# Mononuclear Three-Coordinate Magnesium Complexes of a Highly Sterically Encumbered *β*-Diketiminate Ligand

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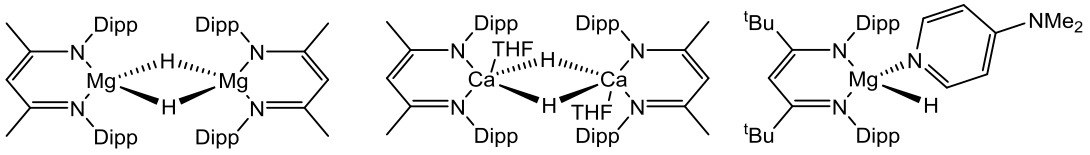
## Abstract

The highly sterically encumbered chelating *β*-diketiminate ligand, [HC{C(Me)N(2,6-CHPh$_2$-4-MeC$_6$H$_2$)}$_2$]$^-$, $^{Ar}$L$^-$, has been used to prepare a series of heteroleptic three-coordinate magnesium complexes. Both the bis(imine) and imine-enamine tautomers of the ligand precursor, $^{Ar}$LH, as well as the diethyl ether adduct of the bromide complex, [$^{Ar}$LMgBr(OEt$_2$)], the monomeric methyl complex, [$^{Ar}$LMgMe], the THF-solvated and unsolvated *n*-butylmagnesium complexes, [$^{Ar}$LMg$^n$Bu(THF)] and [$^{Ar}$LMg$^n$Bu] and the 1-hexynyl analogue, [$^{Ar}$LMgC≡C$^n$Bu] have been crystallographically characterized. Both *n*-butylmagnesium complexes showed remarkable stability in air, both in the solid state and in solution. Single crystals of the highly sensitive magnesium hydride, [$^{Ar}$LMgH], underwent partial hydrolysis by solid-state water diffusion to the isostructural hydroxide compound, [$^{Ar}$LMgOH].

## Introduction

Since the 1970s *β*-diketiminate ligands[1] have found numerous applications as highly tunable monoanionic chelating ligands for the stabilization of main group, as well as late transition metal and f-block elements.[2] Among this ligand class the ease of preparation and steric properties of the [HC{CMeN(Dipp)}$_2$H] (Dipp = 2,6-di-*iso*propylphenyl) derivative, LH,[3] have earmarked it as the pro-ligand of choice for the synthesis of well-defined heteroleptic alkaline earth complexes of the form [LMRD$_n$]$_m$ (M = Be, Mg, Ca, Sr, Ba; R = reactive substituent, e.g. halide, alkoxide, amide, alkyl, etc.; D = neutral donor ligand; m/n = 1–3).

This has enabled the stabilization of even the smallest group 2-bound functionalities.[4-6] The synthesis of well-defined, soluble group 2 hydrides, in particular, remains challenging as low bond energies and primarily ionic bonding often lead to ligand redistribution and the precipitation of highly stable and insoluble $[MH_2]_\infty$ hydrides, especially among the larger congeners. The steric protection afforded by the *β*-diketiminate ligand, L, and other bulky derivatives has enabled the isolation of magnesium and calcium hydride species, readily obtained by σ-bond metathesis of the heteroleptic *n*-butylmagnesium or calcium bis(trimethylsilyl)amide precursors with phenylsilane.[6] While the unsolvated *β*-diketiminate magnesium hydride species, **I**, and the related calcium hydride THF adduct, **II**, form dimers both in solution and the solid state, these may be fragmented to monomeric species by addition of a bulky neutral donor molecule, such as in the 4-dimethylaminopyridine adduct, **III**. Over the last decade these *β*-diketiminate-supported molecular group 2 hydrides have rapidly gained in importance as homogenous catalysts in a variety of transformations, including the hydrosilylation and hydrogenation of activated alkenes,[7] the hydrosilylation of ketones[8] and the hydroboration of pyridines, imines, aldehydes and ketones.[9]

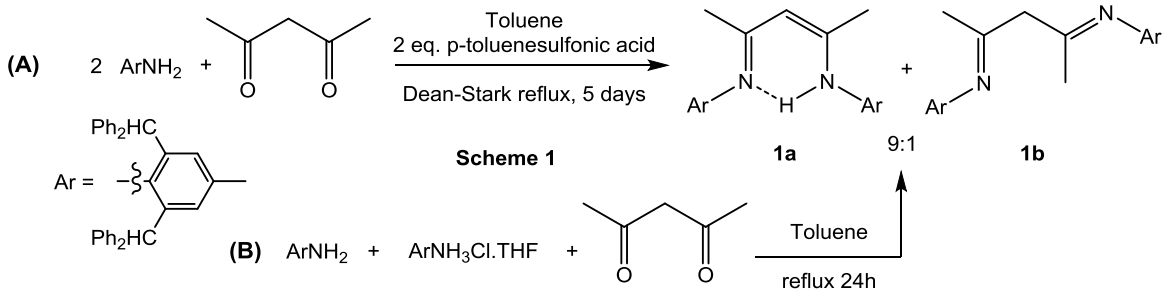



**I** **II** **III**

Dipp = 2,6-$iPr_2C_6H_3$

Other ligands, such as *N*-heterocyclic carbenes or bis(diketiminates) have enabled the isolation of well-defined $Mg_nH_m$ clusters (n = 4, m = 4, 6; n = 8, m = 10).[10] There are, to date however, no reports of three-coordinate monomeric group 2 hydride species. The quest for the stabilization of low-coordinate main group hydride complexes relies on the utilization of new ligands with highly sterically hindering substituents capable of encapsulating the metal center. Heavily substituted terphenyl derivatives, for example, have enabled the successful isolation of the whole series of heavier group 13 dimetallenes and group 14 dimetallynes.[11] Easily accessible in a two-step synthesis the extremely bulky silylanilide derivative, $[N(Ar)(SiMe_3)]^-$ (Ar = 2,6-bis(diphenylmethyl)-*p*-tolyl),[12] has also been successfully used to stabilize group 13 dihydrides, heavier group 14(II) hydrides and even one-coordinate group 13 metal(I) complexes.[13] Herein we report the synthesis of an extremely bulky *β*-diketiminate derivative bearing similar *N*-Ar appendages, and its application in the stabilization of the first monomeric three-coordinate magnesium *n*-butyl, 1-hexynyl, hydrido and hydroxide complexes.

