Accessing Stable Magnesium Acyl Compounds: Reductive Cleavage of Esters by Magnesium(I) Dimers

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Abstract

The first examples of magnesium acyls, [(Nacnac)Mg{μ-C(Ph)O}(μ-OR)Mg(Nacnac)] (R = Me, Bu^t or Ph; Nacnac = [HC(MeCNAr)$_2$]$^-$; Ar = $C_6H_2Me_3$-2,4,6 (^{Mes}Nacnac), $C_6H_3Et_2$-2,6 (^{Dep}Nacnac), $C_6H_3Pr^i_2$-2,6 (^{Dip}Nacnac)), have been prepared by reductive cleavage of a series of esters using dimeric magnesium(I) reducing agents, [{(Nacnac)Mg}$_2$]. Crystallographic studies reveal the complexes to be dimeric, being bridged by both phenyl-acyl and alkoxide/aryloxide fragments. The crystal structures, combined with results of spectroscopic and computational studies suggest that the nature of the acyl ligands within these complexes should be viewed as lying somewhere between anionic umpolung acyl and oxo-carbene. However, reactions of the acyl complexes with a variety of organic electrophiles did not provide evidence of umpolung acyl reactivity. A number of attempts to prepare alkoxide free magnesium acyls were carried out, and while these were unsuccessful, they did lead to unusual products, the crystallographic and spectroscopic details of which are discussed.

Keywords

magnesium acyl, magnesium(I), ester cleavage, reduction, umpolung

Introduction

The use of acyl anion equivalents is of considerable importance to organic synthesis, as these umpolung reagents normally act as nucleophiles through their carbonyl *C*-center, thereby allowing them to participate in otherwise difficult C-C bond forming reactions.[1] Despite their importance, they often require several steps to synthesize, are not thermally stable and/or need to be generated *in situ*. A number of classes of masked acyl anion equivalents are now available to the synthetic chemist, including metalated dithianes used in

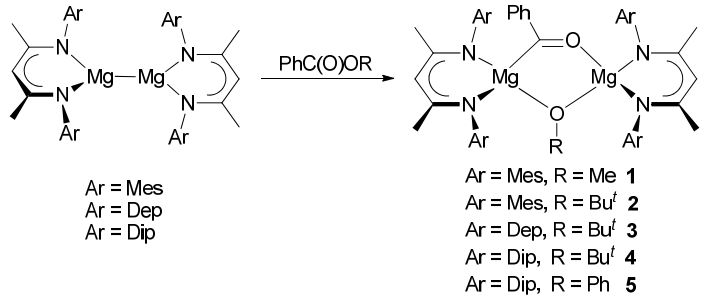
the Corey-Seebach reaction,[2] protected cyanohydrins,[3] metalated enol ethers, silyl acyls etc.[4] In addition, organo-catalysts, such as N-heterocyclic carbenes, have been extensively used to mediate C-C bond forming reactions *via* acyl anion equivalents, e.g. "Breslow intermediates".[5,6] One potential way to circumvent the complexity of procedures involving these reagents would be to have ready access to simple metal acyl complexes, $L_nMC(=O)R$, which could act as direct sources of nucleophilic acyl anions. While many hundreds of examples of d-block metal acyls have been reported,[7] the electronegativities of the metals involved in these systems are generally too high for the complexes to act as acyl anion sources. In contrast, some success has been had using highly polarized lithium acyls, $^{\delta+}Li^{\delta-}C(=O)R$, as direct sources of acyl anions in reactions with electrophiles.[8,9] However, these reagents typically need to be generated at very low temperatures (*ca.* -100 °C) from the reaction of RLi with carbon monoxide, and are unstable at well below room temperature. To the best of our knowledge there are no known examples of stable s-block metal acyls, but if these could be prepared, they may well prove useful as direct sources of acyl anions in their further reactivity.

We have had considerable success using β-diketiminato coordinated magnesium(I) dimers as powerful and selective two-electron reducing agents in both organic and inorganic synthetic methodologies.[10] In organic synthesis, these reagents have proved useful in a variety of reductive element-element bond cleavage and bond formation processes. Throughout this work magnesium(I) dimers have exhibited marked parallels with the reactivity of often used lanthanide(II) reducing agents, e.g. SmI_2, $SmCp^*_2$ etc. One recent demonstration of the synthetic power of samarium diiodide has been its use in the *in situ* formation of samarium acyl radicals *via* reductive cleavage of unactivated esters.[11] In light of this, we wondered if magnesium(I) dimers might reductively cleave esters to give stable magnesium acyl complexes, all prior examples of which exist only transiently at room

temperature.[12] Here we show that this is the case, and while we have not yet had success using these complexes as nucleophilic acyl anion sources in organic synthesis, this possibility remains.

