacH<sup>[51]</sup> were synthesized by variations of literature procedures. All other reagents were used as received.

[ $(^{Dipp}$ Nacnac)MgI(OEt<sub>2</sub>)] (5): A freshly prepared solution of MeMgI (25.4 mmol) in diethyl ether (80 mL) was added over 20 min to a stirred solution of <sup>Dipp</sup>NacnacH (9.50 g, 22.7 mmol) in diethyl ether (100 mL) at -20 °C, yielding a colorless precipitate. The suspension was warmed to room temperature and stirred for 1 h after which time the precipitate of 5 was collected by filtration. The supernatant solution was concentrated to ca. 40 mL and cooled to -30 °C to afford a second crop of 5 (yield = 11.0 g, 75%). The spectroscopic data for the complex were identical to those previously reported.<sup>[18]</sup>

[ $^{Ph}$ Nacnac)MgI(OEt<sub>2</sub>)] (6): The compound was synthesized by using a similar procedure to that employed for the preparation of **5**, but by using  $^{Ph}$ NacnacH (2.5 g, 10.0 mmol). After work-up compound **6** was obtained as a yellow crystalline solid (yield=2.90 g, 61%). M.p. 102–107°C;  $^{1}$ H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta$ =0.54 (t,  $^{3}J_{H-H}$ =7.0 Hz, 6H; CH<sub>2</sub>CH<sub>3</sub>), 1.73 (s, 6H, NCCH<sub>3</sub>), 3.26 (q,  $^{3}J_{H-H}$ =7.0 Hz, 4H; CH<sub>2</sub>CH<sub>3</sub>), 4.75 (s, 1H, CH), 6.61–7.39 ppm (m, 10H; Ar-H);  $^{13}$ C[<sup>1</sup>H] NMR: (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta$ =13.5 (CH<sub>2</sub>CH<sub>3</sub>), 23.7 (NCCH<sub>3</sub>), 639 (CH<sub>2</sub>CH<sub>3</sub>), 97.2 (CH), 124.3 (Ar-C), 125.4 (Ar-C), 129.3 (Ar-C), 149.9 (Ar-C), 168.0 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\bar{\nu}$ =1632 (w), 1595 (m), 1552 (s), 1238 (s), 1298 (m), 1315 (m), 1279 (m), 1194 (m), 1123 (m), 1090 (m), 1073 (m), 1029 (s), 997 (m), 764 (m), 753 (m), 700 cm<sup>-1</sup> (m).

 $[(^{Mes}Nacnac)MgI(OEt_2)]$  (7): The compound was synthesized by using a similar procedure to that employed for the preparation of 5, but by using <sup>Mes</sup>NacnacH (10.0 g, 29.9 mmol). After work-up compound 7 was obtained as a colorless crystalline solid (yield=14.60 g 68%). M.p. 192-194°C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.61$  (brt, <sup>3</sup> $J_{H-H} = 7.0$  Hz, 6H; CH<sub>2</sub>CH<sub>3</sub>), 1.60 (s, 6H; NCCH<sub>3</sub>), 2.19 (s, 12H; o-CH<sub>3</sub>), 2.59 (br s, 6H; p-CH<sub>3</sub>), 3.18 (q,  ${}^{3}J_{H-H} = 7.0$  Hz, 4H; CH<sub>2</sub>CH<sub>3</sub>), 4.91 (s, 1H; CH), 6.80 ppm (s, 4H; Ar-*H*);  ${}^{13}C{}^{1}H$  NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 15.5$ (br; CH<sub>2</sub>CH<sub>3</sub>), 19.1 (br; o-CCH<sub>3</sub>), 21.0 (p-CCH<sub>3</sub>), 23.6 (NCCH<sub>3</sub>), 66.0 (CH<sub>2</sub>CH<sub>3</sub>), 95.4 (CH), 129.0 (Ar-C), 130.2 (Ar-C), 133.6 (Ar-C), 144.1 (Ar-C), 169.2 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1742$  (w), 1624 (m), 1608 (m), 1553 (s), 1513 (s), 1259 (s), 1225 (s), 1192 (s), 1146 (s), 1089 (s), 1014 (s), 893 (m), 858 (s), 832 (m), 798 (m), 776 (m), 747 (m), 729 (m), 650 (w),  $629 \text{ cm}^{-1}$  (m); EIMS: m/z (%): 557.3 (2)  $[M^+-H]$ , 334.3 (12) [<sup>Mes</sup>NacnacH<sup>+</sup>]; elemental analysis calcd (%) for  $C_{27}H_{39}MgIN_2O$  ( $M_r$ = 558.82): C 58.03, H 7.03, N 5.01; found: C 57.74, H 7.13, N 5.07.

[( $^{\text{Dueda}}$ Nacnac)MgI(OEt<sub>2</sub>)] (8): The compound was synthesized by using a similar procedure to that employed for the preparation of 5, but by using  $^{\text{Dueda}}$ NacnacH (2.50 g, 7.70 mmol). After work-up compound 8 was obtained as a colorless crystalline solid (yield=3.50 g, 81%). M.p. 145–150°C; EIMS: m/z (%): 553.4 (10) [ $M^+$ ]; <sup>1</sup>H NMR (300 MHz, 298 K,

 $\begin{array}{l} {\rm C_6D_6): \ \delta=1.03 \ ({\rm t}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 6H; \ {\rm CH}_2{\rm CH}_3), \ 1.15 \ ({\rm d}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 6H; \ {\rm CH}({\rm CH}_{3})_2), \ 1.60 \ ({\rm s}, \ 3H; \ {\rm NCCH}_3), \ 1.65 \ ({\rm s}, \ 3H; \ {\rm NCCH}_3), \ 1.90 \ ({\rm s}, \ 6H; \ {\rm NCH}_3), \ 2.21 \ ({\rm t}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 6H; \ {\rm CH}({\rm CH}_3)_2), \ 1.60 \ ({\rm s}, \ 3H; \ {\rm NCCH}_3), \ 1.65 \ ({\rm s}, \ 3H; \ {\rm NCCH}_3), \ 1.90 \ ({\rm s}, \ 6H; \ {\rm NCH}_3), \ 2.21 \ ({\rm t}, \ {}^3J_{\rm H-H}\!=\!6.0 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_2{\rm N}), \ 3.22 \ ({\rm sep}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_2{\rm N}), \ 2.73 \ ({\rm t}, \ {}^3J_{\rm H-H}\!=\!6.0 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_2{\rm N}), \ 3.22 \ ({\rm sep}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_2{\rm N}), \ 3.22 \ ({\rm sep}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_2{\rm N}), \ 3.22 \ ({\rm sep}, \ {}^3J_{\rm H-H}\!=\!6.9 \, \rm Hz, \ 2H; \ {\rm NCH}_2{\rm CH}_3), \ 4.74 \ ({\rm s}, \ 1H; \ {\rm NCCH}), \ 7.17-7.14 \, {\rm ppm} \ ({\rm m}, \ 3H; \ {\rm Ar-H}); \ {}^{13}{\rm Cl}^{1}{\rm H} \ {\rm NMR} \ (75.5 \, {\rm MHz}, \ 298 \, {\rm K}, \ C_6{\rm D}); \ \delta=15.1 \ ({\rm CH}_2{\rm CH}_3), \ 24.8 \ ({\rm NCCH}_3), \ 24.4 \ ({\rm CH}-({\rm CH}_3)_2), \ 24.6 \ ({\rm NCCH}_3), \ 25.5 \ ({\rm CH}({\rm CH}_3)_2), \ 28.3 \ ({\rm CH}({\rm CH}_3)_2), \ 43.9 \ ({\rm NCH}_2{\rm CH}_2{\rm N}({\rm CH}_3)_2), \ 44.7 \ ({\rm NCH}_3), \ 57.0 \ ({\rm NCH}_2{\rm CH}_2{\rm N}({\rm CH}_3)_2), \ 45.5 \ ({\rm CH}_2{\rm CH}_3), \ 95.6 \ ({\rm CH}), \ 124.0 \ ({\rm Ar-C}), \ 125.5 \ ({\rm Ar-C}), \ 142.3 \ ({\rm Ar-C}), \ 145.5 \ ({\rm Ar-C}), \ 145.5 \ ({\rm Ar-C}), \ 145.5 \ ({\rm M}, \ 1552 \ ({\rm m}), \ 1524 \ ({\rm s}), \ 1399 \ ({\rm m}), \ 1379 \ ({\rm s}), \ 1344 \ ({\rm s}), \ 1315 \ ({\rm m}), \ 1289 \ ({\rm w}), \ 1255 \ ({\rm m}), \ 1185 \ ({\rm w}), \ 1148 \ ({\rm w}), \ 1096 \ ({\rm w}), \ 1043 \ ({\rm m}), \ 1020 \ ({\rm m}), \ 1000 \ ({\rm w}), \ 895 \ ({\rm w}), \ 840 \ ({\rm w}), \ 787 \ {\rm cm}^{-1} \ ({\rm m}). \ 1000 \ ({\rm m}), \ 1000 \ ({\rm$ 