## Results and discussion

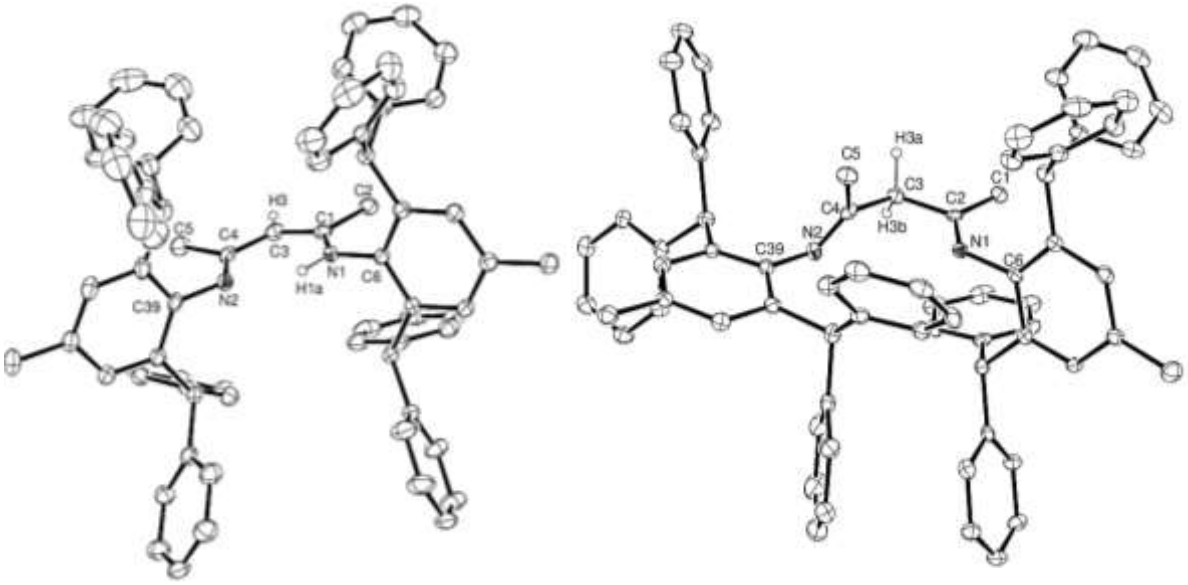



**Scheme 1**

The 2,6-bis(diphenylmethyl)-*p*-tolyl-substituted *β*-diketiminate ligand precursor **1**, $^{Ar}$LH, was synthesized in good yield by Dean-Stark reflux in toluene of 2,4-pentanedione with two equivalents of the corresponding aniline and *p*-toluenesulfonic acid (Scheme 1A). Recrystallization from hot dichloromethane yielded a large crop of colorless crystals. NMR spectroscopic analysis ($CDCl_3$) revealed compound **1** to be a ca. 9:1 mixture of the imine-enamine, compound **1a**, and its bis(imine) tautomer, compound **1b**, respectively. Alternatively $^{Ar}$LH was obtained by heating at reflux one equivalent of the aniline and one equivalent of its hydrochloride salt with 2,4-pentanedione in toluene, followed by a basic work-up (Scheme 1B). At 298 K, the enamine tautomer, **1a**, displayed a characteristic downfield $^1$H NMR N*H* resonance at δ 12.11 ppm and a backbone methine singlet resonance at δ 4.18 ppm, while the bis(imine) compound, **1b**, displayed a 2H backbone methylene singlet at δ 3.07 ppm. Budzelaar *et al.* have previously reported that the synthesis of the *tert*-butyl-substituted *β*-diketiminate ligand precursor [HC{C$^t$BuN(Dipp)}$_2$H], $^{tBu}$LH, also yields a mixture of imine-enamine and bis(imine) tautomers providing similar $^1$H NMR chemical shifts.[14] Most notable for **1a** and **1b** are the chemical shifts of the backbone methyl proton singlets at δ 0.25 and 0.56 ppm, respectively. These are significantly shifted upfield from the corresponding methyl protons in LH, which appear at $\delta_H$ 1.72 ppm.[3] A NOESY experiment revealed a spatial interaction between these methyl groups and the diphenylmethyl moieties, which may account for the extra shielding experienced by the methyl protons. A DOSY experiment on a 0.06 M mixture of **1a** and **1b** in $d_8$-toluene yielded two distinct diffusion coefficients of 4.37 x $10^{-10}$ and 3.02 x $10^{-10}$ $m^2.s^{-1}$, corresponding to Stokes hydrodynamic radii of 8.48 and 12.25 Å, respectively. Subsequent syntheses of **1** always resulted in mixtures of **1a** and **1b** in similar ratios. Single crystals of the enamine tautomer, **1a** (Figure 1, left), were acquired from chloroform or saturated toluene solutions at room temperature while X-ray quality crystals of the bis(imine) compound, **1b** (Figure 1, right), were obtained from a saturated toluene solution at 4 $^o$C. Details of the X-ray crystallographic analyses and selected

bond lengths and angles are displayed in Tables 1 and 2, respectively. For the crystals grown from chloroform the asymmetric unit of the enamine tautomer, **1a**, contains two distinct but structurally similar molecules. In both cases, the amino-proton was located on one of the nitrogen atoms of the molecule and freely refined, with N-H bond lengths of 0.875(19) and 0.847(19) Å. The distance between the imino-nitrogen and the amino-proton [1.99(3) and 2.00(3) Å] suggest the presence of a N---H hydrogen bonding interaction, while the bond lengths within the ligand framework are clearly indicative of an imine-enamine structure. The rather short C-C and C-N single bonds [C3-C4 1.423(6), C74-C75 1.419(6) Å; C1-N1 1.345(5), C72-N3 1.358(5) Å] and slightly elongated C=C and C=N double bonds [C1-C31.383(6), C72-C74 1.373(5) Å; C4-N2 1.314(5), C75-N4 1.313(5) Å] also suggest a degree of delocalization over the ligand framework (see Supplementary Information for structural details of crystals of **1a** grown from toluene). The bis(imine) tautomer, **1b**, crystallizes as the (*Z*,*Z*) conformer, with the backbone methyl groups adopting an *anti* orientation with respect to each other, similar to the solid state structure of the bis(imine) form of $^{tBu}$LH.[15] The C=N bond lengths [1.266(5) and 1.273(5) Å] are characteristic of localized double bonds, while the bond lengths and angles around the $\beta$-carbon, C3, indicate $sp^3$ hybridization [C1-C3 1.512(6), C3-C4 1.503(6) Å; C1-C3-C4 115.1(4)$^o$].

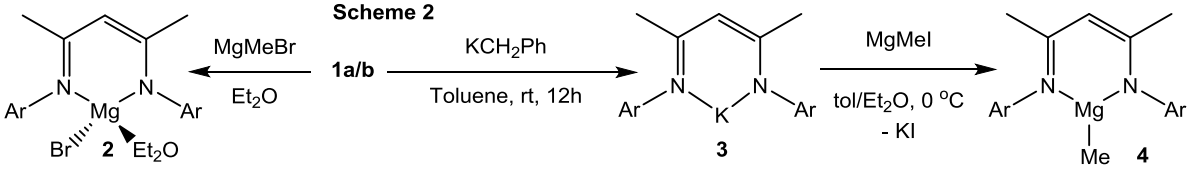
**Figure 1.** ORTEP representations of one of the molecules in the asymmetric unit of the




amino-imine compound, **1a** (left), and its bis(imine) tautomer, **1b** (right). Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity except the amino and methine protons H1A and H3 in **1a**, and the methylene protons H3A and H3B in **1b**.

The reaction of $^{Ar}$LH with methylmagnesium bromide in diethyl ether at room temperature yielded only a very low yield (< 5%) of the desired magnesium bromide complex, [$^{Ar}$LMgBr(OEt$_2$)], compound **2**, after work-up. NMR analysis of the crude reaction mixture also showed the presence of [$^{Ar}$LMgMe] arising from ligand redistribution. While a single crystal X-ray diffraction analysis yielded the unambiguous structure of a four-coordinate magnesium bromide diethyl ether adduct supported by the monoanionic $^{Ar}$L$^-$ chelate ligand, the amount of product isolated was insufficient for further characterization (see Supplementary Information for an ORTEP representation of **2** and details of the X-ray experiment). NMR spectroscopic analysis of the reaction mixture prior to work-up revealed a complex mixture of products, among which only [$^{Ar}$LMgMe] could be identified. Clean deprotonation of the ligand precursor $^{Ar}$LH was, however, achieved using a suspension of benzyl potassium in toluene at room temperature (Scheme 2). The resulting potassium complex, [$^{Ar}$LK], compound **3**, was isolated as a yellow solid from hexanes in good yield (82%). Analysis by $^1$H NMR spectroscopy data indicated a notable downfield shift of the backbone methine proton singlet resonance to δ 4.56 ppm. Reaction of **3** with methylmagnesium iodide in toluene and diethyl ether produced a thick precipitate of potassium iodide. Filtration and addition of hexanes to the filtrate yielded the methylmagnesium complex [$^{Ar}$LMgMe], compound **4**, as colorless crystals in good yield (75%) upon storage at 4 $^o$C (Scheme 2).

**Scheme 2**




NMR spectra of **4** displayed a very characteristic upfield $^1$H NMR singlet resonance integrating for 3 protons at δ –1.27 ppm and a $^{13}$C NMR resonance at δ –18.1 ppm corresponding to the magnesium-bound methyl ligand. These chemical shifts are similar to those observed for the related dimeric unsolvated methylmagnesium *β*-diketiminato complex [LMgMe]$_2$ ($\delta_{1H}$ −1.17, $\delta_{13C}$ −18.6 ppm)[16] and those of Bailey's monomeric three-coordinate *tert*-butyl-substituted complex, [$^{tBu}$LMgMe] ($\delta_{1H}$ −1.37, $\delta_{13C}$ −16.8 ppm).[17]

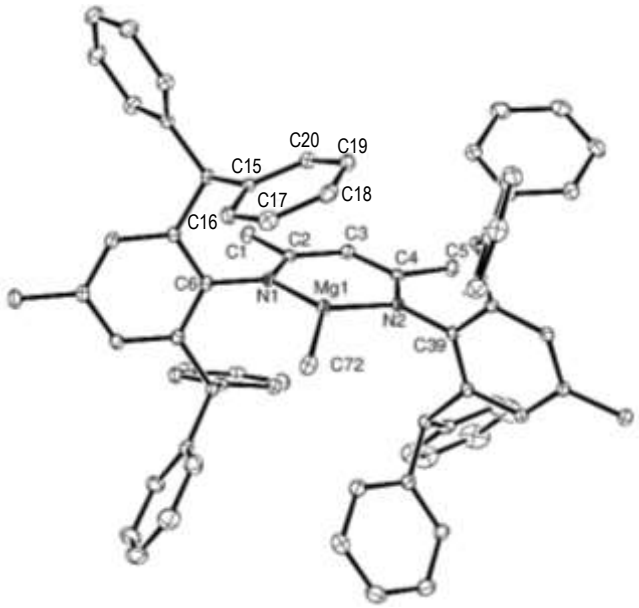
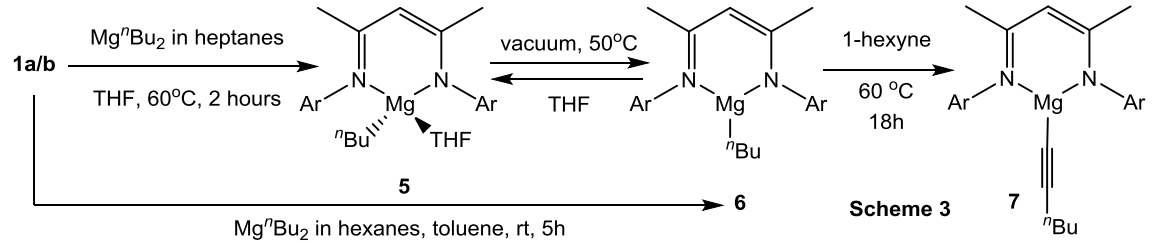