Results and Discussion

Representative reactions of three β-diketiminato magnesium(I) dimers, [{(Nacnac)Mg}$_2$] (Nacnac = [HC(MeCNAr)$_2$]$^-$; Ar = $C_6H_2Me_3$-2,4,6 (^{Mes}Nacnac),[13] $C_6H_3Et_2$-2,6 (^{Dep}Nacnac),[14] $C_6H_3Pr^i_2$-2,6 (^{Dip}Nacnac)[15]), of varying steric bulk, with a series of alkyl and/or aryl substituted esters were carried out at -78 °C, and the reaction mixtures subsequently warmed to ambient temperature. For all reactions carried out, moderate isolated yields of the orange to red, acyl/alkoxide or acyl/aryloxide bridged dimagnesium complexes, **1**-**5**, were obtained (Scheme 1). The mechanism of these reactions presumably involves a two-electron reduction of the ester, leading to cleavage of its (O)C−O linkage. This could proceed *via* attack of the carbonyl oxygen center at magnesium, and formation of a ketyl-like radical intermediate, which is further reduced to give the cleaved product. In this respect, we have previously shown that stable ketyl radicals are formed from the reduction of ketones with magnesium(I) dimers.[16] Following the current reactions by ^{1}H NMR spectroscopy suggested that those involving the smaller esters were clean, and did not generate significant quantities of other products. However, reductions of *tert*-butyl benzoate did yield small quantities of typically unidentifiable by-products. One exception here was the reduction of *tert*-butyl benzoate with the bulkiest magnesium(I) dimer, [{(^{Dip}Nacnac)Mg}$_2$], which in addition to **4**, gave a low isolated yield (*ca.* 6 %) of the known benzoate bridged complex, [{(^{Dip}Nacnac)Mg(μ-O_2CPh)}$_2$].[17] It is possible that there is competitive reductive cleavage of the (O)CO−Bu^t bond in this case, due to the relative stability of the *tert*-butyl radical.



Scheme 1. Synthesis of compounds **1**-**5**.

Complexes **1**-**5** are stable in the solid state or in solution at ambient temperature for weeks, when kept under an atmosphere of dry dinitrogen. Their ^{1}H and ^{13}C{^{1}H} NMR spectra are largely consistent with their proposed structures, though very low field resonances (δ 333-355 ppm) were observed for their acyl carbon centres. These values are, however, comparable to that obtained (δ 327 ppm) for the related dimeric acyl-bridged aluminium complex, [Bu$^t_2$Al{μ-OC(Bu^t)}$_2$AlBu$^t_2$].[18] The intriguing ^{13}C{^{1}H} NMR chemical shifts for **1**-**5** might indicate that their bridging acyl ligands are better viewed as having more oxo-carbenic character (Figure 1). While this possibility was not previously discussed for [Bu$^t_2$Al{μ-OC(Bu^t)}$_2$AlBu$^t_2$], the somewhat related monomeric thorium η^2-acyl complex, [Cp*$_2$Th{η^2-OC(CH$_2$Bu^t)}Cl] ($\delta_{\text{acyl-C}}$ = 318.7 ppm), was described as having significant carbenic character.[19] Unfortunately, confident assignment of the C-O stretching bands in the infrared spectra of **1**-**5** (*cf.* ν_{CO} = 1527 cm^{-1} for [Bu$^t_2$Al{μ-OC(Bu^t)}$_2$AlBu$^t_2$]) was not possible, as these likely lie in the same region (*ca.* ν = 1520-1540 cm^{-1}) as normally observed for C-N stretching bands of magnesium coordinated Nacnac ligands.[10]

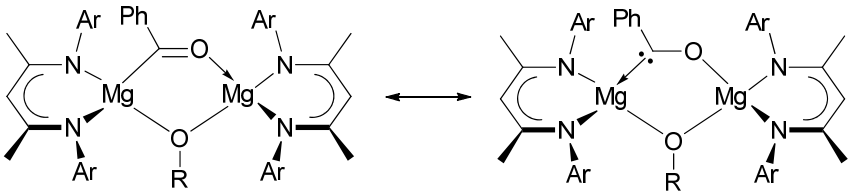


Figure 1. Potential umpolung acyl (left) and oxo-carbene (right) character of **1**-**5**.

In order to confirm the proposed structures of the magnesium acyl complexes, and to shed further light on the nature of the bonding within their acyl ligands, X-ray crystallographic studies of **1**-**4** were carried out. The complexes represent the first structurally authenticated s-block acyls and all possess similar unsymmetrical acyl and alkoxide/aryloxide bridged dimeric structures, as depicted in Figure 2 for the representative complex, **4**. Inspection of relevant metrical data for the compounds (Table 1) reveals that their acyl C-O bonds (*cf.* 1.252(3) Å in $[Bu^t_2Al\{\mu\text{-}OC(Bu^t)\}_2AlBu^t_2]$[18]) are slightly longer than those typically seen in terminal transition metal acyls (e.g. 1.220(6) Å in $[(Ph_3P)_2ClPt\{C(O)Me\}]$[20]), but significantly shorter than normal C-O single bonds (*ca.* 1.42 Å). Moreover, the Mg-C distance for the compounds lie between the means for all crystallographically characterised $Mg_{(4\text{-coord})}$-$C_{(3\text{-coord})}$ covalent bonds (2.19 Å), and all dative Mg-C bonds involving N-heterocyclic carbenes (2.32 Å).[7] These comparisons point toward the bonding in the acyl ligands in **1**-**5** lying between umpolung acyl in character, and carbene-like.