[(<sup>Bu</sup>Nacnac)MgI] (9): MgnBu<sub>2</sub> (1.0м solution in heptane, 3.28 mL, 3.28 mmol) was added to a solution of <sup>tBu</sup>NacnacH (1.60 g, 3.19 mmol) in toluene (40 mL) at 20 °C. The mixture was heated to 100 °C for 16 h. All volatiles were removed in vacuo to give a colorless solid residue. This was dissolved in toluene (30 mL) and a solution of iodine (0.849 g, 3.35 mmol) in toluene (20 mL) was added to it at -20 °C. An immediate color change occurred, leaving a deep-yellow solution that was stirred for 3 h at room temperature. All volatiles were removed in vacuo, the residue was extracted with hexane (50 mL), and the extract was cooled to -30 °C giving colorless crystals of 9. Concentration of the supernatant to ca. 20 mL and storing at -30 °C overnight yielded another crop of 9 (yield = 1.25 g, 60 %). M.p. 176–178 °C; <sup>1</sup>H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta = 1.16$  (s, 18H;  $C(CH_3)_3$ ), 1.24 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H; CH- $(CH_3)_2$ , 1.43 (d,  ${}^{3}J_{H-H} = 6.8 \text{ Hz}$ , 12H; CH $(CH_3)_2$ ), 3.22 (sept,  ${}^{3}J_{H-H} =$ 6.8 Hz, 4H; CH(CH<sub>3</sub>)<sub>2</sub>), 5.44 (s, 1H; CH), 7.00–7.10 ppm (m, 6H; ArH); <sup>13</sup>C[<sup>1</sup>H] NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 23.3$  (CH(CH<sub>3</sub>)<sub>2</sub>), 26.0 (CH-(CH<sub>3</sub>)<sub>2</sub>), 28.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 32.9 (C(CH<sub>3</sub>)<sub>3</sub>), 44.2 (C(CH<sub>3</sub>)<sub>3</sub>), 95.6 (CH), 124.2 (Ar-C), 126.6 (Ar-C), 141.3 (Ar-C), 143.8 (Ar-C), 177.9 ppm (CC-(CH<sub>3</sub>)<sub>3</sub>); IR (Nujol): v=1621 (m), 1317 (m), 1261 (m), 1208 (m), 1155 (m), 1095 (s), 1054 (m), 1029 (m), 932 (m), 806 (m), 778 (m), 753 (m), 671 cm<sup>-1</sup> (m); EIMS: m/z (%): 652.4 (35 [ $M^+$ ], 595.3 (46) [ $M^+$ -C<sub>4</sub>H<sub>9</sub>], 244.2 (100) [tBuCNDipp<sup>+</sup>]: EI accurate mass calcd for C<sub>35</sub>H<sub>53</sub>MgIN<sub>2</sub>: 652.3098; found: 652.3098; elemental analysis calcd (%) for C<sub>35</sub>H<sub>53</sub>MgIN<sub>2</sub> (M<sub>r</sub>=652.02): C 64.37, H 8.18, N 4.29; found: C 64.13, H 8.50, N 4.31.

[(<sup>Dipp</sup>Nacnac)MgI(thf)] (10): Compound 10 was obtained as a colorless solid in quantitative yield by dissolving 5 in THF and subsequently removing all volatiles in vacuo. Colorless crystals suitable for an X-ray diffraction experiments were obtained from a saturated solution of 10 in hexane/THF (2:1). M.p. 266-268 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.20$  (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (m<sub>c</sub>, 4H; OCH<sub>2</sub>CH<sub>2</sub>), 1.35 (brm<sub>c</sub>, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.62 (s, 6H; NCCH<sub>3</sub>), 3.34–3.48 (brm, 4H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.58 (m<sub>c</sub>, 4H; OCH<sub>2</sub>CH<sub>2</sub>), 4.82 (s, 1H; CH), 6.75–7.03 ppm (m, 6H; Ar-H);  ${}^{13}C{}^{1}H$  NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 24.3$ (NCCH<sub>3</sub>), 24.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.7 (OCH<sub>2</sub>CH<sub>2</sub>), 28.4 (br, CH(CH<sub>3</sub>)<sub>2</sub>), 70.5 (br, OCH<sub>2</sub>CH<sub>2</sub>), 95.1 (CH), 124.2 (Ar-C), 125.8 (Ar-C), 143.0 (br, Ar-C), 144.8 (Ar-C), 169.6 ppm (NCCH<sub>3</sub>); IR (Nujol): v=1621 (w), 1557 (m), 1455 (s), 1376 (s), 1313 (m), 1263 (m), 1174 (m), 1103 (m), 1056 (m), 1016 (s), 936 (m), 919 (m), 869 (m), 853 (m), 794 (s), 756 (s), 629 cm<sup>-1</sup> (m); EIMS: m/z (%): 568.2 (4) [ $M^+$ -THF], 418.4 (16)  $[^{Dipp}NacnacH^{+}]$ , 403.4 (42)  $[^{Dipp}NacnacH^{+}-CH_{3}]$ , 202.3 (100) [MeCCN-Dipp<sup>+</sup>].

[(<sup>Mes</sup>Nacnac)MgI(thf)] (11): Compound 11 was obtained as a colorless solid in quantitative yield by dissolving 7 in THF and subsequently removing all volatiles in vacuo. Colorless crystals suitable for an X-ray diffraction experiments were obtained by recrystallizing 11 from a minimum volume of THF. M.p. 218–220 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta =$ 0.95 (brm<sub>c</sub>, 4H; CH<sub>2</sub>CH<sub>2</sub>), 1.61 (s, 6H; NCCH<sub>3</sub>), 2.15 (s, 6H; *p*-CH<sub>3</sub>), 2.35 (brs, 12H; *o*-CH<sub>3</sub>), 3.20 (brt, <sup>3</sup>J<sub>H-H</sub>=6.6 Hz, 4H; OCH<sub>2</sub>CH<sub>2</sub>), 4.90 (s, 1H; CH), 6.82 ppm (s, 4H; Ar-H); <sup>13</sup>C[<sup>1</sup>H] NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta =$  19.6 (*o*-CH<sub>3</sub>), 20.8 (*p*-CH<sub>3</sub>), 23.1 (OCH<sub>2</sub>CH<sub>2</sub>), 24.7 (NCCH<sub>3</sub>), 69.9 (OCH<sub>2</sub>CH<sub>3</sub>), 94.9 (CH), 129.4 (Ar-C), 132.2 (Ar-C), 133.6 (Ar-C), 144.9 (Ar-C), 168.7 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} =$ 1625 (w), 1556 (m), 1515 (m), 1258 (m), 1229 (s), 1200 (m), 1147 (m), 1098 (w), 1014 (m), 958 (vw), 920 (vw), 856 (m), 803 (w), 773 (w), 723 cm<sup>-1</sup> (w); EIMS: *m*/z (%): 690.3 (6) [(<sup>Mes</sup>Nacnac)<sub>2</sub>Mg<sup>+</sup>], 675.3 (4) [(<sup>Mes</sup>Nacnac)<sub>2</sub>Mg<sup>+</sup>-Me], 557.3 (4) [ $M^+$ +H], 334.1 (92) [<sup>Mes</sup>NacnacH<sup>+</sup>]; elemental analysis calcd (%) for C<sub>27</sub>H<sub>36</sub>MgIN<sub>2</sub>O ( $M_r$ =555.80): C 58.24, H 6.70, N 5.03; found: C 58.17, H 6.84, N 4.96.

[(<sup>nBu</sup>Nacnac)MgI(DMAP)] (12): DMAP (32 mg, 0.26 mmol) was added at 20°C to a solution of 9 (0.115 g, 0.23 mmol) in toluene (6 mL), affording a colorless crystalline precipitate of 12. The precipitate was collected by filtration, the supernatant was concentrated to ca. 3 mL and stored overnight at 4°C to yield a second crop of 12 (yield = 0.11 g, 60 %). M.p. slow decomposition above ca. 250 °C; <sup>1</sup>H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta =$ 1.07 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d,  ${}^{3}J_{H-H}$  6.9 Hz, 6H; CH- $(CH_3)_2$ , 1.27 (s, 18H; C(CH<sub>3</sub>)<sub>3</sub>), 1.48 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.58 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 2.03 (s, 6H; N(CH<sub>3</sub>)<sub>2</sub>), 3.13 (sept,  ${}^{3}J_{H-H} = 6.9$  Hz, 2H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.75 (br sept,  ${}^{3}J_{H-H}$  ca. 6.9 Hz, 2H; CH-(CH<sub>3</sub>)<sub>2</sub>), 5.61 (s, 1H; CH), 5.82 (brm<sub>c</sub>, 2H; DMAP *m*-Ar-H), 6.97–7.11 (m, 6H; Ar-H), 8.59 ppm (brm<sub>c</sub>, 2H: DMAP-o-Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 23.2$ , 24.1, 27.1, 28.4, 28.8, 29.1 (4×CH-(CH<sub>3</sub>)<sub>2</sub>, 2×CH(CH<sub>3</sub>)<sub>2</sub>), 33.2 (C(CH<sub>3</sub>)<sub>3</sub>), 38.1 (N(CH<sub>3</sub>)<sub>2</sub>), 44.4 (C(CH<sub>3</sub>)<sub>3</sub>), 95.9 (CH), 106.0 (DMAP m-Ar-C), 123.1 (Ar-C), 123.4 (Ar-C), 124.2 (Ar-C), 125.2 (Ar-C), 142.2 (Ar-C), 143.2 (Ar-C), 145.9 (Ar-C), 149.9 (DMAP p-Ar-C), 178.0 ppm (CC(CH<sub>3</sub>)<sub>3</sub>); IR (Nujol): v=1621 (s), 1543 (m), 1492 (m), 1364 (m), 1316 (m), 1261 (m), 1214 (m), 1154 (m), 1091 (s), 1012 (s), 802 (s), 757 cm<sup>-1</sup> (m); EIMS: m/z (%): 652.2 (3) [ $M^+$ -DMAP], 595.2 (8) [ $M^+$ -DMAP $-C_4H_9$ ], 244.4 (100) [ $tBuCNDipp^+$ ].