**Figure 2.** ORTEP representation of complex **4**. Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.

A single crystal X-ray diffraction experiment yielded a monomeric structure displaying a three-coordinate magnesium center (Figure 2). This is only the second example of a crystallographically characterized, monomeric three-coordinate methylmagnesium complex.[17] Details of the experiment and selected bond lengths and angles are provided in Tables 1 and 2, respectively. While the methyl carbon atom C72 lies in the mean plane of the $\beta$-diketiminate framework the magnesium atom lies ca. 0.33 Å above this plane, distorting it from a trigonal planar geometry. The Mg-C bond length of 2.114(2) Å is longer than that observed in [$^{tBu}$LMgMe] [2.077(2) Å][17] but still significantly shorter than those in the four-coordinate dimer, [LMgMe]$_2$, containing two asymmetrically bridging methyl fragments [2.220(2), 2.245(2) Å].[16] The N1-Mg-N2 bite angle [94.65(5)$^o$] of the ligand is smaller than that in [$^{tBu}$LMgMe] [95.68(7)$^o$][17] but significantly larger than in [LMgMe]$_2$ [91.30(6)$^o$].[16] This reflects the relative combined steric strain of the nitrogen appendages and the backbone methyl or *tert*-butyl substituents. In order to relieve the steric strain in complex **4** seven of the phenyl groups on the diphenylmethyl substituents rotate away from the methylmagnesium moiety, while the [C15-C20] ring is oriented towards the Mg coordination sphere, shielding the methyl ligand on that side. There is, however, no Mg···C contact involving that phenyl group of < 3.2 Å indicating that any significant bonding interaction between it and the Mg center is unlikely.




Scheme 3

Stirring $^{Ar}$LH with one equivalent of di-*n*-butylmagnesium in THF/heptanes at 60 $^o$C for two hours yielded the heteroleptic THF-solvated *β*-diketiminato *n*-butylmagnesium complex **5** as a colorless crystalline solid in high yield (77%) after recrystallization (Scheme 3). NMR spectroscopic data for the compound were consistent with the monomeric formulation [$^{Ar}$LMg$^n$Bu(THF)]. The $^1$H NMR singlet resonance of the ligand backbone methine proton at δ 4.67 ppm was shifted 0.1 ppm downfield of that of **4**. The characteristic upfield multiplet of the MgC$H_2$ methylene protons appeared at δ –0.40 ppm, correlating with a $^{13}$C NMR resonance at δ 6.5 ppm, in accordance with the values reported for the complex [$^{tBu}$LMg$^n$Bu(THF)] ($\delta_{1H}$ −0.54, $\delta_{13C}$ 6.4 ppm).[18]

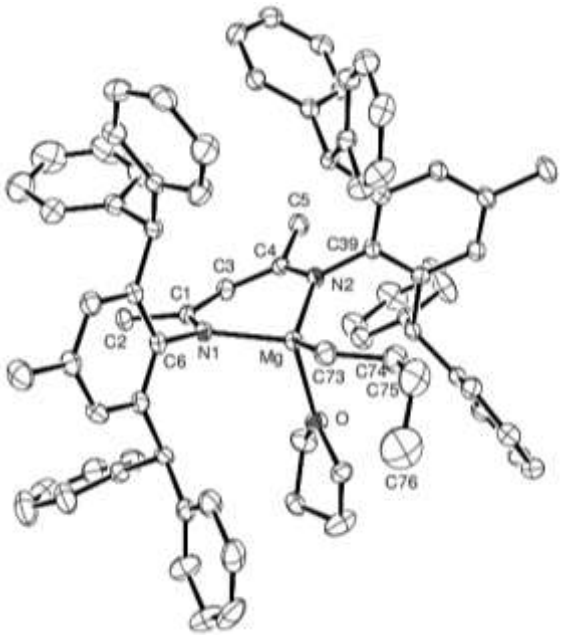



**Figure 3.** ORTEP representation of complex **5**. Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.

Single crystals of compound **5** suitable for X-ray crystallographic analysis were obtained from a 10:1 toluene/THF mixture at room temperature. Details of the X-ray crystallographic experiment and selected bond lengths and angles are provided in Tables 1 and 2, respectively.

Similar to other crystallographically characterized four-coordinate *β*-diketiminate butylmagnesium complexes, compound **5** crystallizes as a monomer (Figure 3).[18,19] Coordination at the *pseudo*-tetrahedral magnesium center is provided by the bidentate *β*-diketiminate ligand, the *n*-butyl substituent and one THF molecule. As expected when comparing a four-coordinate and a three-coordinate complex, the N1-Mg-N2 bite angle of the *β*-diketiminate ligand in complex **5** [90.97(13)$^{o}$] is significantly more acute than that in the methyl derivative, **4**, [94.65(5)$^{o}$], and the Mg-N bonds are elongated by ca. 0.04 Å [**5** 2.082(3), 2.084(4) Å; **4** 2.0320(13), 2.0434(13) Å]. Unlike any other known magnesium alkyl complexes, compound **5** displayed remarkable solid state and solution stability in $C_6D_6$ when exposed to air, showing no sign of hydrolysis or decomposition over a period of one week.

Complete removal of the adducted THF molecule from **5** was achieved by heating the isolated compound at 60$^{o}$C under vacuum for two hours to yield the unsolvated *n*-butylmagnesium complex [$^{Ar}$LMg$^{n}$Bu], **6**. Alternatively, compound **6** could be obtained by adding one equivalent of di-*n*-butylmagnesium in hexanes to ligand precursor **1** in toluene (Scheme 3). The $^{1}$H NMR chemical shift of the MgC*H*$_2$ methylene multiplet at $\delta$ –0.62 ppm is ca. 0.2 ppm upfield from that in the THF-solvated species.

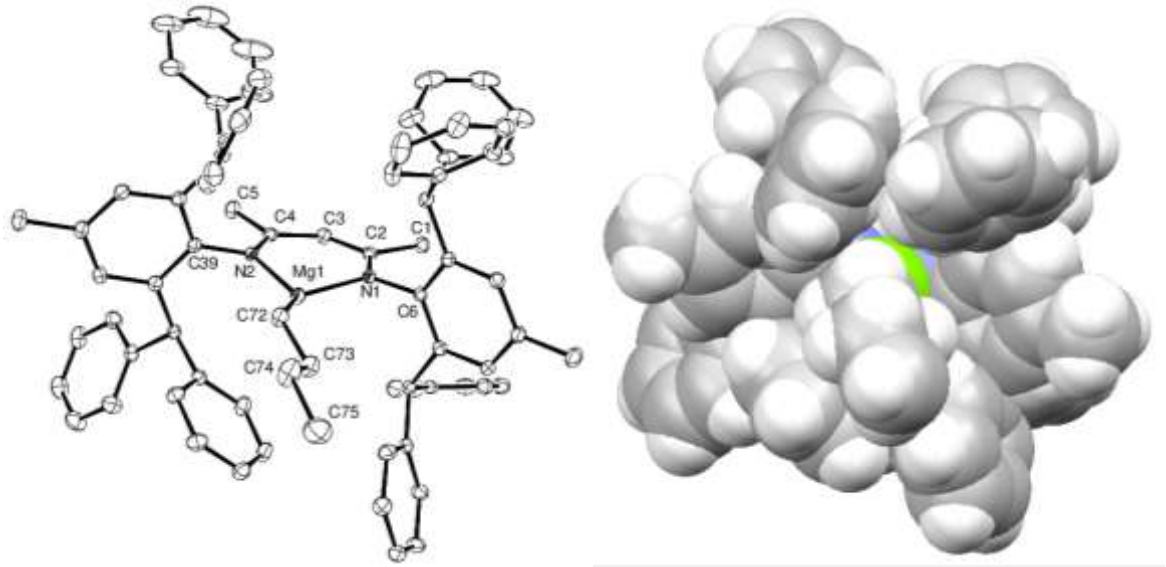



**Figure 4.** ORTEP representation of complex **6** (left) and its space-filling model in the same orientation (right). Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.

Upon dilution of a saturated toluene solution of **6** with hexanes and cooling to 4$^{o}$C overnight, single crystals were obtained. Tables 1 and 2 provide details of the structural analysis and selected structural parameters, respectively. As was the case for the methyl analogue, **4**, the

resulting X-ray crystallographic analysis confirmed the monomeric, three-coordinate nature of complex **6** (Figure 4). In contrast the analogous *β*-diketiminato magnesium butyl complex bearing smaller xylyl or Dipp substituents are dimeric both in solution and in the solid state.[5a,d] The only major structural difference between **4** and **6** is a narrowing of the N1-Mg-N2 bite angle [**4** 94.65(5); **6** 92.31(5)$^{o}$] to accommodate the *n*-butyl ligand. Similar to the THF-solvated analogue, **5**, complex **6** proved effectively stable in the solid state and in $C_6D_6$ solution exposed to air for up to a week at room temperature, as determined by $^{1}$H NMR spectroscopic monitoring (< 5% hydrolysis to LH and [LMg(OH)]). A space-filling model (Figure 4, right) evidences the tight encapsulation of the metal center by the *β*-diketiminate ligand and the *n*-butyl co-ligand, leading to this remarkable stability. In terms of reactivity, however, the steric bulk of the (2,6-diphenylmethyl)-*p*-tolyl appendages proved highly restrictive. A hydroamination experiment using 1-amino-2,2-diphenyl-4-pentene with 2 mol% of isolated crystalline **6** only provided complete conversion to the corresponding pyrrolidine after more than 10 hours at room temperature. This drastic reduction in catalytic activity, compared to the less sterically hindered precatalyst [LMg$^{n}$Bu] (which yielded quantitative conversion in less 2 hours under the same conditions[20]) is most likely caused by reduced access to the metal center for both substrate pre-coordination and concerted insertion/protonolysis.