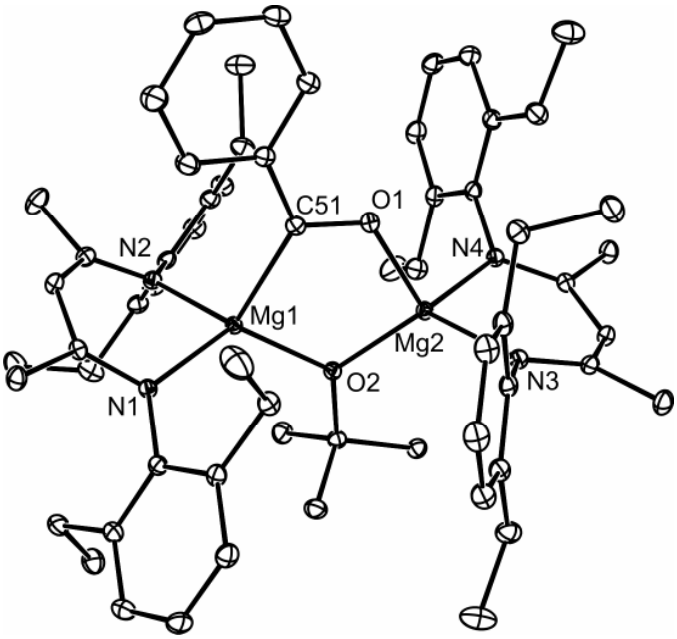


Figure 2. Molecular structure of compound **4**.

Table 1. Selected Interatomic Distances (Å) and Angles (°) for **1**-**4**.

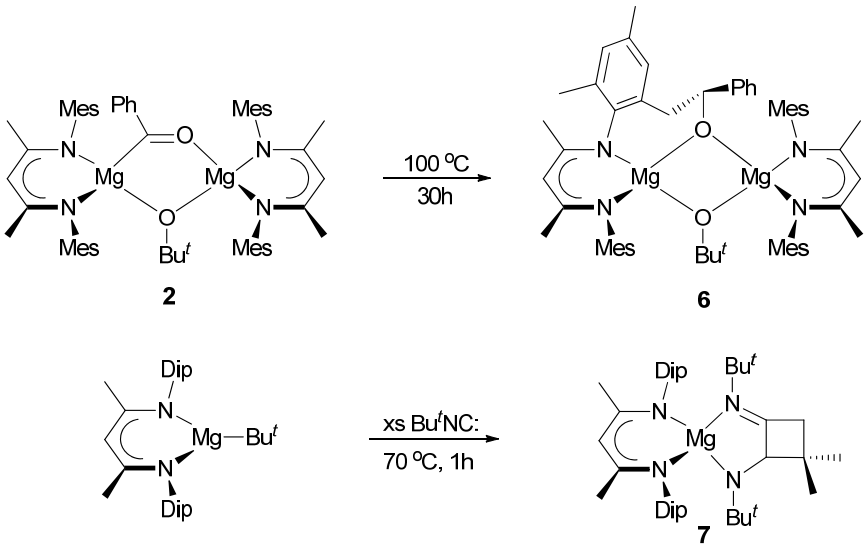
	1	**2**	**3**	**4**
Mg-N (mean)	2.036	2.062	2.066	2.108
Mg(2)-O(1)	1.993(1)	1.964(1)	1.982(1)	1.980(2)
Mg(1)-O(2)	1.939(1)	1.973(1)	1.974(1)	1.996(2)
Mg(2)-O(2)	1.940(1)	1.964(1)	1.960(1)	1.983(2)
Mg(1)-C_{acyl}	2.224(2)	2.225(1)	2.239(1)	2.256(2)
C_{acyl}-O(1)	1.267(2)	1.265(2)	1.267(2)	1.276(3)
Mg(1)-O(2)-Mg(2)	112.30(6)	111.32(5)	112.28(4)	116.6(7)
Mg(1)-C_{acyl}-O(1)	117.3(1)	115.7(1)	114.1(1)	115.8(2)
Mg(2)-O(1)-C_{acyl}	117.7(1)	120.6(9)	121.6(1)	123.8(2)

So as to provide further insight into the nature of the acyl bonding and charge distribution in **1**-**5**, DFT calculations (B3PW91/D3BJ) were carried out on **1** in the gas phase (*viz.* **1'**). The geometry of the molecule optimized to be very similar to that of **1** in the solid state, but with a slightly elongated acyl C-O bond (1.273 Å) and a marginally shorter Mg-C bond (2.210 Å). The Wiberg bond index calculated for the C-O bond was 1.50, which indicates that it has significant π-bond character. This is in line with the HOMO-12 of the compound, which indeed exhibits attributes of a C-O π-bond (see Supporting Information). Although these results perhaps suggest greater umpolung-acyl than oxo-carbene character for **1'**, the results of an NPA charge analysis of the compound give a different view. That is, the acyl carbon actually possesses a slight positive charge (+0.1), whereas the acyl oxygen is significantly negative (-0.8). This is comparable to the charge on the methoxide oxygen (-1.1), while the magnesium centers have similar positive charges (+1.5 and +1.6). The sum of the crystallographic and computational results, combined with the very low field ^{13}C NMR spectroscopic chemical shift for **1**, lead to the conclusion that the bonding situation for the acyl ligands of complexes **1**-**5**, is best described as lying between umpolung-acyl and oxo-carbene.