[(MesNacnac)BeI] (13): A Schlenk tube fitted with a Young's tap was charged with beryllium powder (0.18 g, ca. 20.0 mmol) and diethyl ether (20 mL) and then cooled to -80 °C. I<sub>2</sub> (1.86 g, 7.33 mmol) and a catalytic amount of  $HgI_2$  (ca. 10 mg) was added and the reaction vessel sealed. The mixture was then allowed to slowly warm to room temperature with rapid stirring. The ensuing exothermic reaction was controlled by cooling the reaction flask when necessary. After the most vigorous stage of the reaction had ceased, the resultant slurry was stirred at room temperature for 6 h yielding a grey precipitate of [BeI2(OEt2)2]. This suspension was cooled to 0°C and a slurry of [K(MesNacnac)] (5.53 mmol, prepared in situ from the reaction of MesNacnacH with K[N(SiMe<sub>3</sub>)<sub>2</sub>] in toluene) in toluene (20 mL)/diethyl ether (10 mL) was added over 5 min. The resultant suspension was stirred vigorously at 20 °C for one day. It was then filtered and the residue was extracted with a mixture of toluene (15 mL) and diethyl ether (10 mL). The combined extracts were concentrated to ca. 12 mL and cooled to -30 °C to give colorless crystals of 13. Concentration of the supernatant solution and cooling to -30°C yielded a second crop of the compound (yield=1.67 g, 66%). Data for isolated crystals of  $[BeI_2(OEt_2)_2]^{[22]}$  M.p. 48–49 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 1.05$  (t,  ${}^{3}J_{H-H} = 7.0$  Hz, 12 H; CH<sub>2</sub>CH<sub>3</sub>), 3.96 ppm (q,  ${}^{3}J_{H-H} =$ 7.0 Hz, 8H;  $CH_2CH_3$ );  ${}^{13}C{}^{1}H$  NMR (100.6 MHz,  $C_6D_6$ , 298 K):  $\delta = 13.8$ (CH<sub>3</sub>), 59.9 ppm (OCH<sub>2</sub>); IR (Nujol):  $\tilde{\nu} = 1326$  (m), 1190 (m), 1146 (m), 1091 (m), 1012 (m), 885 (m), 834 (m), 767 cm<sup>-1</sup> (m). Data for [(<sup>Mes</sup>Nacnac)BeI] **13**: M.p. 199–201 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.55$  (s, 6H; NCCH<sub>3</sub>) 2.08 (s, 12H; o-CH<sub>3</sub>), 2.13 (s, 6H; p-CH<sub>3</sub>), 4.80 (s, 1H; CH), 6.83 ppm (s, 4H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 19.3$  (o-CH<sub>3</sub>), 21.4 (p-CH<sub>3</sub>), 22.3 (NCCH<sub>3</sub>), 101.3 (CH), 130.1 (Ar-C), 132.4 (Ar-C), 136.0 (Ar-C), 143.1 (Ar-C), 168.6 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1607$  (w), 1538 (s), 1376 (s), 1318 (m) 1239 (m), 1024 (s), 930 (s) 738 cm<sup>-1</sup> (m); EIMS: m/z (%): 469.3 (45) [M<sup>+</sup>], 342.4 (100) [M<sup>+</sup> -I]; EI accurate mass calcd for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>BeI: 469.1492; found: 469.1495. CAUTION: Bervllium metal and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, a breathing apparatus, and a well ventilated fume cupboard) should be taken for all manipulations involving them. The reaction of beryllium metal with I2 in diethyl ether can be rapid.

[ $\{(^{Dipp}Nacnac)Cal(OEt_2)\}_2$ ] (14): Iodine (1.22 g, 4.81 mmol) was added to a mixture of freshly filed calcium metal (0.23 g, 5.74 mmol) in diethyl ether (60 mL) at 20 °C. The resultant mixture was stirred vigorously for 7 days at 20 °C to give a fine white slurry. To this, a solution of [ $K(^{Dipp}Nacnac)$ ] (4.33 mmol, prepared in situ from the reaction of  $^{Dipp}NacnacH$  with  $K[N(SiMe_3)_2]$  in toluene) in a mixture of toluene (30 mL) and diethyl ether (10 mL) was slowly added at 20 °C. The resultant mixture was stirred for 2 days and then filtered. Volatiles were re-

www.chemeurj.org

A EUROPEAN JOURNAL

moved in vacuo and hexane (40 mL) added to the residue yielding a suspension. Compound 14 was isolated by filtration as a colorless solid and dried under vacuum (note that a 28% yield of the known complex, [Ca(<sup>Dipp</sup>Nacnac)<sub>2</sub>],<sup>[28(b,c)]</sup> was crystallized from the hexane mother liquor). Crystals of 14 that were suitable for X-ray structural analysis were obtained by recrystallization from diethyl ether (yield=0.90 g, 32%). M.p. > 350 °C (decomp); <sup>1</sup>H NMR (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.94$ (brm<sub>c</sub>, 12H; OCH<sub>2</sub>CH<sub>3</sub>), 1.15 and 1.16 (two overlapping d,  ${}^{3}J_{H-H}$ = 6.8 Hz, 24H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12 H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.63 (s, 12 H; CCH<sub>3</sub>), 3.12–3.28 (m, 16H; CH(CH<sub>3</sub>)<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 4.85 (s, 2H; CH), 7.06-7.18 ppm (m, 12H; ArH);  ${}^{13}C{}^{1}H$  NMR (100.6 MHz, 298 K; C<sub>6</sub>D<sub>6</sub>):  $\delta = 14.7$  (OCH<sub>2</sub>CH<sub>3</sub>), 20.4, 22.7, 23.4, 24.2, 25.4 (4×CH(CH<sub>3</sub>)<sub>2</sub>, 1×CCH<sub>3</sub>), 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 65.5 (OCH<sub>2</sub>CH<sub>3</sub>), 93.9 (CH), 123.0, 123.8, 124.8, 125.5, 136.0, 141.9 (ArC), 166.1 ppm (CCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1621$  (m), 1552 (m), 1377 (s), 1261 (s), 1097 (s), 1019 (s), 866 (m), 797 (s), 758 cm<sup>-1</sup> (m); EIMS: m/z (%): 418.4 (33) [<sup>Dipp</sup>NacnacH<sup>+</sup>], 403.4 (80) [<sup>Dipp</sup>NacnacH<sup>+</sup> -CH<sub>3</sub>], 202.3 (43) [MeCCNDipp<sup>+</sup>], 167.0 (100) [CaI<sup>+</sup>], 127.0 (50) [I<sup>+</sup>].

[Mg(<sup>Ph</sup>Nacnac)<sub>2</sub>] (15): Method 1: Complex 6 (1.0 g, 2.1 mmol) was dissolved in toluene (50 mL). The solution was stirred over a potassium mirror (0.70 g, 17.9 mmol) for 24 h at 20 °C. The resultant solution was filtered and volatiles were removed in vacuo. The residue was dissolved in hexane and the extract was cooled to -30 °C yielding yellow crystals of 15 overnight (yield=0.09 g, 16%). Method 2: MgnBu<sub>2</sub> (1.0м solution in heptane, 0.30 mL, 0.30 mmol) was added to a solution of <sup>Ph</sup>NacnacH (0.15 g, 0.60 mmol) in hexane (8 mL) at 20 °C. The mixture was stirred at 50°C for 20 min, concentrated to ca. 1.5 mL, and cooled to 4°C overnight yielding 15 as large yellow crystals (yield=0.12 g, 76%). M.p. 131-133 °C; <sup>1</sup>H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta = 1.83$  (s, 12H; NCCH<sub>3</sub>), 4.81 (s, 2H; CH), 6.80–7.30 ppm (m, 20H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ=23.1 (NCCH<sub>3</sub>), 96.8 (CH), 123.4 (Ar-C), 124.7 (Ar-C), 128.8 (Ar-C), 150.3 (Ar-C), 166.9 ppm (NCCH<sub>3</sub>); IR (Nujol): v=1634 (w), 1594 (m), 1551 (s), 1522 (s), 1261 (s), 1187 (s), 1169 (s), 1072 (s), 1021 (s), 932 (m), 905 (m), 834 (m), 802 (m), 750 (s), 698 (s), 661 (m), 630 (m), 614 cm<sup>-1</sup> (m); EIMS: m/z (%): 522.2 (10) [ $M^+$ ], 250.0 (50)  $[^{Ph}NacnacH^+]$ ; elemental analysis calcd (%) for  $C_{34}H_{34}MgN_4$  ( $M_r =$ 522.97): C 78.09, H 6.55, N 10.71; found: C 77.47, H 6.51, N 10.49.