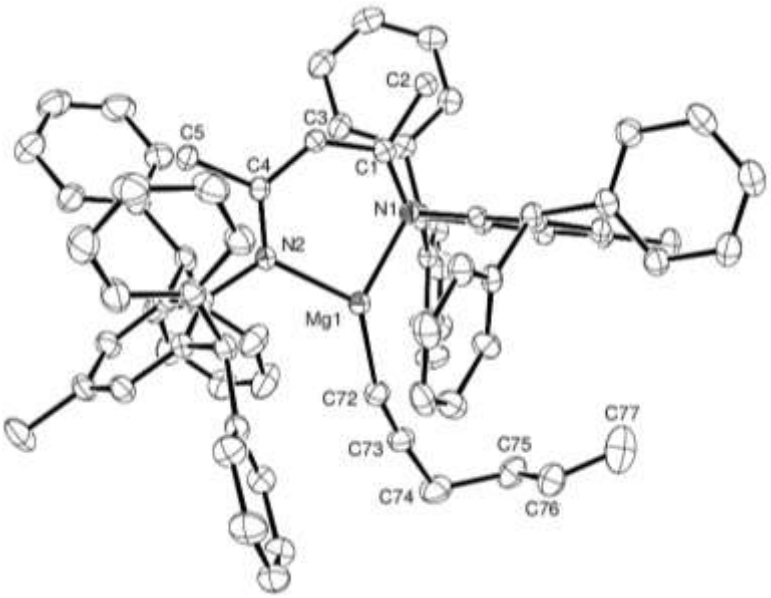
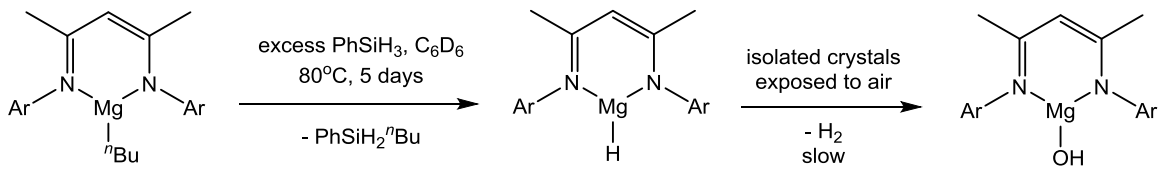



**Figure 5.** ORTEP representation of complex **7**. Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity.

Complex **6** was reacted with 1-hexyne at 60 °C to give the 1-hexynylmagnesium complex [$^{Ar}$LMgC≡C$^{n}$Bu], **7**, in essentially quantitative yield. In contrast to dimeric magnesium *β*-diketiminato acetylide complexes, the $^{1}$H NMR spectra of which exhibit diastereotopic resonances for the aryl substituents indicative of hindered rotation,[21] the $^{1}$H NMR spectrum of complex **7** evidenced a single ligand environment, suggesting a monomeric three-coordinate species. The $^{13}$C NMR spectrum displayed two characteristic Mg*C*≡C and MgC≡*C* resonances at δ 103.5 and δ 111.9 ppm, respectively. These both appeared significantly upfield from the acetylenic $^{13}$C NMR resonances of the analogous dimeric *β*-diketiminato 1-hexynylmagnesium complex, [LMgC≡C$^{n}$Bu]$_2$, at δ 121.0 and δ 112.2 ppm, respectively.[21] In the latter compound, decreased shielding of the acetylenic carbons may be attributed to π-interactions between the bridging alkynyl fragments and the magnesium centers. Single crystals of **7** were isolated from a saturated toluene solution at room temperature and its structure was deduced through a further X-ray diffraction analysis. The structure, displayed in Figure 5, confirms the monomeric three-coordinate nature of the complex. Details of the X-ray diffraction experiment and structural parameters are provided in Tables 1 and 2, respectively. Bond lengths and angles of the *β*-diketiminate framework are very similar to those in the *n*-butyl derivative, **6**. The N1-Mg-N2 bite angle [94.38(10)°] is, however, much closer to that in the methyl derivative, **4** [94.65(5)°], than to that in the *n*-butyl analogue, **6** [92.31(5)°]. The Mg-C72 bond [2.049(3) Å] is, to the best of our knowledge, the shortest crystallographically characterized Mg-C bond. The Mg-C73-C74-C75 moiety, with its characteristically short C73-C74 triple bond [1.224(4) Å], deviates slightly from linearity, with Mg-C73-C74 and C73-C74-C75 angles of 165.7(3) and 173.8(4)°, respectively.

**Scheme 4**




**6** **8** **9**

The slow reaction of **6** with phenylsilane at 80 °C in $C_6D_6$ provided quantitative conversion to the corresponding heteroleptic magnesium hydride species [$^{Ar}$LMgH], **8**, together with one equivalent of the metathesis by-product, PhSi$^{n}$BuH$_2$ (Scheme 4). Removal of volatiles and recrystallization from a 2:1 $C_6D_6$/hexanes solution at room temperature yielded **8** as colorless crystals in ca. 90% yield. The complex displayed a characteristic $^{1}$H NMR singlet resonance

at δ 4.07 ppm, slightly downfield of the bridging hydride resonances observed for the dimeric *β*-diketiminate magnesium hydride species reported by Jones and co-workers (δ 3.83–3.92 ppm) but significantly upfield of the terminal hydride resonance observed at δ 4.65 ppm for the four-coordinate monomeric species [{HC{C$^t$BuN(2,6-$^i$Pr$_2$C$_6$H$_3$)}$_2$}MgH(DMAP)] (DMAP = 4-dimethylaminopyridine).[6d] The magnesium deuteride analogue, **D-8**, synthesized by the same method using $PhSiD_3$, displayed a single $^2$H NMR Mg*D* resonance at δ 3.96 ppm. Although the IR (KBr) spectra of **8** and **D-8** differ slightly it was not possible to unambiguously assign the Mg–H and Mg–D absorptions as they overlap with the ligand absorptions in the fingerprint region.[22] A DOSY experiment yielded a diffusion coefficient of 4.17 x $10^{-10}$ $m^2.s^{-1}$ in $C_6D_6$ (0.06 M solution), corresponding to a Stokes radius of 8.62 Å, close to that of the ligand precursor, **1a**. This confirms the mononuclear three-coordinate nature of compound **8** in solution.

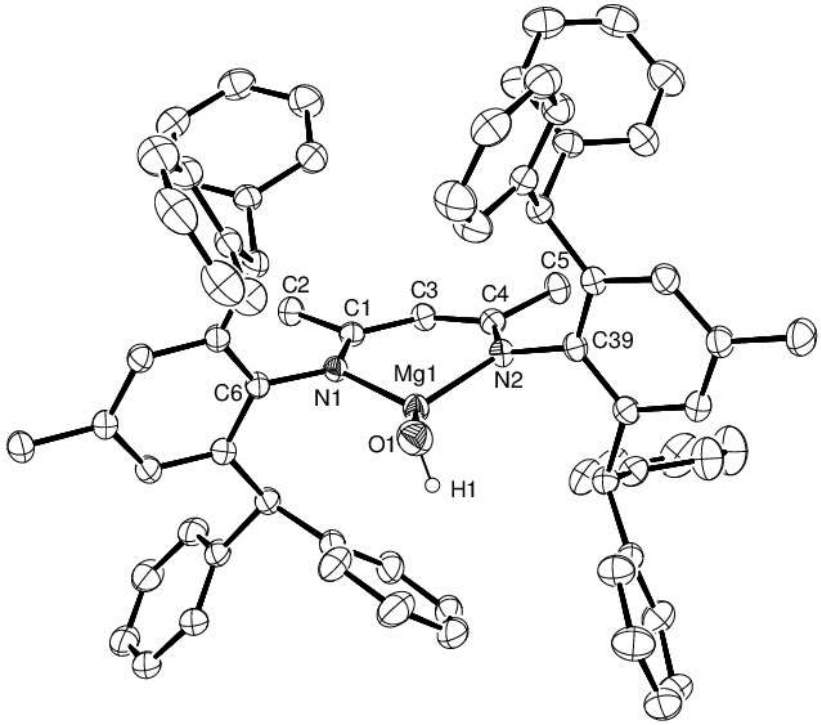



**Figure 6.** ORTEP representation of complex **9** (crystals containing 85:15 mixture of **8** and **9**). Ellipsoids drawn at 30% probability. Hydrogen atoms omitted for clarity, except for the hydroxyl proton H1.