As a further means of determining the nucleophilicity of the acyl fragments of **1**-**5**, several of these compounds were reacted with a series of electrophiles, largely with inconclusive results. For example, reaction of **5** with acetone or benzaldehyde led to complex product mixtures, which upon quenching did not contain the α-hydroxyketones that would be expected if **5** was acting as an umpolung-acyl source. Similarly, alkyl halides (e.g. MeI) and silyl halides (e.g. Me_3SiCl) were reacted with **2** to give an unidentifiable mixtures of products, as was the case when **3** was treated with a series of nitriles or carbodiimides. The only magnesium acyl reaction that afforded any isolable product was that between **1** and an excess of phenylisocyanate, PhNCO. This gave a good yield of the known triphenyl isocyanurate,

{(Ph)CN(=O)}$_3$, presumably *via* a catalyzed trimerization process. It cannot be sure how the trimerization reaction was catalysed, though this could have involved the methoxide fragment of **1**, considering that isocyanate trimerizations are known to be catalyzed by metal alkoxides.[21] Moreover, the complex product mixtures obtained from the other reactions with electrophiles might, in part, be due to competition between the magnesium bound acyl and alkoxide/aryloxide nucleophiles in these reactions. Because of this, attempts were made to prepare symmetrical acyl bridged complexes, [{(Nacnac)Mg[μ-OC(R)]}$_2$], for purposes of comparison.

In the first instance, solutions of several of the magnesium acyl complexes were heated at 100 °C, with the expectation that they would undergo redistribution reactions, yielding 1:1 mixtures of magnesium acyls, [{(Nacnac)Mg[μ-OC(R)]}$_2$], and magnesium alkoxides, [{(Nacnac)Mg(μ-OR)}$_2$]. However, the complexes proved to be remarkably resilient and typically showed no reaction at this temperature. The only exception was **2** which, over 30 hours, cleanly rearranged to the unusual chiral bis(alkoxide) product, **6**, in very high yield (Scheme 2). In this intramolecular reaction, an *ortho*-methyl group from one of the mesityl substituents has been C-H activated by the acyl carbon centre of **2**. Such C-H activation reactions are rare for mesityl substituted Nacnac ligands, but are common for related mesityl substituted N-heterecyclic carbenes.[7] Both the NMR spectroscopic data and the metrical parameters of complex **6** determined from its X-ray crystal structure (Figure 3), are consistent with its proposed structure, and need no further comment.



Scheme 2. Synthesis of compounds **6** and **7**.

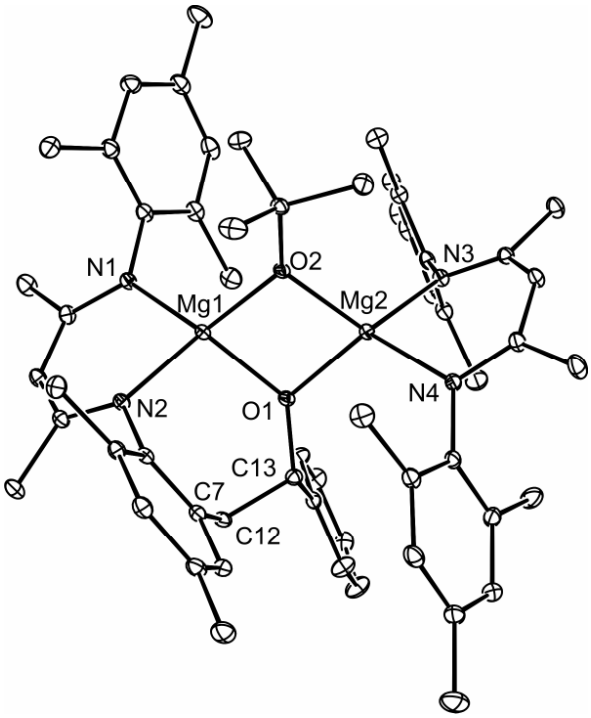


Figure 3. Molecular structure of **6** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Mg(1)-O(2) 1.9550(14), Mg(1)-O(1) 1.9693(14), Mg(1)-N(2) 2.0295(16), Mg(1)-N(1) 2.0687(17), O(1)-C(13) 1.420(2), C(12)-C(13) 1.541(3), Mg(2)-O(1)-Mg(1) 96.12(6), Mg(1)-O(2)-Mg(2) 96.39(6), O(2)-Mg(1)-O(1) 83.33(6), O(1)-Mg(2)-O(2) 83.11(6).