[(MesNacnac)MgMg(MesNacnac)] (16): Toluene (80 mL) and diethyl ether (ca. 2 mL) were added to 7 (1.68 g, 1.52 mmol). The resultant solution was rapidly stirred over a sodium mirror (0.70 g, 30.4 mmol) for 5 days to vield a vellow-green suspension. This was filtered, the vellow filtrate was concentrated to ca. 20 mL and placed at -30 °C overnight to give yellow crystals of 16. A second crop of 16 was isolated after further concentration and cooling of the supernatant solution (yield=0.56 g, 51 %). M.p. 201–203 °C; <sup>1</sup>H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta = 1.55$  (s, 12 H; NCCH<sub>3</sub>), 1.91 (s, 24H; o-CH<sub>3</sub>), 2.30 (s, 12H; p-CH<sub>3</sub>), 4.80 (s, 2H; CH), 6.86 ppm (s, 8H; Ar-H);  ${}^{13}C{}^{1}H$  NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 19.2$  (o-CH<sub>3</sub>), 21.2 (p-CH<sub>3</sub>), 23.2 (NCCH<sub>3</sub>), 95.4 (CH), 129.3 (Ar-C), 131.5 (Ar-C), 132.7 (Ar-C), 145.5 (Ar-C), 166.6 ppm (NCCH<sub>3</sub>); IR (Nujol)  $\tilde{\nu} = 1624$  (w), 1610 (w), 1526 (s), 1260 (s), 1197 (s), 1146 (s), 1016 (m), 958 (w), 854 (m), 727 (m),  $693 \text{ cm}^{-1}$  (w); EIMS: m/z (%): 715.2 (30) [M<sup>+</sup>], 690.3 (25) [Mg(MesNacnac)<sub>2</sub>], 334.3 (40) [MesNacnacH<sup>+</sup>]; elemental analysis calcd (%) for  $C_{46}H_{58}Mg_2N_4$  ( $M_r$ =715.59): C 77.21, H 8.17%, N 7.83; found: C 76.42, H 8.19, N 7.66.

[(<sup>Bu</sup>Nacnac)MgMg((<sup>Bu</sup>Nacnac)] (17): A solution of 9 (0.65 g, 0.99 mmol) in toluene (40 mL) was stirred vigorously for 16 h over a potassium mirror (0.70 g, 17.9 mmol) at 20 °C. The resultant suspension was filtered, the orange solution was concentrated under reduced pressure to ca. 20 mL, and then cooled to 5 °C overnight to give orange crystals of **17**. The supernatant was further concentrated at room temperature to ca. 10 mL and cooled to -30 °C to afford a second crop of **17** (yiel=0.31 g, 59%). M.p. 278–280 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =0.96 (brd, <sup>3</sup>*J*<sub>H-H</sub> ca. 6.8 Hz, 24H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (s, 36H; C(CH<sub>3</sub>)<sub>3</sub>) 1.34 (d, <sup>3</sup>*J*<sub>H-H</sub>=6.8 Hz, 24H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.30 (brsept, 8H; CH(CH<sub>3</sub>)<sub>2</sub>), 5.54 (s, 2H; CH), 6.92–7.02 ppm (m, 12H; Ar-H); <sup>13</sup>C[<sup>1</sup>H] NMR (100.6 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =23.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.0 (br, CH(CH<sub>3</sub>)<sub>2</sub>), 27.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 32.9 (C(CH<sub>3</sub>)<sub>3</sub>), 43.6 (C(CH<sub>3</sub>)<sub>3</sub>), 96.8 (CH), 123.4 (Ar-C), 124.6 (Ar-C), 142.5 (Ar-C), 145.9 (Ar-C), 176.2 ppm (CC(CH<sub>3</sub>)<sub>3</sub>); IR (Nujol):  $\tilde{\nu}$ =1621 (m), 1537 (m), 1493 (s), 1363 (s), 1310 (m), 1259 (m), 1213 (m), 1183 (m), 1153 (m), 1098 (s), 1020 (s), 932 (w), 873 (w), 798 (s), 777 (s), 708 (m), 694 (m), 667 cm<sup>-1</sup> (m); EIMS: m/z (%): 1050.9 (1)  $[M^+]$ , 525.5 (42)  $[M/2^+]$ , 502.5 (10)  $[^{16u}NacnacH_2^+]$ , 445.4 (73)  $[^{16u}NacnacH^+-C_4H_9]$ ; elemental analysis calcd (%) for  $C_{70}H_{106}N_4Mg_2$  ( $M_r$ =1052.23): C 79.90, H 10.15, N 4.62; found: C 79.65, H 10.02, N 4.77.

 $[(^{Dipp}Nacnac)Mg(\mu-H)(\mu-I)Mg(^{Mes}Nacnac)]$  (18): Complex 5 (1.00 g, 1.55 mmol) and 7 (0.87 g, 1.55 mmol) were dissolved in toluene (50 mL). The resultant solution was stirred over a potassium mirror (0.70 g, 17.9 mmol) for 24 h. The solution was filtered, volatiles were removed in vacuo, and the residue was extracted into hot benzene. Yellow crystals of 18 were isolated from the solution upon cooling to 20 °C (yield = 0.12 g, 8%). M.p. 147–150°C; <sup>1</sup>H NMR (300 MHz, 298 K,  $C_6D_6$ ):  $\delta = 1.11$  (d,  ${}^{3}J_{H-H} = 6.9 \text{ Hz}, 12 \text{ H}; \text{ CH}(\text{CH}_{3})_{2}), 1.14 \text{ (d, } {}^{3}J_{H-H} = 6.9 \text{ Hz}; 12 \text{ H}, \text{ CH-}$ (CH3)2), 1.42 (s, 6H; NCCH3), 1.49 (s, 12H; o-CH3), 1.90 (s, 6H; NCCH<sub>3</sub>), 2.30 (s, 6H; *p*-CH<sub>3</sub>), 3.25 (sept,  ${}^{3}J_{H-H} = 6.9$  Hz, 4H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.92 (s, 1H; µ-H), 4.80 (s, 1H; CH), 5.35 (s, 1H; CH), 6.57-7.25 ppm (m, 10H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 21.2$  (o-CH<sub>3</sub>), 23.3 (p-CH<sub>3</sub>), 23.8 (NCCH<sub>3</sub>), 24.0 (NCCH<sub>3</sub>), 24.4 (C(CH<sub>3</sub>)<sub>2</sub>), 24.8 (C-(CH<sub>3</sub>)<sub>2</sub>), 28.4 (C(CH<sub>3</sub>)<sub>2</sub>), 95.6 (CH), 95.8 (CH), 123.7 (Ar-C), 124.3 (Ar-C), 125.9 (Ar-C), 129.3 (Ar-C), 130.0 (Ar-C), 131.3 (Ar-C), 132.9 (Ar-C), 142.7 (Ar-C), 169.1 (NCCH<sub>3</sub>), 169.9 ppm (NCCH<sub>3</sub>); IR (Nujol): v=1624 (m), 1555 (m), 1261 (m), 1022 (m), 854 (w), 798 cm<sup>-1</sup> (m); EIMS: m/z(%): 417.3 (35) [<sup>Dipp</sup>Nacnac<sup>+</sup>], 333.2 (8) [<sup>Mes</sup>Nacnac<sup>+</sup>].

[Mg(<sup>Mes</sup>Nacnac)<sub>2</sub>] (19): Method 1: <sup>Mes</sup>NacnacH (2.50 g, 7.5 mmol) was dissolved in toluene (20 mL). MgnBu<sub>2</sub> (7.7 mmol, as a 1.0 M solution in heptane) was added and the resultant solution was stirred at 20°C for 1 hr. This was then heated at 60 °C for 2 h, and the volatiles were removed in vacuo. The residue was dissolved in hexane (40 mL), PhSiH<sub>3</sub> (1 mL, 0.88 g, 8.07 mmol) was added, and the solution was heated at reflux for 3 days. Colorless crystals of 19 were isolated from the reaction mixture upon cooling to -30 °C (yield=0.90 g, 17%). Method 2: MgnBu<sub>2</sub> (1.0 M solution in heptane, 0.79 mL, 0.79 mmol) was added to a solution of MesNacnacH (0.50 g, 1.49 mmol) in toluene (7 mL) at 20 °C. The mixture was stirred at 50°C for 1 h, then concentrated to ca. 2 mL. Hexane (6 mL) was added and the mixture cooled to 4°C, yielding 19 as colorless crystals (yield = 0.35 g, 68%). M.p. 260-264°C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.55$  (s, 12H; NCCH<sub>3</sub>), 1.94 (s, 24H; o-CH<sub>3</sub>), 2.22 (s, 12H; *p*-CH<sub>3</sub>), 4.96 (s, 2H; CH), 6.76 ppm (s, 8H; Ar-H);  ${}^{13}C{}^{1}H$  NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ=19.0 (o-CH<sub>3</sub>), 21.2 (p-CH<sub>3</sub>), 24.1 (NCCH<sub>3</sub>), 96.8 (CH), 129.7 (Ar-C), 133.1 (Ar-C), 133.2 (Ar-C), 146.8 (Ar-C),169.2 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1611$  (w), 1513 (s), 1253 (s), 1195 (s), 1146 (s), 1016 (s), 957 (w), 924 (w), 856 (s), 761 (m), 744 (m), 728 (m), 598 cm<sup>-1</sup> (s); EIMS: m/z (%): 690.5 (100) [ $M^+$ ], 675.4 (40) [ $M^+$ -Me], 334.2 (30) [MesNacnacH+]; EI accurate mass calcd for C46H58MgN4: 690.4506; found: 690.4505; elemental analysis calcd (%) for  $C_{46}H_{58}MgN_4$  ( $M_r$ =691.28): C 79.92, H 8.46, N 8.10; found: C 78.78, H 8.43, N 7.97.