Although single crystals of **8** and **D-8** suitable for X-ray diffraction analysis could be isolated, these underwent slow hydrolysis of the hydride moiety during crystal selection in the microscopy oil. This was evidenced by bubbling of $H_2$ from the crystal surface, albeit without loss of crystallinity (Scheme 4). Over a series of crystallographic determinations, the

resulting structures were all shown to contain various proportions of the co-crystallized, three-coordinate hydroxide species, [$^{Ar}$LMg(OH)], complex **9**, depending on how long it took to mount the crystals on the diffractometer. As a result, the hydride atom of **8** could not be located during structural refinement. The details of the X-ray crystallographic analyses and selected bond lengths and angles for a sample containing an 85:15 mixture of **8** and **9**, respectively, are provided in Table 1 and Table 2. The asymmetric unit contains two crystallographically independent molecules, both modelled with the same 85:15 mixture of **8** and **9**. Figure 6 shows one of the molecules of hydroxide complex, **9**. Structures containing larger proportions of **9** also displayed significantly more solvent disorder and solvent loss, as well as poorer $R_{int}$ and $R_1$ values. Monitoring of the unit cell of a single crystal of **8** left at room temperature did not result in significant lattice parameter changes over a period of five hours. A subsequent X-ray crystallographic experiment performed at 150 K, however, showed that the crystal now contained an approximately 1:1 ratio of **8** and **9**, but with such a degree of solvent loss and disorder that full refinement was not possible. The bond lengths and angles of the *β*-diketiminate ligand, as well as the N1-Mg-N2 bite angles [94.20(9), 93.26(9)$^{o}$] are all very similar to those in the three-coordinate 1-hexynyl complex, **7**. As expected for a three-coordinate magnesium hydroxide species, the Mg-O bond lengths [1.73(2), 1.747(18) Å] are much shorter than in the four- and five-coordinate dimeric *β*-diketiminate complexes, $[LMg(OH)]_2$ and $[LMg(OH)(THF)]_2$, in which the hydroxide units bridge between two magnesium centers $[LMg(OH)]_2$ 1.957(2), 1.962(2) Å; $[LMg(OH)(THF)]_2$ 1.9878(17) Å].[4b, 23] To our knowledge compound **9** is the sole reported example of a structurally characterized three-coordinate magnesium hydroxide. Multiple attempts to synthesize **9** by controlled addition of one equivalent of water to a toluene solution of **6** or **8** at low temperature, or reaction with a molecular stoichiometric water source, such as copper sulfate pentahydrate, inevitably resulted in significant amounts of protonation of the *β*-diketiminate ligand, as evidenced by the appearance of the characteristic $^1$H NMR N*H* resonance at δ 12.11 ppm. Exposure of isolated crystals of **8** to atmospheric conditions for prolonged periods of time never yielded complete conversion to the hydroxide, presumably due to crystal size-limited solid-state water diffusion. Conversely, ground samples of **8** underwent both hydride and *β*-diketiminate hydrolysis when exposed to air over longer periods of time.

## Conclusion

The use of the extremely sterically hindered 2,6-bis(diphenylmethyl)-*p*-tolyl-substituted *β*-diketiminate ligand has enabled the isolation of a number of three-coordinate magnesium alkyl, alkynyl, hydride and hydroxide species, presenting pseudo-trigonal planar geometries at magnesium. The bulky nitrogen aryl appendages afford remarkable kinetic stability to the otherwise highly reactive magnesium *n*-butyl functionality, making it virtually air-stable both in solution and in the solid state at room temperature. This, however, also limits its usefulness in catalytic transformations which require substrate pre-coordination. In the case of the three-coordinate magnesium hydride complex, the exposed hydride moiety underwent solid state diffusion controlled partial hydrolysis to the analogous magnesium hydroxide complex.

**Table 1.** Details of X-ray crystallographic analyses for compounds **1a**, **1b**, **4-7** and an 85:15 mixture of **8** and **9**.

| | **1a** | **1b** | **4** | **5** | **6** | **7** | **8/9 85:15** |
|---|---|---|---|---|---|---|---|
| Chemical formula | $2(C_{71}H_{62}N_2)\bullet 2.3(CHCl_3)$ | $C_{71}H_{62}N_2$ | $C_{85}H_{86}MgN_2$ | $C_{86}H_{86}MgN_2O$ | $C_{75}H_{70}MgN_2$ | $C_{77}H_{69}MgN_2\bullet C_7H_8$ | $C_{71}H_{61.15}MgN_2O_{0.15}\bullet 2(C_6H_6)$ |
| Formula Mass | 2161.00 | 943.23 | 1159.87 | 1187.88 | 1023.64 | 1138.78 | 1125.29 |
| Temperature/K | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1$ | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 14.8918(2) | 11.2164(12) | 12.7608(5) | 13.9290(5) | 12.0964(4) | 13.1791(6) | 13.19320(10) |
| $b$/Å | 22.3244(4) | 13.1293(14) | 16.0274(7) | 15.8762(7) | 17.2910(6) | 13.2304(6) | 13.29930(10) |
| $c$/Å | 18.9375(3) | 18.8572(18) | 18.0554(8) | 15.5792(7) | 28.0393(10) | 19.0177(7) | 36.9496(4) |
| $\alpha$/° | 90.00 | 72.216(9) | 78.316(4) | 90 | 90.00 | 97.035(3) | 87.7914(5) |
| $\beta$/° | 109.1590(10) | 86.223(8) | 71.938(4) | 96.364(2) | 99.854(3) | 100.793(3) | 88.9917(4) |
| $\gamma$/° | 90.00 | 81.205(9) | 73.385(4) | 90 | 90.00 | 91.552(2) | 89.9024(5) |
| Unit cell volume/Å$^3$ | 5947.07(16) | 2612.6(5) | 3337.8(2) | 3423.9(2) | 5778.1(3) | 3228.6(2) | 6477.37(10) |
| No. of formula units per unit cell, $Z$ | 2 | 2 | 2 | 2 | 4 | 2 | 4 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.218 | 0.068 | 0.074 | 0.075 | 0.077 | 0.075 | 0.075 |
| $\theta$ range measured/$^o$ | 3.46 to 25.04 | 2.18 to 25.00 | 2.39 to 27.00° | 4.07 to 25.08 | 2.06 to 27.00 | 3.61 to 27.08 | 3.08 to 25.06 |
| No. of reflections measured | 87101 | 15931 | 26819 | 35511 | 31490 | 37589 | 87706 |
| No. of independent reflections | 20791 | 9140 | 14571 | 11921 | 12502 | 13469 | 22262 |
| $R_{int}$ | 0.0719 | 0.0701 | 0.0218 | 0.1168 | 0.0279 | 0.1063 | 0.0646 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0682 | 0.0686 | 0.0495 | 0.0658 | 0.0469 | 0.0739 | 0.0666 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1738 | 0.1063 | 0.1273 | 0.1330 | 0.1049 | 0.1480 | 0.1531 |
| Final $R_1$ values (all data) | 0.0906 | 0.1481 | 0.0665 | 0.1202 | 0.0677 | 0.1614 | 0.1074 |
| Final $wR(F^2)$ values (all data) | 0.1912 | 0.1418 | 0.1394 | 0.1581 | 0.1158 | 0.1856 | 0.1720 |

**Table 2.** Selected bond lengths and angles for compounds **1a**, **1b**, **4**-**7** and an 85:15 mixture of **8** and **9**.