Considering that reactions of alkyl complexes of electropositive metals with CO are known to give metal acyls,[8,9,18] it was believed that treatment of β-diketiminato magnesium organyl systems with CO might lead to similar results. To this end benzene solutions of the monomeric magnesium compounds, [(^{Dip}Nacnac)MgR] (R = Bu^t or Ph), were placed under an atmosphere of CO gas in sealed J-Young's NMR tubes and heated at 100 °C for several hours. However, no reaction was observed in either case. Given the isolobal relationship between CO and isonitriles, and for sake of comparison, a benzene solution of [(^{Dip}Nacnac)MgBu^t] was treated with an excess of Bu^{t}NC:, and subsequently heated at 70 °C for one hour. In this case a reaction did take place and the unusual chiral amido/imino-magnesium complex, **7** was formed in good yield (Scheme 2). Clearly, two molecules of Bu^{t}NC: are involved in this reaction, the mechanism of which is so far undefined. However, it likely involves insertion of one molecule of Bu^{t}NC: into the Mg-C bond of [(^{Dip}Nacnac)MgBu^t], in its initial stages, though the insertion product was not spectroscopically observed or isolated. That said, the proposed reaction is similar to known insertions of isonitriles into the M-H (M = Mg or Ca) bonds of [(Nacnac)MH] compounds.[14,22] The cyclobutane backbone in the ultimate product, **7**, seemingly arises from a C-H activation process involving the *tert*-butyl group which originates from the magnesium starting material, and the second equivalent of Bu^{t}NC:. The solid state structure of the compound was verified by an X-ray crystallographic study (Figure 4), while the NMR spectroscopic data for **7** imply that it retains this structure in solution.

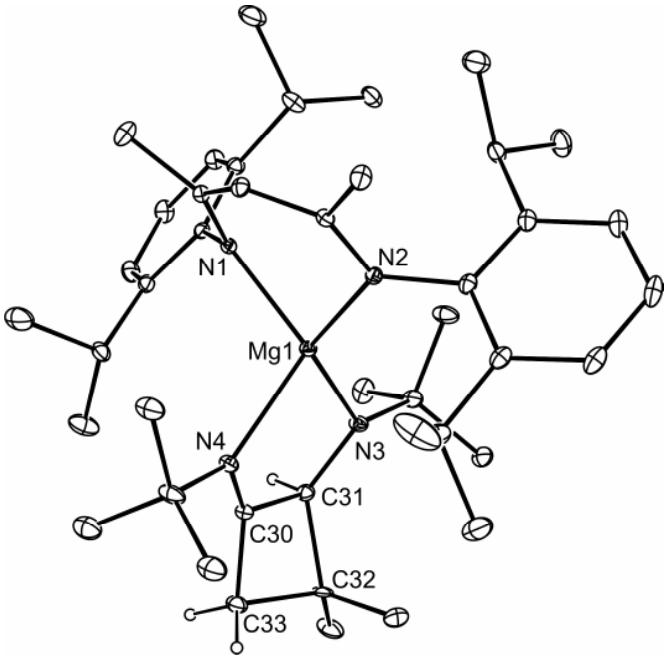


Figure 4. Molecular structure of **7** (25% thermal ellipsoids; hydrogen atoms, except those attached to the cyclobutane moiety, omitted). Selected bond lengths (Å) and angles (°): Mg(1)-N(3) 1.9865(14), Mg(1)-N(4) 2.206(6), N(3)-C(31) 1.412(3), N(4)-C(30) 1.257(6), C(30)-C(31) 1.504(3), N(3)-Mg(1)-N(4) 84.50(16), C(31)-N(3)-Mg(1) 109.13(12), C(30)-N(4)-Mg(1) 103.1(4).

Conclusions

In summary, the first examples of magnesium acyls have been prepared by reductive cleavage of a series of esters using dimeric magnesium(I) reducing agents. The combined results of crystallographic, spectroscopic and computational studies suggest that the acyl ligands within these complexes should be viewed as lying somewhere between anionic umpolung acyl and oxo-carbene in nature. Reactions of the acyl complexes with a variety of organic electrophiles were largely inconclusive, and did not provide evidence of umpolung acyl reactivity. While attempts to prepare alkoxide free magnesium acyls by reaction of organo-magnesium compounds with CO were not successful, a related reaction between a β-diketiminato magnesium alkyl and an isonitrile afforded an unusual amido/imino-magnesium

complex *via* an isonitrile coupling/C-H activation process. The development and synthetic utility of magnesium acyls continues to be explored in our laboratory.

Experimental Section

General methods. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene was distilled over molten potassium, while pentane and diethyl ether were distilled from Na/K (1:1) alloy. ^{1}H, and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DPX300, AvanceIII 400 or Varian Inova 500 spectrometers at 296 K in deuterated solvents, and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. IR spectra were recorded on solid samples, or as Nujol mulls, using a Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid state probe. Microanalyses were carried out at the Science Centre, London Metropolitan University, UK. [{(^{Dip}Nacnac)Mg}$_2$],[15] [{(^{Dep}Nacnac)Mg}$_2$],[14] [{(^{Mes}Nacnac)Mg}$_2$][13] and [(^{Dip}Nacnac)MgBu^{t}][17] were prepared by literature procedures. All other reagents were used as received. Toluene solutions of the esters were dried over molecular sieves prior to use.