[{Na( $^{rBu}$ Nacnac)}<sub>2</sub>] (20): A solution of [{( $^{rBu}$ Nacnac)CaI(thf)}<sub>2</sub>] (0.70 g, 0.47 mmol) in toluene (50 mL) was stirred vigorously for 6 days over a sodium mirror (0.420 g, 18.3 mmol) at 20°C. The resultant suspension was filtered, all volatiles were removed in vacuo, and the residue was extracted with benzene (30 mL). The brown-yellow filtrate was concentrated under reduced pressure to ca. 5 mL and yellow crystals of 20 were obtained after 3 days upon standing at 20 °C (yield = 0.25 g, 50 %). M.p. 244–252 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.10$  (d, <sup>3</sup>J<sub>H-H</sub>=6.9 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d,  ${}^{3}J_{H-H}$ =6.9 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (s, 18H;  $C(CH_3)_3$ , 3.43 (sept,  ${}^{3}J_{H-H} = 6.9$  Hz, 4H;  $CH(CH_3)_2$ ), 4.99 (s, 1H; CH), 6.95-7.19 ppm (m, 6H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 23.6 (CH(CH_3)_2), 25.6 (CH(CH_3)_2), 27.5 (CH(CH_3)_2), 33.1 (C(CH_3)_3),$ 44.7 (C(CH<sub>3</sub>)<sub>3</sub>), 90.3 (CH), 119.2 (Ar-C), 123.5 (Ar-C), 137.2 (Ar-C), 151.8 (Ar-C), 168.5 ppm (CC(CH<sub>3</sub>)<sub>3</sub>); IR (Nujol): ṽ=1621 (m), 1548 (m), 1325 (m), 1260 (s), 1215 (m), 1142 (m), 1095 (s), 1020 (s), 935 (m), 794 (s), 761 (m), 678 (cm)<sup>-1</sup> (m); EIMS: m/z (%): 502.5 (10) [<sup>tBu</sup>NacnacH<sub>2</sub><sup>+</sup>], 445.4 (96) [<sup>tBu</sup>NacnacH<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 244.4 (100) [tBuCNDipp<sup>+</sup>]; elemental analysis calcd (%) for  $C_{35}H_{53}N_2Na$  ( $M_r = 524.80$ ): C 80.10, H 10.18, N 5.34; found: C 79.27, H 10.30, N 5.21.

952 -

[(<sup>Mes</sup>Nacnac)Mg(thf)Mg(thf)(<sup>Mes</sup>Nacnac)] (21): Compound 16 (0.10 g, 0.14 mmol) was dissolved in THF (5 mL) to give a red solution. Compound 21 was isolated from the solution as red plates after concentrating to ca. 2 mL and cooling to -30 °C (yield=0.094 g, 79%). M.p. 86–89 °C (yellows with THF loss, then decomposes at 246–248 °C); <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =1.38 (m<sub>c</sub>, 8H; OCH<sub>2</sub>CH<sub>2</sub>), 1.56 (s, 12H; NCCH<sub>3</sub>), 1.98 (s, 24H; *o*-CH<sub>3</sub>), 2.30 (s, 12H; *p*-CH<sub>3</sub>), 3.44 (m<sub>c</sub>, 8H; OCH<sub>2</sub>CH<sub>2</sub>), 4.80 (s, 2H; CH), 6.88 ppm (s, 8H; Ar-H); <sup>13</sup>C[<sup>1</sup>H] NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta$ =19.2 (*o*-CH<sub>3</sub>), 20.9 (*p*-CH<sub>3</sub>), 23.3 (NCCH<sub>3</sub>), 25.4 (OCH<sub>2</sub>CH<sub>2</sub>), 68.1 (OCH<sub>2</sub>CH<sub>2</sub>), 94.6 (CH), 128.9 (Ar-C), 131.4 (Ar-C), 131.9 (Ar-C), 146.9 (Ar-C), 165.2 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\bar{\nu}$ =1625 (w), 1608 (w), 1547 (m), 1400 (s), 1302 (w), 1260 (m), 1194 (m), 1144 (m), 1073 (m), 1019 (m), 958 (m), 915 (s), 876 (m), 853 (m), 802 (m), 740 (w), 696 cm<sup>-1</sup> (s); EIMS: *m/z* (%): 334.3 (100) [<sup>Mes</sup>NacnacH<sup>+</sup>].

[(MesNacnac)Mg(DMAP)Mg(DMAP)(MesNacnac)] (22): Compound 16 (0.10 g, 0.14 mmol) was dissolved in toluene (15 mL). The solution was cooled to -78°C and DMAP (0.031 g, 0.25 mmol) was added. The reaction mixture changed color from yellow to brown as it was warmed to room temperature. Red-brown crystals of 22 were isolated from the reaction mixture upon cooling to -30°C. A second crop was isolated after further concentration and cooling of the supernatant solution (vield 0.056 g, 36%). M.p. 142–143°C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta =$ 1.74 (s, 12H; NCCH<sub>3</sub>), 1.99 (s, 24H; o-CH<sub>3</sub>), 2.19 (br s, 12H; N(CH<sub>3</sub>)<sub>2</sub>), 2.33 (s, 12H; *p*-CH<sub>3</sub>), 4.97 (s, 2H; CH), 6.01 (d,  ${}^{3}J_{H-H}=5.3$  Hz, 4H; DMAP Ar-H), 6.93 (s, 8H; Ar-H), 8.22 ppm (d,  ${}^{3}J_{H-H}=5.3$  Hz, 4H; DMAP Ar-*H*); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 19.6$  (*o*-*C*H<sub>3</sub>), 21.2 (p-CH<sub>3</sub>), 23.8 (NCCH<sub>3</sub>), 38.1 (N(CH<sub>3</sub>)<sub>2</sub>), 93.8 (CH), 106.0 (DMAP Ar-C), 128.9 (Ar-C), 131.2 (Ar-C), 132.1 (Ar-C), 148.5 (Ar-C), 150.0 (DMAP Ar-C), 154.2 (DMAP Ar-C), 164.6 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{v} = (\text{cm}^{-1})$ : 1621 (m), 1609 (m), 1538 (m), 1519 (m), 1409 (m), 1260 (m), 1224 (w), 1195 (m), 1144 (m), 1098 (w), 1008 (m), 950 (w), 854 (m), 807 (m), 757 (w), 727 (m), 668 (m); EIMS: m/z (%): 715.3 (30)  $[{(^{Mes}Nacnac)Mg}_2^+].$ 

[("BuNacnac)Mg(µ-AdN<sub>6</sub>Ad)Mg("BuNacnac)] (27): A solution of 1-azidoadamantane (0.017 g, 0.096 mmol) in toluene (4 mL) was added to a solution of 17 (0.050 g, 0.048 mmol) in toluene (15 mL) at -78 °C. An immediate color change from orange to colorless occurred. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. It was then filtered, concentrated to ca. 4 mL, and cooled to  $-30\,^{\circ}\text{C}$  overnight yielding 27 as colorless crystals (yield 0.034 g, 51%). M.p. 292-294°C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.47$  (d, <sup>3</sup> $J_{H-H} = 6.8$  Hz, 12 H; CH- $(CH_3)_2$ , 1.13 (s, 36 H; C(CH<sub>3</sub>)<sub>3</sub>), 1.31 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12 H; CH(CH<sub>3</sub>)<sub>2</sub>). 1.38 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.51 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.69–1.92 (m, 18H, Ad-CH; Ad-CH<sub>2</sub>), 1.89 (m<sub>c</sub>, 12H; Ad-CH<sub>2</sub>), 3.27–3.50 (overlapping sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 8H; CH(CH<sub>3</sub>)<sub>2</sub>), 5.46 (s, 2H; CH), 6.98–7.11 ppm (m, 12H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 22.5$  (CH(CH<sub>3</sub>)<sub>2</sub>), 26.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.4 (Ad-C), 33.2 (C(CH<sub>3</sub>)<sub>3</sub>), 37.2 (Ad-C), 44.6 (Ad-C), 56.7 (Ad-C), 96.1(CH), 125.7 (Ar-C), 129.4 (Ar-C), 137.9 (Ar-C), 142.6 (Ar-C), 143.0 (Ar-C), 146.0 (Ar-C), 178.2 ppm (CC(CH<sub>3</sub>)<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1615$  (m), 1365 (m), 1260 (s), 1104 (s), 1060 (s), 1020 (s), 935 (m), 888 (m), 801 (s), 678 cm<sup>-1</sup> (m); EIMS: m/z (%): 701.5 (6)  $[(M/2)^+-H]$ , 502.5 (15)  ${}^{Bu}$ NacnacH<sub>2</sub><sup>+</sup>], 445.6 (84) [ ${}^{Bu}$ NacnacH<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 224.3 (100) [C<sub>17</sub>H<sub>26</sub>N<sup>+</sup>]. [(MesNacnac)Mg(µ-AdN<sub>6</sub>Ad)Mg(MesNacnac)] (28): 1-Azidoadamantane