| | **1a**[a] | **1b** | **4** | **5**[a] | **6** | **7**[a] | **8/9 85:15**[a] |
|---|---|---|---|---|---|---|---|
| N1-C2 | 1.345(5), 1.358(5) | 1.277(4) | 1.336(2) | 1.326(5) | 1.3359(19) | 1.329(3) | 1.339(3), 1.341(3) |
| C2-C3 | 1.383(6), 1.373(5) | 1.507(4) | 1.407(2) | 1.404(6) | 1.407(2) | 1.414(4) | 1.402(4), 1.404(4) |
| C3-C4 | 1.423(6), 1.419(6) | 1.502(4) | 1.410(2) | 1.403(6) | 1.401(2) | 1.401(4) | 1.403(4), 1.404(4) |
| C4-N2 | 1.314(5), 1.313(5) | 1.268(4) | 1.338(2) | 1.335(5) | 1.3380(19) | 1.339(3) | 1.337(3), 1.334(3) |
| Mg-N1 | – | – | 2.0320(13) | 2.082(3) | 2.0463(13) | 2.021(2) | 2.020(2), 2.019(2) |
| Mg-N2 | – | – | 2.0434(13) | 2.084(4) | 2.0326(13) | 2.027(2) | 2.030(2), 2.030(2) |
| Mg-O | – | – | – | 2.105(3) | – | – | 1.73(2), 1.747(18) |
| Mg-C72 | – | – | 2.1142(18) | 2.131(5) | 2.089(4), 2.135(7) | 2.049(3) | – |
| C72-C73 | – | – | – | 1.533(6) | 1.515(4) | 1.224(4) | – |
| N1-C2-C3 | 122.1(3), 120.5(3) | 117.6(3) | 123.54(13) | 122.8(3) | 123.71(13) | 123.2(3) | 123.6(2), 123.2(2) |
| C2-C3-C4 | 125.8(3), 127.3(3) | 115.9(3) | 130.58(14) | 130.0(4) | 129.84(14) | 130.4(3) | 130.9(2), 129.9(2) |
| C3-C4-N2 | 121.7(3), 121.0(3) | 118.6(3) | 124.32(13) | 123.5(4) | 123.47(13) | 124.0(3) | 123.1(2), 123.8(2) |
| C2-N1-Mg | – | – | 122.89(10) | 122.0(2) | 124.53(10) | 123.41(19) | 122.66(17), 124.54(17) |
| C4-N2-Mg | – | – | 121.56(10) | 121.6(3) | 125.11(10) | 122.40(19) | 123.14(17), 123.94(17) |
| N1-Mg-N2 | – | – | 94.65(5) | 90.97(13) | 92.31(5) | 94.38(10) | 94.20(9), 93.26(9) |
| N1-Mg-O | – | – | – | 103.58(13) | – | – | 132.5(7), 133.3(6) |
| N2-Mg-O | – | – | – | 105.67(13) | – | – | 125.2(7), 125.4(5) |
| N1-Mg-C72 | – | – | 132.29(6) | 121.88(16) | 132.47(13), 128.8(2) | 127.45(12) | – |
| N2-Mg-C72 | – | – | 127.26(6) | 130.09(16) | 129.44(11), 138.4(2) | 128.51(12) | – |
| C6-N1-Mg | – | – | 117.52(9) | 118.6(3) | 115.25(9) | 116.65(17) | 117.09(16), 115.07(16) |
| C39-N2-Mg | – | – | 120.38(9) | 119.4(3) | 116.35(9) | 118.96(17) | 115.34(16), 116.04(16) |
| Mg-C72-C73 | – | – | – | 124.0(3) | 125.4(3) | 165.7(3) | – |
| C72-C73-C74 | – | – | – | 118.6(4) | 114.6(3) | 173.8(4) | – |

[a] For compounds **1a**, **5** and **7** and the 85:15 mixture of **7**/**8** C1 and C2 are inverted.

## Experimental

### General Methods

All manipulations were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen or argon. Toluene, hexane, THF, and benzene were distilled over molten potassium, whereas diethyl ether was distilled over a Na/K alloy (25:75). Potassium benzyl and 2,6-diphenylmethyl-*p*-toluidine were prepared by literature procedures.[24] All other reagents were used as received. $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra were recorded on either Bruker DPX 400 or Bruker AV-300 spectrometers in deuterated solvents and were referenced to the residual $^{1}$H or $^{13}$C resonances of the solvent used. IR spectra were recorded using a Perkin–Elmer RXI FTIR spectrometer as Nujol mulls between NaCl plates or using a Nexus FT-IR spectrometer as KBr pellets.

### Crystallographic data

Crystals of all structurally characterized compounds were mounted in silicone oil. Crystallographic measurements of **1b**, **4** and **6** were carried out at 150 K with an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å), those of **1a**, **5**, **7** and the 85:15 mixture of **8** and **9** at 150 K with a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite-monochromated Mo Kα radiation. Data were processed using the Nonius Software.[25] Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.80 suite of programs throughout.[26]

*Compound **1a**:* The asymmetric unit contains two independent molecules of the ligand and three independent molecules of solvent $CHCl_3$. Amino protons were located in the difference Fourier map and freely refined with idealized bond lengths. Prior to data collection the crystals had been lying in oil for several days causing solvent loss. This is reflected in the fact that all $CHCl_3$ molecules in the lattice have an occupation factor between 70 and 80 %. The $CHCl_3$ molecule with 70% occupation also displays a 1:1 disorder in one of the chlorine atoms. Bond lengths in this disorder have been restrained and ADPs equalized. The Flack parameter of 0.47 indicates a potential for a centrosymmetric space group. Trying to solve the structure in $P2_1/n$, however, resulted in total disorder of the one remaining ligand in the asymmetric unit and unreasonably short bond lengths between ligand and solvent molecules.

*Compound **4**:* The asymmetric unit contains one molecule of hexane and one of toluene.

*Compound **5***: Each asymmetric unit contains one magnesium complex and one molecule of toluene, which is disordered over two sites in the ratio 56:44. Bond lengths of the two $CH_3$ groups had to be restrained. The adducted THF molecule displays a 75:25 disorder in C79. The C78-C79A bond length had to be restrained.

*Compound **6***: The *n*-butyl ligand displays a 62:38 disorder in all four carbon atoms. Bond lengths in this ligand had to be restrained. Bond lengths in the phenyl substituent C67-C71 were restrained.

*Compound **7**:* The asymmetric unit contains one molecule of toluene. The 1-hexynyl ligand displays a 50:50 disorder in the two methylene carbons C75 and C76.

*85:15 mixture of compounds **8** and **9**:* Due to high moisture sensitivity the microscopy oil had to be thoroughly degassed and the microscopy slide cooled to –36°C in the glovebox prior to crystal selection. The asymmetric unit contains four benzene molecules, two of which are disordered, one in a 72:28 ratio, the other in a 70:30 ratio. The two independent magnesium complexes are composed of a 85:15 ratio of the hydride complex **8** and the hydroxide complex **9**. As a result the hydride atom of **8** could not be located in the difference Fourier map.

**Synthetic procedures**

*Synthesis of ligand precursor $^{Ar}$LH, **1a/b**.*

2,4-pentanedione (1.37 g, 13.6 mmol) and 2,6-diphenylmethyl-*p*-toluidine (12 g, 27.3 mmol) were refluxed with *p*-toluenesulfonic acid (5.19 g, 27.3 mmol) in toluene (300 mL) under Dean-Stark conditions for five days. Upon cooling of the resulting brown mixture a cream-colored solid precipitated, which was filtered, neutralised with 500 mL of a 5% aqueous NaOH solution and extracted into 800 mL of $CH_2Cl_2$. After drying over $MgSO_4$ the solvent was removed *in vacuo* yielding an off-white solid which was purified by flash chromatography with a 50:50 hexane/THF mixture. Crystallization from hot chloroform (20 mL) afforded compound **1** as colorless needles (6.70 g, 7.11 mmol, 52% yield). $^1$H NMR ppm (300 MHz, 298 K, $CDCl_3$), **1a** (88%): δ 12.11 (s, 1H, N*H*), 7.26-7.28 (m, 16H, Ph-*H*), 7.00-7.05 (m, 24H, Ar-*H*), 6.85 (s, 4H, *m*-tol-*H*), 5.95 (s, 4H, C*H*Ph$_2$), 4.18 (s, 1H, *β*-C*H*), 2.24 (s, 6H, tol-C*H$_3$*), 0.25 (s, 6H, *α*-C*H$_3$*); **1b** (12%): δ 7.08-7.23 (m, 40H, Ar-*H*), 6.69 (s, 4H, *m*-tol-*H*), 5.42 (s, 4H, C*H*Ph$_2$), 3.07 (s, 2H, *β*-C*H$_2$*), 2.17 (s, 6H, tol-C*H$_3$*), 0.56 (s, 6H, *α*-C*H$_3$*). $^{13}$C{$^1$H} NMR ppm (75 MHz, 298 K, $CDCl_3$), **1a**: δ 164.0 (N=*C*), 144.8 (*i*-tol-*C*),

142.3 (*i*-Ph-*C*), 138.6 (*p*-tol-*C*), 133.4 (*o*-tol-*C*), 130.0, 129.4 (*m*-Ph-*C*), 128.2, 128.0 (*o*-Ph-*C*), 126.1 (*m*-tol-*C*), 125.8 (*p*-Ph-*C*), 94.8 (*β*-C), 52.1 (*C*HPh$_2$), 21.5 (*α*-*C*H$_3$), 19.5 (tol-*C*H$_3$); **1b**: δ 164.0 (N=*C*), 144.0 (*i*-tol-*C*), 141.2 (*i*-Ph-*C*), 138.6 (*p*-tol-*C*), 132.5 (*o*-tol-*C*), 129.9, 129.3 (*m*-Ph-*C*), 128.3, 127.9 (*o*-Ph-*C*), 126.1 (*m*-tol-*C*), 125.9 (*p*-Ph-*C*), 77.0 (*β*-C), 51.5 (*C*HPh$_2$), 21.5 (*α*-*C*H$_3$), 19.5 (tol-*C*H$_3$). IR (nujol, cm$^{-1}$): 1621w, 1600w, 1537w, 1389s, 1365s, 1261w, 1231m, 1076w, 1030m, 795w, 756w, 698m. MS (ESI, m/z): 944.48 ([MH]$^+$, 100%). Elemental analysis for $C_{71}H_{62}N_2$ (Mw = 943.3): Calc. C, 90.41; H, 6.63; N, 2.97%. Found: C, 90.36; H, 6.58; N, 2.94%.