[(^{Mes}Nacnac)Mg(μ-OMe){μ-OC(Ph)}Mg(^{Mes}Nacnac)] (1). To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.11 g, 0.147 mmol) in toluene (100 mL) at -78 ºC was added a solution of PhC(O)OMe in toluene (0.336 M, 0.85 mL, 0.285 mmol) over 5 min. The reaction solution turned ruby-red on addition, slowly changing to a red-orange colour on warming to ambient temperature. The reaction solution was then reduced *in vacuo* to *ca.* 35 mL and cooled to -30 °C overnight to give pink-orange crystals of **1**. Upon isolation of the crystals, reduction of the mother liquor *in vacuo* gave a second crop of the title compound (yield 0.052 g, 42%). M.p.

decomp > 180 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 1.44 (s, 6H; ArCH_3), 1.59 (s, 6H; NCCH_3), 1.63 (s, 6H; NCCH_3), 1.86 (s, 6H; ArCH_3), 2.17 (s, 6H; ArCH_3), 2.25 (s, 6H; ArCH_3), 2.33 (s, 6H; ArCH_3), 2.39 (s, 6H; Ar ArCH_3), 3.38 (s, 3H; OCH_3), 4.92 (s, 1H; NCC*H*), 5.07 (s, 1H; NCC*H*), 6.70 (s, 2H; Ar*H*), 6.73 (s, 2H; Ar*H*), 6.82 (s, 2H; Ar*H*), 6.86 (s, 2H; Ar*H*), 7.05-7.27 (m, 3H; Ph*H*), 8.01-8.03 (m, 2H; Ph*H*); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ = 17.6 (Ar*C*H_3), 17.9 (Ar*C*H_3), 18.5 (Ar*C*H_3), 21.0 (Ar*C*H_3), 21.0 (Ar*C*H_3), 23.1 (Ar*C*H_3), 23.1 (NC*C*H_3), 23.2 (NC*C*H_3), 51.4 (O*C*H_3), 94.2 (NC*C*H), 94.7 (NC*C*H), 125.6, 128.5, 128.7, 129.0, 129.1, 129.3, 129.7, 129.9, 130.1, 130.9, 131.4, 131.5, 131.6, 131.7, 132.0, 132.2, 145.4, 145.8 (Ar*C*), 168.0 (N*C*CH), 168.7 (N*C*CH), 333.8 (Ph*C*O); IR (ATR, Nujol); $\tilde{\upsilon}$(cm^{-1}) = 1521(s), 1451(s), 1397(s), 1258(m), 1199(m), 1146(m), 1099(m), 1013(m), 853(s), 743(m); EI/MS (70eV): *m/z* (%): 850.8 (M^+, 5), 690.6 (M^+-MesNCMe, 4), 516.4 (M^+-^{Mes}Nacnac, 4), 357.3 (^{Mes}NacnacMg$^+$, 70), 160.2 (MesNCMe$^+$, 100). A reproducible microanalysis could not be obtained for this compound as it consistently crystallized with small amounts (*ca.* 5%) of protonated ligand, ^{Mes}NacnacH, which could not be separated by repeated fractional crystallizations.

[(^{Mes}Nacnac)Mg(μ-OBu^{t}){μ-OC(Ph)}Mg(^{Mes}Nacnac)] (2). To a stirred solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.21 g, 0.293 mmol) in toluene (90 mL) at -78 ºC was added a solution of PhC(O)OBu^{t} in toluene (1.68 M, 0.17 mL 0.293 mmol) over 5 min. The initially deep red solution changed to a red-orange colour on warming to ambient temperature. The reaction solution was then reduced *in vacuo* to *ca.* 30 mL and cooled to -30 ºC yielding red-orange plates of **2**. After isolation of these crystals, the mother liquor was concentrated to *ca.* 10 mL, yielding a second crop of the title compound upon cooling (yield 0.132 g, 50 %). M.p. = 227-229 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6) δ = 0.89 (s, 9H; C(CH_3)$_3$), 1.34 (s, 6H; ArCH_3), 1.66 (s, 6H; NCCH_3), 1.68 (s, 6H; NCCH_3), 2.17 (s, 6H; ArCH_3), 2.19 (s, 6H;