[(""Nachac)Mg(II-Adix<sub>6</sub>Ad)Mg(""Nachac)] (28): 1-A21doadamantane (0.014 g, 0.08 mmol) in toluene (3 mL) was added to a solution of **16** (0.050 g, 0.07 mmol) in toluene (8 mL) at -78 °C. The yellow solution changed to colorless during the addition. The resultant solution was warmed to 20 °C, volatiles were removed in vacuo, and the residue was dissolved in benzene (5 mL). Colorless crystals of **28** deposited from the extract after it had been allowed to stand at room temperature overnight. A second crop of **28** was isolated after further concentration of the supernatant solution (yield 0.017 g, 27%). M.p. 180–182 °C; <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.45-1.54$  (m, 18 H, Ad-CH; Ad-CH<sub>2</sub>), 1.65 (s, 12 H; NCCH<sub>3</sub>), 1.88 (m<sub>c</sub>, 12 H; Ad-CH<sub>2</sub>), 2.20 (s, 12 H; *p*-CH<sub>3</sub>), 2.25 (s, 12 H; *o*-CH<sub>3</sub>), 2.26 (s, 12 H; *o*-CH<sub>3</sub>), 4.83 (s, 2 H; CH), 6.86 (s, 4 H; Ar-H), 7.09 ppm (s, 8 H; Ar-H) ; <sup>13</sup>C[<sup>1</sup>H] NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 18.7$ (*o*-CH<sub>3</sub>), 18.9 (*o*-CH<sub>3</sub>), 21.0 (*p*-CH<sub>3</sub>), 23.3 (NCCH<sub>3</sub>), 30.1 (Ad-C), 36.8 (Ad-C), 42.9 (Ad-C), 55.6 (Ad-C), 94.9 (CH), 129.1 (Ar-C), 129.5 (Ar-C), 131.3 (Ar-C), 132.5 (Ar-C), 133.0 (Ar-C), 145.2 (Ar-C), 168.6 ppm (NCCH<sub>3</sub>); IR (Nujol):  $\tilde{\nu} = 1624$  (m), 1524 (s), 1396 (s), 1269 (s), 1220 (s), 1199 (m), 1101 (s), 1018 (s), 855 (m), 800 cm<sup>-1</sup> (m); EIMS: *m/z* (%): 1068.4 (2) [*M*]<sup>+</sup>, 357.3 (100) [(<sup>Mes</sup>Nacnac)Mg<sup>+</sup>], 334.3 (48) [<sup>Mes</sup>NacnacH<sup>+</sup>]; elemental analysis calcd (%) for C<sub>66</sub>H<sub>88</sub>Mg<sub>2</sub>N<sub>10</sub> (*M*<sub>r</sub>=1070.08): C 74.08, H 8.29, N 13.08; found: C 73.05, H 8.46, N 12.32.

[(<sup>Mes</sup>Nacnac)Mg(µ-*t*Bu<sub>2</sub>N<sub>2</sub>C<sub>2</sub>O<sub>2</sub>)Mg(<sup>Mes</sup>Nacnac)] tBuNCO (29): (0.035 mL, 0.030 g, 0.31 mmol) was added to a solution of 16 (0.10 g, 0.14 mmol) in toluene (14 mL) at -78 °C. The reaction mixture changed color from yellow to colorless during the addition. It was warmed to 20°C, volatiles were removed in vacuo and the residue was extracted with hexane (20 mL). Colorless crystals of 29 were isolated upon cooling of the solution to -30°C overnight. A second crop of 29 was isolated after further concentration and cooling of the supernatant solution (yield 0.02 g, 15%). <sup>1</sup>H NMR (300 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.87$  (s, 12 H; o-CH<sub>3</sub>), 1.10 (s, 12H; o-CH<sub>3</sub>), 1.23 (brs, 18H; C(CH<sub>3</sub>)<sub>3</sub>), 1.65 (s, 6H; NCCH<sub>3</sub>), 1.67 (s, 6H; NCCH<sub>3</sub>), 2.07 (s, 6H; p-CH<sub>3</sub>), 2.27 (s, 6H; p-CH<sub>3</sub>), 4.94 (s, 1H; CH), 4.99 (s, 1H; CH), 6.82 (s, 4H; Ar-H), 6.83 ppm (s, 4H; Ar-H);  ${}^{13}C{}^{1}H{}$  NMR (75.5 MHz, 298 K,  $C_6D_6$ ):  $\delta = 18.4$  (o-CH<sub>3</sub>), 19.3 (o-CH<sub>3</sub>), 20.7 (p-CH<sub>3</sub>), 22.7 (p-CH<sub>3</sub>), 22.9 (NCCH<sub>3</sub>), 28.6 (NCCH<sub>3</sub>), 31.8 (C-(CH<sub>3</sub>)<sub>3</sub>), 51.9 (C(CH<sub>3</sub>)<sub>3</sub>), 94.4 (CH), 96.9 (CH), 128.8 (Ar-C), 129.2 (Ar-C), 131.4 (Ar-C), 131.4 (Ar-C), 131.9 (Ar-C), 132.6 (Ar-C), 132.8 (Ar-C), 145.4 (Ar-C), 168.5 (NCCH<sub>3</sub>), 168.6 ppm (NCCH<sub>3</sub>); IR (Nujol):v=1660 (w), 1584 (s), 1561 (m), 1542 (m), 1516 (m), 1394 (s), 1325 (m), 1307 (m), 1261 (m), 1222 (w), 1197 (m), 1146 (m), 1086 (w), 1015 (m), 981 (w), 952 (w), 852 (w), 801 cm<sup>-1</sup> (w); EIMS: m/z (%): 912.4 (100) [ $M^+$ ], 334.4 (22) [MesNacnacH<sup>+</sup>].

[(<sup>Bu</sup>Nacnac)Mg(µ-H)<sub>2</sub>Mg(<sup>Bu</sup>Nacnac)] (30): MgnBu<sub>2</sub> (1.0 M solution in heptane, 4.10 mL, 4.10 mmol) was added to a solution of "BuNacnacH (2.00 g, 3.98 mmol) in toluene (40 mL) and the mixture was heated to 100°C for 16 h. After cooling to room temperature, PhSiH<sub>3</sub> (0.51 mL, 0.45 g, 4.18 mmol) was added and the mixture was heated at reflux for 48 h. After cooling, all volatiles were removed in vacuo and the residue was extracted with hexane (50 mL). Concentration of the solution to ca. 25 mL and cooling to 5°C yielded colorless crystals of 30 overnight. The supernatant was further concentrated to ca. 10 mL and was cooled to -30°C to give a second crop of 30 (yield 0.83 g, 40%). M.p. 256-258°C; <sup>1</sup>H NMR (300 MHz, 353 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 1.12$  (brd, <sup>3</sup> $J_{H-H}$  ca. 6.8 Hz, 24 H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (s, 36H; C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (d,  ${}^{3}J_{H-H}$ =6.8 Hz, 24H; CH- $(CH_3)_2$ ), 3.26 (sept,  ${}^{3}J_{H-H} = 6.8 \text{ Hz}$ , 8H;  $CH(CH_3)_2$ ), 3.83 (s, 2H; MgH), 5.53 (s, 2H; CH), 6.95–7.02 ppm (m, 12H; Ar-H); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 24.2$  (br; CH(CH<sub>3</sub>)<sub>2</sub>), 26.4 (br; CH(CH<sub>3</sub>)<sub>2</sub>), 28.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 33.2 (C(CH<sub>3</sub>)<sub>3</sub>), 44.2 (C(CH<sub>3</sub>)<sub>3</sub>, 96.8 (br; CH), 123.7 (Ar-C), 125.1 (br; Ar-C), 142.6 (br; Ar-C), 145.9 (br; Ar-C), 178.2 (br;  $CC(CH_3)_3$ ; IR (Nujol)  $\tilde{\nu} = 1537$  (m), 149 (s), 1392 (s), 1364 (s), 1309 (m), 1275 (m), 1256 (m), 1214 (m), 1184 (m), 1154 (m), 1099 (s), 1021 (m), 932 (w), 875 (w), 798 (m), 779 (s), 712 (m), 672 cm<sup>-1</sup> (m); EIMS: m/z(%): 502.6 (8) [<sup>'Bu</sup>NacnacH<sub>2</sub><sup>+</sup>], 445.6 (60) [<sup>'Bu</sup>NacnacH<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 224.3 (100)  $[C_{17}H_{26}N^+]$ ; elemental analysis calcd (%) for  $C_{70}H_{108}N_4Mg_2$  ( $M_r =$ 1054.24): C 79.75, H 10.33, N 5.31; found: C 78.99, H 10.43, N 4.91.

[(<sup>Bu</sup>Nacnac)Mg(H)(DMAP)] (31): DMAP (0.018 g, 0.142 mmol) was added to a solution of 30 (0.075 g, 0.071 mmol) in toluene (9 mL) at 20 °C and the mixture was stirred for 30 min. The reaction solution was concentrated to ca. 4 mL and cooled to -30°C yielded colorless crystals of 31 overnight (yield 0.055 g, 60 %). M.p. 160-180 °C (decomp); <sup>1</sup>H NMR  $(300 \text{ MHz}, 298 \text{ K}, \text{ C}_6\text{D}_6): \delta = 0.99 \text{ (br } \text{m}_c, 6 \text{ H}; \text{ CH}(\text{CH}_3)_2), 1.33 \text{ (s, 18 H; C-}$ (CH<sub>3</sub>)<sub>3</sub>), 1.38–1.52 (brm, 12H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (brm<sub>c</sub>, 6H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.90 (brs, 6H; N(CH<sub>3</sub>)<sub>2</sub>, 3.33 (brm<sub>c</sub>, br, 2H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.87 (brm<sub>c</sub>, 2H; CH(CH<sub>3</sub>)<sub>2</sub>), 4.65 (s, 1H; Mg-H), 5.64 (s, 1H; CH), 5.77 (brs, 2H; DMAP *m*-Ar-*H*), 6.95–7.12 (m, 6H; Ar-*H*), 7.90 ppm (brs, 2H; DMAP *o*-Ar-*H*); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 21.2$  (br; CH(CH<sub>3</sub>)<sub>2</sub>), 23.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (br; CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.3 (br; CH(CH<sub>3</sub>)<sub>2</sub>), 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 38.1 (N(CH<sub>3</sub>)<sub>2</sub>), 43.6 (C(CH<sub>3</sub>)<sub>2</sub>), 94.5 (CH), 106.7 (DMAP m-Ar-C), 122.8 (Ar-C), 123.0 (br; Ar-C), 123.7 (br; Ar-C), 124.6 (Ar-C), 150.2 (DMAP p-Ar-C), 176.1 (CC(CH<sub>3</sub>)<sub>3</sub> (note that not all resonances are observed owing to peak broadening); IR (Nujol):  $\tilde{\nu} = 1614$  (s), 1537 (m), 1495 (m), 1365 (m), 1316 (m), 1261 (m), 1149 (m), 1096 (s), 1008 (s), 800 (s), 728 cm<sup>-1</sup> (m); EIMSI m/z (%): 502.5 (10)