*Synthesis of [$^{Ar}$LK], compound **3***

A suspension of ligand precursor **1** (1.00 g, 1.06 mmol) and benzyl potassium (0.146 g, 1.12 mmol) were stirred for 12 hours at room temperature in toluene (30 mL). The reaction was relatively slow due to the poor solubility of benzyl potassium in toluene. The solution was then concentrated to a dry residue which was triturated with hexane (10 mL) to give [$^{Ar}$LK] as a yellow solid (0.850 g, 0.870 mmol, 82%). $^1$H NMR (400 MHz, 303 K, $C_6D_6$): δ 7.36 (d, $^3J$ = 7.2 Hz, 8H, Ar-*H*), 7.14 (t, $^3J$ = 7.6 Hz, 8H, Ph-*H*), 7.08 (d, $^3J$ = 6.8 Hz, 8H, Ar-*H*), 7.00-7.05 (m, 8H, Ar-*H*), 6.76-6.85 (m, 12H, Ar-*H*), 5.99 (s, 4H, C*H*Ph$_2$), 4.56 (s, 1H, *β*-C*H*), 2.02 (s, 6H, tol-C*H*$_3$), 1.41 (s, 6H, *α*-C*H*$_3$). $^{13}$C{$^1$H} NMR (100 MHz, 303 K, $C_6D_6$): δ 163.1 (N=*C*), 151.9 (*i*-tol-*C*), 146.9, 144.2 (*i*-Ph-*C*), 136.8 (*p*-tol-*C*), 130.4, 129.8, 129.3, 129.1, 128.5, 128.2, 126.2, 126.0 (*p*-Ph-*C*), 92.0 (*β*-C), 52.0 (*C*HPh$_2$), 24.8 (*α*-*C*H$_3$), 21.2 (tol-*C*H$_3$). IR (nujol, cm$^{-1}$): 2919m, 2851m, 1543w, 1491m, 1459m, 1446m, 1405m, 1286m, 1220m, 1171m, 1117m, 1075m, 1029m, 1006m, 976m, 916m, 855m, 670m, 741m. MS (CI, m/z): 980.6 ([M]$^+$, 100%). Elemental analysis for $C_{71}H_{61}N_2K$ (Mw = 981.36): Calc. C, 86.90; H, 6.27; N, 2.85%. Found: C, 86.70; H, 6.94; N, 2.67%.

*Synthesis of [$^{Ar}$LMgMe], compound **4***

MeMgI (0.68 mL, 1.1 M in Et$_2$O, 0.68 mmol) was added to a solution of **3** (0.70 g, 0.71 mmol) in toluene (15 mL) and diethyl ether (15 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature, concentrated to approximately a quarter of the volume and then filtered. Hexane (20 mL) was added and the resultant mixture cooled at 4 °C overnight to give the product, [$^{Ar}$LMgMe] as colorless crystals (0.52 g, 74 %). $^1$H NMR (400 MHz, 303 K, $C_6D_6$): δ 7.31 (d, $^3J$ = 7.6 Hz, 8H, Ph-*H*), 7.28 (d, $^3J$ = 7.6 Hz, 8H, Ph-*H*), 7.11 (t, $^3J$ = 7.2 Hz, 8H, Ph-*H*), 7.00-7.07 (m, 16H, Ar-H), 6.86 (t, $^3J$ = 7.2 Hz, 4H, *p*-Ph-H), 5.83 (s, 4H, C*H*Ph$_2$), 4.62 (s, 1H, *β*-C*H*), 1.86 (s, 6H, tol-C*H*$_3$), 1.00 (s, 6H, *α*-C*H*$_3$), –1.27 (s, 3H,

MgC$H_3$). $^{13}$C{$^1$H} NMR (100 MHz, 303 K, $C_6D_6$): δ 169.6 (N=*C*), 143.5 (*i*-tol-*C*), 143.1, 141.7 (*i*-Ph-*C*), 137.8 (*p*-tol-*C*), 132.8 (*o*-tol-*C*), 129.1, 128.8 (*m*-Ph-*C*), 128.4, 127.7 (*o*-Ph-*C*), 127.4 (*m*-tol-*C*), 125.6, 125.3 (*p*-Ph-*C*), 95.0 (*β*-*C*H), 51.5 (*C*HPh$_2$), 21.9 (*α*-*C*H$_3$), 19.8 (tol-*C*H$_3$), –18.1 (Mg*C*H$_3$). IR (nujol, cm$^{-1}$): 3059w, 3025w, 1598w, 1521.2m, 1493m, 1443m, 1377s, 1324m, 1265m, 1266m, 1198m, 1126m, 1078m, 1030m, 931w, 865w, 786w, 744w, 726w, 695s. Elemental analysis for $C_{72}H_{64}MgN_2$ (Mw = 981.6): Calc. 88.10; H, 6.57; N, 2.85%. Found: C, 87.82; H, 6.50; N, 2.73 %.

*Synthesis of [$^{Ar}$LMg$^n$Bu(THF)], compound **5**, and [$^{Ar}$LMg$^n$Bu], compound **6**.*

Mg($^n$Bu)$_2$ (0.318 mL of a 1 M solution in heptane, 0.318 mmol) and ligand precursor **1** (300 mg, 0.318 mmol) were heated in THF (20 mL) at 60 $^o$C for 2 hours. The solvent was removed *in vacuo* and the crude product was recrystallized at room temperature from a 10:1 toluene/THF mixture (5 mL) to yield colorless crystals of [$^{Ar}$LMg$^n$Bu(THF)], compound **5** (270 mg, 0.246 mmol, 77% yield). $^1$H NMR ppm (300 MHz, 298 K, $C_6D_6$): 7.40 (dd, $^3J$ = 6.8, 5.4 Hz, 16H, Ph-*H*), 7.23 (s, 4H, *m*-tol-*H*), 7.16-7.21 (m, 20H, Ph-*H*), 7.10 (t, $^3J$ = 7.3 Hz, 4H, *p*-Ph-*H*), 7.00 (t, $^3J$ = 7.3 Hz, 4H, *p*-Ph-*H*), 5.95 (s, 4H, C*H*Ph$_2$), 4.67 (s, 1H, *β*-C*H*), 3.74 (m, 4H, THF), 1.96 (s, 6H, tol-C$H_3$), 1.41-1.46 (m, 8H, THF + Bu-(C$H_2$)$_2$), 1.09 (t, $^3J$ = 6.7 Hz, 3H, Bu-C$H_3$), 1.03 (s, 6H, *α*-C$H_3$), –0.40 (m, 2H, Mg-C$H_2$). $^{13}$C{$^1$H} NMR ppm (75 MHz, 298 K, $C_6D_6$): 171.0 (N=*C*), 145.1 (*i*-tol-*C*), 144.5, 143.2 (*i*-Ph-*C*), 137.0 (*p*-tol-*C*), 134.0 (*o*-tol-*C*), 130.2 (*m*-Ph-*C*), 129.9, 128.9, 128.7 (*m*-Ph-*C*), 128.5 (*m*-tol-*C*), 128.3, 128.1, 128.0, 127.9 (*o*-Ph-*C*), 126.9, 126.7 (*p*-Ph-*C*), 96.2 (*β*-C), 66.1 (THF), 52.8 (*C*HPh$_2$), 32.0 + 31.9 (Bu-(*C*H$_2$)$_2$), 23.3 (*α*-*C*H$_3$), 21.4 (THF), 21.2 (tol-*C*H$_3$), 14.2 (Bu-*C*H$_3$), 6.5 (Mg-*C*H$_2$). Elemental analysis for $C_{79}H_{78}MgN_2O$ (1095.8): C, 86.59; H, 7.17; N, 2.56%. Found: C, 86.62, H, 7.09, N 2.52%. Prolonged drying of **5** *in vacuo* at 50 $^o$C resulted in complete removal of the adducted THF molecule to yield [$^{Ar}$LMg$^n$Bu], compound **6**. The latter was later synthesized independently by adding Mg($^n$Bu)$_2$ (1.52 mL, 1.00 M solution in heptane, 1.52 mmol) to a slurry of **1** (1.30 g, 1.38 mmol) in toluene (20 mL) and stirring for 5 hours at room temperature prior to concentration and dilution with hexanes (50 mL). The solution was cooled at 4 °C overnight to give the product as colorless crystals (1.14 g, 1.11 mmol, 82.6%). $^1$H NMR ppm (300 MHz, 298 K, $d_8$-tol): 7.27 (dd, $^3J$ = 6.8, 5.4 Hz, 16H, Ph-*H*), 7.02-7.12 (m, 20H, Ph-*H*), 6.97 (t, $^3J$ = 7.3 Hz, 4H, *p*-Ph-*H*), 6.89 (t, $^3J$ = 7.3 Hz, 4H, *p*-Ph-*H*), 5.78 (s, 4H, C*H*Ph$_2$), 4.59 (s, 1H, *β*-C*H*), 1.91 (s, 6H, tol-C$H_3$), 1.20-1.31 (m, 4H, Bu-(C$H_2$)$_2$), 0.97 (t, $^3J$ = 6.7 Hz, 3H, Bu-C$H_3$), 0.94 (s, 6H, *α*-C$H_3$), –0.62 (m, 2H, Mg-C$H_2$). $^{13}$C{$^1$H} NMR ppm (75 MHz, 298 K, $d_8$-tol): 171.0 (N=*C*), 145.0 (*i*-tol-*C*), 144.3, 143.2 (*i*-Ph-*C*), 136.1 (*p*-tol-*C*),

135.5 (*o*-tol-*C*), 130.4, 129.8, 128.9, 128.7 (*m*-Ph-*C*), 128.4 (*m*-tol-*C*), 128.3, 128.2 (*o*-Ph-*C*), 126.9, 126.6 (*p*-Ph-*C*), 96.0 (*β*-C), 53.0 (*C*HPh$_2$), 31.9 + 31.8 (Bu-(*C*H$_2$)$_2$), 23.1 (*α*-*C*H$_3$), 21.1 (tol-*C*H$_3$), 14.2 (Bu-*C*H$_3$), 6.4 (Mg-*C*H$_2$). IR (nujol, cm$^{-1}$): 3060w, 3025w, 1599w, 1542m, 1520m, 1493m, 1444m, 1388s, 1267m, 1196m, 1125m, 1076m, 1030m, 930.5m, 862m, 762m, 745m, 697s. Elemental analysis for $C_{75}H_{70}MgN_2$ (1023.7): Calc. C, 88.00; H, 6.89; N, 2.74%. Found: C, 87.92; H, 7.03; N, 2.81%.