ArC*H*$_3$), 2.22 (s, 6H; ArC*H*$_3$), 2.26 (s, 6H; ArC*H*$_3$), 2.52 (s, 6H; ArC*H*$_3$), 5.01 (s, 1H; NCC*H*), 5.21 (s, 1H; NCC*H*), 6.73 (s, 2H; Ar*H*), 6.78 (s, 4H; Ar*H*), 6.94 (s, 2H; Ar*H*), 7.13-7.39 (m, 3H; Ph*H*) 8.27-8.28 (m, 2H; Ph*H*); ^{13}C{^{1}H} NMR (100MHz, C_6D_6) δ = 17.2 (Ar*C*H$_3$), 17.9 (Ar*C*H$_3$), 18.0 (Ar*C*H$_3$), 18.7 (Ar*C*H$_3$), 19.6 (Ar*C*H$_3$), 19.6 (Ar*C*H$_3$), 22.5 (2xNC*C*H$_3$), 31.9 (C(*C*H$_3$)$_3$), 66.4 (*C*(CH$_3$)$_3$), 93.5 (NC*C*H), 94.5 (NC*C*H), 126.4, 126.6, 126.9, 127.1, 127.1, 127.6, 127.9, 128.1, 128.2, 128.4, 129.9, 130.3, 130.7, 130.9, 131.1, 131.3 144.8, 145.1 (Ar*C*), 166.7 (N*C*CH), 1967.2 (N*C*CH), 355.3 (Ph*C*O); IR (ATR, Nujol); $\tilde{\upsilon}$(cm^{-1}) = 1519(m), 1260(s), 1196(m), 1144(m), 1094(m), 1018(s), 854(m), 800(m); EI/MS (70eV): *m/z* (%): 892.5 (M$^+$, 8), 819.8 ((M$^+$-OBu^t, 13), 357.3 (^{Mes}NacnacMg$^+$, 80), 160.2 (MeCNMes$^+$, 100), 119.2 (Mes$^+$, 32); elemental analysis: calc. for $C_{57}H_{72}Mg_2N_4O_2$; C, 76.59%; H, 8.12%; N, 6.27%; found: C, 76.45%; H, 8.22%; N, 6.37%.

[(^{Dep}Nacnac)Mg(μ-OBu^t){μ-OC(Ph)}Mg(^{Dep}Nacnac)] (3). To a stirred solution of [{(^{Dep}Nacnac)Mg}$_2$] (0.30 g, 0.389 mmol) in toluene (60 mL) at -78 ºC was added a solution of PhC(O)OBu^t in toluene (1.68 M, 0.23 mL, 0.389 mmol) over 5 min. The reaction solution was deep orange following the addition, and upon warming darkened to brown, then became an intense green on further warming to ambient temperature. Volatiles were removed *in vacuo* and the residue dissolved in pentane (15 mL), then cooled to 8 ºC to afford a red-brown crystalline material. This was recrystallised from pentane, to remove a deep green coloured impurity, giving red-orange crystals of **3** (yield 0.13 g, 37 %). M.p. = 135-145 ˚C; ^{1}H NMR (500 MHz, C_6D_6) δ = 0.52 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 6H; CH$_2$C*H*$_3$), 0.90 (s, 9H; C(C*H*$_3$)$_3$), 1.15 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 6H; CH$_2$C*H*$_3$), 1.26 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 6H; CH$_2$C*H*$_3$), 1.36 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 6H; CH$_2$C*H*$_3$), 1.62 (s, 6H; NCC*H*$_3$), 1.63 (s, 6H; NCC*H*$_3$), 1.97 (dq, $^2J_{H\text{-}H}$ = 15 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H; C*H*$_2$CH$_3$), 2.47 (m,3 x overlapping dq, 6H; C*H*$_2$CH$_3$), 2.66 (dq, $^2J_{H\text{-}H}$ = 15 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H; C*H*$_2$CH$_3$), 2.75 (dq, $^2J_{H\text{-}H}$ = 15 Hz, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H; C*H*$_2$CH$_3$), 3.09 (dq,

$^{2}J_{H\text{-}H}$ = 15 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H; C*H*$_2$CH$_3$), 3.19 (dq, $^{2}J_{H\text{-}H}$ = 15 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 2H; C*H*$_2$CH$_3$), 4.95 (s, 1H; NCC*H*), 5.18 (s, 1H; NCC*H*), 6.98-6.99 (m, 2H; Ar*H*), 7.05-7.10 (m, 8H; Ar*H*), 7.19-7.21 (m, 3H; Ar*H*/Ph*H*), 7.34-7.37 (m, 2H; Ph*H*), 8.14-8.16 (m, 2H; Ph*H*); ^{13}C{^{1}H} NMR (100MHz, C_6D_6) δ = 13.1 (CH$_2$*C*H$_3$), 13.6 (CH$_2$*C*H$_3$), 14.4 (CH$_2$*C*H$_3$), 15.0 (CH$_2$*C*H$_3$), 23.6 (*C*H$_2$CH$_3$), 24.1 (*C*H$_2$CH$_3$), 24.3 (*C*H$_2$CH$_3$), 24.6 (*C*H$_2$CH$_3$), 24.8 (NC*C*H$_3$), 24.9 (NC*C*H$_3$), 33.2 (C(*C*H$_3$)$_3$), 67.9 (*C*(CH$_3$)$_3$), 95.0 (NC*C*H), 95.2 (NC*C*H), 124.1, 124.7, 125.2, 125.5, 125.8, 127.0, 129.2, 132.3, 137.1, 137.4, 138.1, 138.3, 146.4, 147.9, 148.1 (Ar*C*, some signals obscured), 168.4 (N*C*CH), 168.7 (N*C*CH), 334.4 (Ph*C*O); IR (ATR, Nujol); ῡ(cm^{-1}) = 1509(m), 1434(s), 1390(s), 1324(s), 1262(s), 1175(m), 1017(m), 929(m), 751(s), 686(m); EI/MS (70eV): *m/z* (%): 948.6 (M$^+$, 57), 385.2 (^{Dep}NacnacMg$^+$, 23), 362.2 (^{Dep}NacnacH$^+$, 43), 174.0 (MeCNDep$^+$, 100). A reproducible microanalysis could not be obtained for this compound as it consistently crystallized with small amounts (*ca.* 3%) of protonated ligand, ^{Dep}NacnacH, which could not be separated by repeated fractional crystallizations.