Chem. Eur. J. 2010, 16, 938-955

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

C. Jones, A. Stasch et al.

[<sup>IBu</sup>NacnacH<sub>2</sub>+], 445.5 (84) [<sup>IBu</sup>NacnacH<sup>+</sup>-C<sub>4</sub>H<sub>9</sub>], 224.3 (100) [C<sub>17</sub>H<sub>26</sub>N<sup>+</sup>]; elemental analysis calcd (%) for C<sub>42</sub>H<sub>64</sub>N<sub>4</sub>Mg ( $M_r$ =649.28): C 77.69, H 9.94, N 8.63; found: C 76.83, H 9.50, N 8.27.

**Crystallography**: Crystals of **6–20**, **22**, **27–31**, and [(<sup>Mes</sup>Nacnac)Mg( $\mu$ -I)<sub>2</sub>Mg(<sup>Mes</sup>Nacnac)] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made by using either a Nonius Kappa CCD or Bruker X8 CCD diffractometer using a graphite monochromator with Mo<sub>Ka</sub> radiation ( $\lambda$ =0.71073 Å). The data were collected at 123 K and the structures were solved by direct methods and refined on F<sup>2</sup> by using full-matrix least-squares techniques (SHELX97)<sup>[52]</sup> and including all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms (except hydrides) included in calculated positions (riding model). The hydride ligands in the crystal structures of compounds **18**, **30**, and **31** were refined with no positional restraints.

A crystal of 16 that was suitable for a neutron diffraction experiment was mounted in the helium flow cryostat of the instrument VIVALDI<sup>[53]</sup> at the Institut Laue-Langevin, Grenoble. Laue patterns were recorded from the stationary crystal at a temperature of 123 K. The refinement of the structure was undertaken by using the CRYSTALS<sup>[54]</sup> suite of programs and was commenced by using atomic positions of non-hydrogen atoms taken from the X-ray crystal structure of the compound. After refinement of this model, all hydrogen atoms were clearly visible from difference maps and were introduced into the model. Subsequent refinement of the positional and isotropic displacement parameters for all atoms of the structure led to its convergence with a final R(F) of 14.5% for 1993 independent reflections with  $[I > 2\sigma(I)]$ . In the final difference map for the structure there was no significant residual nuclear density, which is consistent with the absence of hydride ligands bridging the magnesium centers of the compound. Full details of the neutron diffraction experiment can be found in the Supporting Information.

A table containing crystal data, details of data collections and refinement for all compounds, selected metrical parameters and/or ORTEP diagrams for the structures of **6**, **10–12**, **15**, **19**, **20**, and [(<sup>Mes</sup>Nacnac)Mg(µ-I)<sub>2</sub>(<sup>Mes</sup>Nacnac)], as well as full details of the neutron diffraction experiment on **16** can be found in the Supporting Information. CCDC-745078 **(6)**, 745079 **(7)**, 745080 **(8)**, 745081 **(9)**, 745082 **(10)**, 745083 **(11)**, 745084 **(12)**, 745085 **(13)**, 745086 **(14)**, 745087 **(15)**, 745088 **(16:** X-ray structure), 745099 **(16:** neutron structure), 745094 **(20)**, 745095 **(22:** 3 toluene), 745096 **(27:** 2 benzene), 745097 **(28:** 3 benzene), 745098 **(29)**, 745099 **(30:** benzene), 745100 **(31:** 2 benzene), and 745077 ([[(<sup>Mes</sup>Nacnac)Mg(µ-I)<sub>2</sub>]<sub>2</sub>]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### Acknowledgements

We thank the Australian Research Council (fellowships for C.J., A.S., and S.N. and a studentship for S.J.B.) and the US Air Force Asian office of Aerospace Research and Development for funding. Funding from the AMRF program of the Australian Nuclear and Technology Organisation is acknowledged. Thanks also go to the EPSRC Mass Spectrometry Service, Swansea, UK.

[3] See, for example: a) R. Köppe, P. Henke, H. Schnöckel, Angew. Chem. 2008, 120, 8868–8872; Angew. Chem. Int. Ed. 2008, 47, 8740– 8744; b) X. Wang, L. Andrews, J. Phys. Chem. A 2004, 108, 11511-11520.

- [4] It is of note that quasi  $Mg_2^{2+}$  units have been reported to be present in the superconducting binary material,  $MgB_2$ , and related ternary hydride materials such as  $Mg_4IrH_5$ . See, for example: R. B. King, *Polyhedron* **2002**, *21*, 2347–2350, and references therein.
- [5] a) L. A. Tjurina, V. V. Smirnov, D. A. Potapov, S. A. Nikolaev, S. E. Esipov, I. P. Beletskya, *Organometallics* 2004, 23, 1349–1351;
  b) L. A. Tjurina, V. V. Smirnov, G. B. Barkovskii, E. N. Nikolaev, S. E. Esipov, I. P. Beletskya, *Organometallics* 2001, 20, 2449–2450. Related magnesium(I) dimers, RMgMgX, have been proposed as intermediates in the formation of Grignard reagents, see, for example: P. G. Jasien, C. E. Dykstra, *J. Am. Chem. Soc.* 1983, *105*, 2089–2090.
- [6] a) Y.-H. Kan, J. Mol. Struct. 2009, 894, 88–92; b) L. Gong, X. Wu, C. Qi, W. Li, J. Xiong, W. Guo, Mol. Phys. 2009, 107, 197–204; c) J. M. Mercero, M. Piris, J. M. Matxain, X. Lopez, J. M. Ugalde, J. Am. Chem. Soc. 2009, 131, 6949–6951; d) T. Pankewitz, W. Klopper, P. Henke, H. Schnöckel, Eur. J. Inorg. Chem. 2008, 4879–4890; e) A. Velazquez, I. Fernandez, G. Frenking, G. Merino, Organometallics 2007, 26, 4731–4736; f) M. Westerhausen, M. Gärtner, R. Fischer, J. Langer, L. Yu, M. Reiher, Chem. Eur. J. 2007, 13, 6292–6306; g) Q. S. Li, Y. Xu, J. Chem. Phys. 2006, 124-125, 11898–11902; h) Y. Xie, H. F. Schaefer III, E. D. Jemmis, Chem. Phys. Lett. 2005, 402, 414–421.
- [7] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* 2004, 305, 1136–1138.
- [8] a) E. Carmona, A. Galindo, Angew. Chem. 2008, 120, 6626–6637; Angew. Chem. Int. Ed. 2008, 47, 6526–6536; b) A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Rio, R. A. Andersen, J. Am. Chem. Soc. 2007, 129, 693–703; c) J. F. Van der Maelen, E. Gutierrez-Puebla, A. Monge, S. Garcia-Granda, I. Resa, E. Carmona, M. T. Fernandez-Diaz, G. J. McIntyre, P. Pattison, H.-P. Weber, Acta Crystallogr. Sect. A 2007, 63, 862–868.
- [9] a) Y. Liu, S. Li, X.-J. Yang, P. Yang, J. Gao, Y. Xia, B. Wu, Organometallics 2009, 28, 5270-5272; b) S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser, R. Boese, Angew. Chem. 2009, 121, 5859-5862; Angew. Chem. Int. Ed. 2009, 48, 5748-5751; c) D. Schuchmann, U. Westphal, S. Schulz, U. Florke, D. Bläser, R. Boese, Angew. Chem. 2009, 121, 821-824; Angew. Chem. Int. Ed. 2009, 48, 807-810; d) S. Schulz, D. Schuchmann, U. Westphal, M. Bolte, Organometallics 2009, 28, 1590-1592; e) Y.-C. Tsai, J.-K. Hwang, Y.-M. Lin, D.-Y. Lu, J.-S. K. Yu, Chem. Commun. 2007, 4125-4127; f) X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer III, Y. Liang, B. Wu, Chem. Commun. 2007, 2363-2365; g) I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, Angew. Chem. 2007, 119, 4380-4383; Angew. Chem. Int. Ed. 2007, 46, 4302-4305; h) Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead, P. P. Power, J. Am. Chem. Soc. 2007, 129, 10847-10857; i) Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda, P. P. Power, Angew. Chem. 2006, 118, 5939-5942; Angew. Chem. Int. Ed. 2006, 45, 5807-5810; j) Y. Wang; B. Quillian; P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer III, G. H. Robinson, J. Am. Chem. Soc. 2005, 127, 11944-11945; B. Quillian; P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer III, G. H. Robinson, J. Am. Chem. Soc. 2005, 127, 11944-11945
- [10] S. P. Green, C. Jones, A. Stasch, Science 2007, 318, 1754-1757.
- [11] M. Westerhausen, Angew. Chem. 2008, 120, 2215–2217; Angew. Chem. Int. Ed. 2008, 47, 2185–2187.
- [12] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* 2008, 2832– 2838.
- [13] S. P. Green, C. Jones, A. Stasch, Angew. Chem. 2008, 120, 9219– 9223; Angew. Chem. Int. Ed. 2008, 47, 9079–9083.
- [14] J. Overgaard, C. Jones, A. Stasch, B. B. Iversen, J. Am. Chem. Soc. 2009, 131, 4208–4209.