*Synthesis of [$^{Ar}$LMgC≡C$^{n}$Bu], compound **7***

To a $C_6D_6$ solution (0.5 mL) of compound **6** (40 mg, 39 μmol) was added one equivalent of 1-hexyne (4.44 μL, 39 μmol). The reaction mixture was heated at 60 $^{o}$C for 18 hours at which point NMR data indicated full conversion to **7**. The compound was recrystallized at room temperature from a minimal amount of toluene, yielding colorless single crystals (25 mg, 24 μmol, 61% yield). $^{1}$H NMR ppm (400 MHz, 298 K, $C_6D_6$): 7.40 (d, $^{3}J$ = 7.4 Hz, 8H, Ph-*H*), 7.07-7.15 (m, 16H, Ph-*H*), 6.98 (s, 4H, *m*-tol-*H*), 6.91, 6.93 (t, $^{3}J$ = 7.4 Hz, 8H, *m*-Ph-*H*), 6.85 (t, $^{3}J$ = 7.4 Hz, 4H, *p*-Ph-*H*), 6.76 (t, $^{3}J$ = 7.4 Hz, 4H, *p*-Ph-*H*), 5.62 (s, 4H, C*H*Ph$_2$), 4.29 (s, 1H, *β*-C*H*), 2.11 (t, $^{3}J$ = 6.7 Hz, 2H, C≡CC*H$_2$*), 1.68 (s, 6H, tol-C*H$_3$*), 1.35 (dt, $^{3}J$ = 6.7 Hz, 2H, $^{n}$Bu-C*H$_2$*), 1.19 (dq, $^{3}J$ = 6.7 Hz, 2H, $^{n}$Bu-C*H$_2$*), 0.73 (s, 6H, *α*-C*H$_3$*), 0.69 (t, 3H, $^{n}$Bu-C*H$_3$*, $^{3}J$ = 6.7 Hz). $^{13}$C{$^{1}$H} NMR ppm (100 MHz, 298 K, $C_6D_6$): 171.7 (N=*C*), 145.6 (*i*-tol-*C*), 143.1 (*i*-Ph-*C*), 139.6 (*p*-tol-*C*), 134.6 (*o*-tol-*C*), 131.0 (*m*-Ph-*C*), 130.7 (*m*-tol-*C*), 130.4 (*m*-Ph-*C*), 129.6, 129.0 (*o*-Ph-*C*), 127.3, 127.0 (*p*-Ph-*C*), 111.9 (MgC≡*C*), 103.5 (Mg*C*≡C), 96.9 (*β*-C), 53.2 (*C*HPh$_2$), 33.0 (C≡C*C*H$_2$), 23.3 (*α*-*C*H$_3$), 22.6 ($^{n}$Bu-*C*H$_2$), 21.6 (tol-*C*H$_3$), 21.3 ($^{n}$Bu-*C*H$_2$), 14.4 ($^{n}$Bu-*C*H$_3$). IR (KBr, cm$^{-1}$): 3063s, 3022s, 2962m, 2923m, 1942s, 1622m, 1597m, 1564w, 1521m, 1489m, 1445w, 1397w, 1366s, 1261w, 1242m, 1192m, 1125m, 1074s, 1027w, 926s, 862s, 799w, 745m, 698m. Three successive attempts to obtain elemental analysis data proved unsatisfactory due to the extreme air- and moisture-sensitivity of the complex. NMR spectra are provided in Supplementary Information as corroborative proof of purity.

*Synthesis of [$^{Ar}$LMgH], compound **8***

To a $C_6D_6$ solution (0.5 mL) of compound **6** (50 mg, 49 μmol) were added three equivalents of phenylsilane (18 μL, 0.15 mmol). The reaction mixture was heated at 80 $^{o}$C for 7 days at which point NMR data indicated >95% conversion to **8**. The compound was recrystallized at room temperature in a 2:1 $C_6D_6$/hexanes mixture (0.5 mL), yielding large colorless crystals (41 mg, 42 μmol, 86% yield). $^{1}$H NMR ppm (400 MHz, 298 K, $C_6D_6$): 7.36 (d, $^{3}J$ = 7.4 Hz,

8H, *o*-Ph-*H*), 7.28 (d, $^{3}J$ = 7.4 Hz, 8H, *o*-Ph-*H*), 7.11 (t, $^{3}J$ = 7.3 Hz, 8H, *m*-Ph-*H*), 7.04 (t, 12H, *m/p*-Ph-*H*), 7.01 (s, 4H, *m*-tol-*H*), 6.84 (t, $^{3}J$ = 7.3 Hz, 4H, *p*-Ph-*H*), 5.87 (s, 4H, C*H*Ph$_2$), 4.57 (s, 1H, *β*-C*H*), 4.07 (s, 1H, Mg*H*), 1.92 (s, 6H, tol-C*H*$_3$), 0.99 (s, 6H, *α*-C*H*$_3$). $^{13}$C{$^{1}$H} NMR ppm (100 MHz, 298 K, $C_6D_6$): 171.3 (N=*C*), 145.3 (*i*-Ph-*C*), 144.8 (*i*-tol-*C*), 143.0 (*i*-Ph-*C*), 139.7 (*p*-tol-*C*), 134.5 (*o*-tol-*C*), 130.9 (*o*-Ph-*C*), 130.7 (*m*-tol-*C*), 130.2 (*o*-Ph-*C*), 129.4 (*o*-Ph-*C*), 129.1 (*o*-Ph-*C*), 127.4 (*p*-Ph-*C*), 127.1 (*p*-Ph-*C*), 97.0 (*β*-C), 53.1 (*C*HPh$_2$), 23.4 (*α*-*C*H$_3$), 21.6 (tol-*C*H$_3$). IR (KBr, cm$^{-1}$) for **8**: 3056s, 3021s, 2961w, 2910w, 1600s, 1518m, 1492s, 1445w, 1385w, 1311w, 1268w, 1236w, 1195m, 1150s, 1125m, 1074s, 1027m, 983m, 862s, 745m, 701m. IR (KBr, cm$^{-1}$) for **D-8**: 3060s, 3019s, 2955w, 2917w, 1597m, 1521w, 1496m, 1448w, 1388w, 1318s, 1268m, 1242m, 1230m, 1198m, 1154s, 1122m, 1103m, 1078m, 1027m, 982s, 935s, 865m, 741m, 697m. Elemental analysis for $C_{75}H_{70}MgN_2$ (967.6): Calc. C, 88.13; H, 6.46; N, 2.90%. Found: C, 87.99; H, 6.51; N, 2.83%.

## Supporting Information

Alternative synthetic procedure for $^{Ar}$LH, compound **1** and synthetic details for [$^{Ar}$LMgBr(OEt$_2$)], compound **2**, NMR spectra for compounds **7** and **8**. Details of the X-ray analyses of compounds **1a** and **2**. Crystallographic information files (CIF) for **1a**, **1b**, **2**, **4**, **5**, **6**, **7** and **8**/**9**. This material is available free of charge at http://pubs.acs.org.

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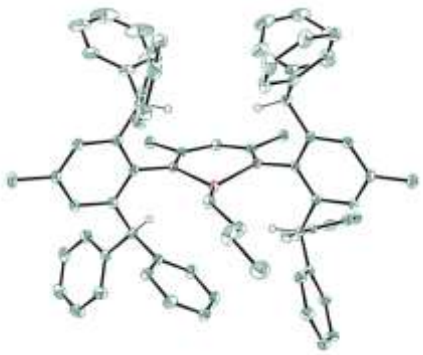

The highly sterically encumbered chelating *β*-diketiminate ligand, [HC{C(Me)N(2,6-$CHPh_2$-4-$MeC_6H_2$)}$_2$]$^-$, $^{Ar}L^-$, has been used to prepare a variety of magnesium complexes including the first three-coordinate terminal magnesium hydride and some unusually air-stable magnesium alkyl complexes.