954

Of most relevance to this study is the chemistry of Group 13–15 element(I) dimers, REER (R=bulky aryl, alkyl etc.,). For recent reviews in this area, see: a) E. Rivard, P. P. Power, *Inorg. Chem.* 2007, 46, 10047–10064; b) P. P. Power, *Organometallics* 2007, 26, 4362–4372; c) A. Sekiguchi, *Pure Appl. Chem.* 2008, 80, 447–457; d) T. Sasamori, N. Tokitoh, *Dalton Trans.* 2008, 1395–1408.

<sup>[2]</sup> See, for example: S. Petrie, Aust. J. Chem. 2003, 56, 259-262, and references therein.

- [15] S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, Angew. Chem. 2009, 121, 3017–3021; Angew. Chem. Int. Ed. 2009, 48, 2973–2977.
- [16] Y. Liu, S. Li, X.-J Yang, P. Yang, B. Wu, J. Am. Chem. Soc. 2009, 131, 4210–4211.
- [17] S. Krieck, H. Görls, L. Yu, M. Reiher, M. Westerhausen, J. Am. Chem. Soc. 2009, 131, 2977–2985.
- [18] J. Prust, K. Most, I. Müller, E. Alexopoulos, A. Stasch, I. Uson, H. W. Roesky, Z. Anorg. Allg. Chem. 2001, 627, 2032–2037.
- [19] J. Emsley, The Elements, 2nd ed., Clarendon, Oxford, 1995.
- [20] A. P. Dove, V. C. Gibson, P. Hormnirun, E. L. Marshall, J. A. Segal, A. J. P. White, D. J. Williams, *Dalton Trans.* 2003, 3088–3097.
- [21] As determined from a survey of the Cambridge Crystallographic Database, August, 2009.
- [22] C. Jones, A. Stasch, Anal. Sci. X-ray Struct. Anal. Online 2007, 23, x115-x116.
- [23] S. Nembenna, H. W. Roesky, S. Nagendran, A. Hofmeister, J. Magull, P.-J. Wilbrandt, M. Hahn, Angew. Chem. 2007, 119, 2564– 2566; Angew. Chem. Int. Ed. 2007, 46, 2512–2514.
- [24] C. Ruspic, S. Harder, Inorg. Chem. 2007, 46, 10426-10433.
- [25] See, for example: Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* 2007, *129*, 12412–12413, and references therein. Note that intermolecular isopropyl hydride abstraction cannot be ruled out as contributing to the mechanism of formation of 18. Similar abstraction processes have been noted previously as giving rise to magnesium hydride complexes, see, for example: D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* 2002, 376–377.
- [26] Theoretical studies have predicted significantly shorter and stronger Be–Be bonds in compounds of the type RBeBeR (e.g., for R=Cp: Be–Be distances of ca. 2.06–2.08 Å; BDEs of ca. 70 kcalmol<sup>-1</sup>) than the Mg–Mg bonds of magnesium(I) dimers RMgMgR (see Ref. [6]).
  [27] See the Supporting Information for further details.
- [27] See the supporting information for further details.
- [28] a) H. M. El-Kaderi, M. J. Heeg, C. H. Winter, *Polyhedron* 2006, 25, 224–234; b) S. Harder, *Organometallics* 2002, 21, 3782–3787; c) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* 2003, 48–49.
- [29] Theoretical studies have predicted significantly longer and weaker Ca-Ca bonds in compounds of the type RCaCaR (Ca-Ca distances of ca. 3.73-3.82 Å; BDEs of <30 kcal mol<sup>-1</sup>) than the Mg-Mg bonds of magnesium(I) dimers RMgMgR (see Ref. [6]).
- [30] The steric profiles of the ligands <sup>Dipp</sup>Nacnac and <sup>(Bu</sup>Nacnac have previously been compared: P. L. Holland, Acc. Chem. Res. 2008, 41, 905-914.
- [31] The effect of the steric bulk of β-diketiminate ligands upon the planarity of their metallacyclic complexes has been previously noted, see, for example: P. B. Hitchcock, M. F. Lappert, D.-S. Liu, J. Chem. Soc. Chem. Commun. 1994, 1699–1700.
- [32] A very low yield (<2%) of the compound [( $^{rBu}$ Nacnac)Mg(C<sub>6</sub>D<sub>5</sub>)-(DMAP)] was obtained from the reaction of **17** with DMAP in [D<sub>6</sub>]benzene after several days. A poor-quality crystal structure of the compound confirmed it to be monomeric in the solid state. No spectroscopic data were obtained. The mechanism of formation of this compound is unknown.
- [33] The X-ray crystal structure of **21**, although of low quality, ambiguously revealed the connectivity of the compound and showed it to have a similar geometry to that of **22**.
- [34] L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, Organometallics 2006, 25, 1012–1020.

- [35] It is of note that the reduction of the unfunctionalized unsaturated substrate 1,3,5,7-cyclooctatetraene by 2 does occur, but only in toluene heated at reflux.
- [36] It is of note that other magnesium reagents that can act as one electron reductants have been described. These include Mg/MgI<sub>2</sub> mixtures, which have been proposed to be in equilibrium with univalent magnesium, MgI, in solution. See, for example: M. D. Rausch, W. E. McEwen, J. Kleinberg, *Chem. Rev.* 1957, 57, 417–437, and references therein.
- [37] It is of note that none of the magnesium(I) dimers 2, 16, or 17 react with the bulkier carbodiimide DippN = C = NDipp in toluene at 20 °C.
- [38] R. E. Cowley, J. Elhaïk, N. A. Eckert, W. W. Brennessel, E. Bill, P. L. Holland, J. Am. Chem. Soc. 2008, 130, 6074–6075.
- [39] See, for example: a) D. Mackay, D. D. McIntyre, N. J. Taylor, J. Org. Chem. 1982, 47, 532–535; b) C. M. Fitchett, C. Richardson, P. J. Steel, Org. Biomol. Chem. 2005, 3, 498–502.
- [40] See, for example: a) H. Zhou, H. Guo, Y. Yao, L. Zhou, H. Sun, H. Sheng, Y. Zhang, Q. Shen, *Inorg. Chem.* **2007**, *46*, 958–964; b) F. Yuan, Q. Shen, J. Sun, *Polyhedron* **1998**, *17*, 2009–2012.
- [41] A. Datta, J. Phys. Chem. C 2008, 112, 18727-18729.
- [42] B. Bogdanovic, A. Ritter, B. Spielthoff, Angew. Chem. 1990, 102, 239–250; Angew. Chem. Int. Ed. Engl. 1990, 29, 223–234, and references therein.
- [43] The formation of MgH<sub>2</sub> complexes through treatment of MgnBu<sub>2</sub> with PhSiH<sub>3</sub> in donor solvents (L) has previously been shown to yield amorphous materials, formulated as [{MgH<sub>2</sub>(L)}<sub>n</sub>]: M. Michalczyk, Organometallics **1992**, *11*, 2307–2309.
- [44] It is of note that a variety of dimeric magnesium hydride complexes of the type [{RMg(μ-H)}<sub>2</sub>] (R=amide, alkyl etc.,) had been previously prepared but not structurally characterized. See, for example: E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1978**, *17*, 1862–1866.
- [45] Another structurally characterized cluster compound exhibiting Mg-(μ-H)-Mg moieties, namely, [Mg<sub>4</sub>H<sub>6</sub>(IPr)<sub>2</sub>[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>] (IPr=:C-{(Dipp)NCH}<sub>2</sub>) has recently been described: M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem.* 2009, *121*, 4073–4076; *Angew. Chem. Int. Ed.* 2009, *48*, 4013–4016.
- [46] A good yield (76%) of the related complex  $[Mg(^{Ph}Nacnac)_2]$  **15** can similarly be obtained by treating <sup>Ph</sup>NacnacH with MgnBu<sub>2</sub> in hexane at 50 °C for 20 min.
- [47] G. A. Molander, C. R. Harris, Chem. Rev. 1996, 96, 307-338.
- [48] M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky, P. P. Power, J. Chem. Soc. Dalton Trans. 2001, 3465– 3469.
- [49] L.-M. Tang, Y.-Q. Duan, X.-F. Li, Y.-S. Li, J. Organomet. Chem. 2006, 691, 2023–2030.
- [50] X. Xu, X. Xu, Y. Chen, J. Sun, Organometallics 2008, 27, 758-763.
- [51] P. H. M. Budzelaar, A. B. van Oort, A. G. Orpen, Eur. J. Inorg. Chem. 1998, 1485–1494.
- [52] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997.
- [53] a) C. Wilkinson, J. A. Cowan, D. A. A. Myles, F. Cipriani, G. J. McIntyre, *Neutron News* **2002**, *13*, 37–41; b) G. J. McIntyre, M.-H. Lemée-Cailleau, C. Wilkinson, *Physica B* **2006**, *385–386*, 1055–1058.
- [54] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, J. Appl. Crystallogr. 2003, 36, 1487.

Received: September 2, 2009 Published online: November 30, 2009