[(^{Dip}Nacnac)Mg(μ-OBu^t){μ-OC(Ph)}Mg(^{Dip}Nacnac)] (4). To a stirred solution of [{(^{Dip}Nacnac)Mg}$_2$] (0.32 g, 0.365 mmol) in toluene (60 mL) at -78 ºC, was added a solution of PhC(O)OBu^t in toluene (1.68 M, 0.22 mL, 0.365 mmol). On addition, the solution turned a dark straw colour and then darkened to an amber colour on warming to -60 ºC, persisting until ambient temperature. Fine orange crystals of **4** were obtained by reducing the reaction solution *in vacuo* to *ca.* 20 mL and then cooling to -30 ºC overnight (yield 0.126 g, 32%). Colourless blocks of the known magnesium carboxylate complex, [{(^{Dip}Nacnac)Mg(μ-COOPh)}$_2$],[17] were obtained by removal of solvent from the mother liquor *in vacuo* and re-crystallising the residue from diethyl ether, yielding *ca.* 25 mg of the material. M.p. = 207-213 ºC; (^{1}H, 500 MHz, C_6D_6) δ = -0.17 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 0.67 (d, $^{3}J_{H\text{-}H}$ = 7 Hz,

6H; CH(C*H*$_3$)$_2$), 0.71 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.21 (s, 9H; C(C*H*$_3$)$_3$), 1.22 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.24 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.37 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.54 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H; CH(C*H*$_3$)$_2$), 1.56 (s, 6H; NCC*H*$_3$), 1.60 (s, 6H; NCC*H*$_3$), 2.73 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H; C*H*(CH$_3$)$_2$), 3.24 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H; C*H*(CH$_3$)$_2$), 3.53 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H; C*H*(CH$_3$)$_2$), 4.00 (sept, $^3J_{H\text{-}H}$ = 7 Hz, 2H; C*H*(CH$_3$)$_2$), 4.87 (s, 1H; NCC*H*), 5.15 (s, 1H; NCC*H*), 6.88-7.14 (m, 12H; Ar*H*), 7.24 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 1H; Ph*H*), 7.34-7.36 (m, 2H; Ph*H*), 8.41-8.42 (m, 2H; Ph*H*); ^{13}C{^{1}H} NMR (100MHz, C_6D_6) δ = 14.3 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 25.4 (*C*H(CH$_3$)$_2$), 25.9 (*C*H(CH$_3$)$_2$), 26.2 (*C*H(CH$_3$)$_2$), 26.8 (*C*H(CH$_3$)$_2$), 29.2 (NC*C*H$_3$), 32.0 (NC*C*H$_3$), 34.7 (CH(*C*H$_3$)$_3$), 67.3 (*C*H(CH$_3$)$_3$), 95.2 (NC*C*H), 95.3 (NC*C*H), 123.5 124.1, 124.4, 124.6, 125.2, 125.6, 130.0, 132.6, 141.9, 143.2, 143.3, 143.5, 145.4, 147.5, 148.0 (Ar*C*, some signals obscured), 169.2 (N*C*CH), 169.9 (N*C*CH), 334.7 (Ph*C*O); IR (ATR, Nujol); ῡ(cm^{-1}) = 1515(s), 1462(s), 1360(s), 1256(s), 1163(m), 1019(m), 926(s), 791(s), 757(s); EI/MS (70eV): *m/z* (%): 1061.8 (M$^+$, 7), 441.3 (^{Dip}NacnacMg$^+$, 22), 418.3 (^{Dip}NacnacH$^+$, 50), 403.3 (^{Dip}NacnacH$^+$-Me, 100), 202.1 (MeCNDip$^+$, 76); elemental analysis: calc. for $C_{69}H_{96}Mg_2N_4O_2$: C, 78.03%; H, 9.11%; N, 5.27%; found: C, 77.89%; H, 9.17%; N, 5.38%.

[(^{Dip}Nacnac)Mg(μ-OPh){μ-OC(Ph)}Mg(^{Dip}Nacnac)] (5). To a stirred solution of [{(^{Dip}Nacnac)Mg}$_2$] (0.32 g, 0.328 mmol) in toluene (100 mL) at -78 ºC, was added a solution of PhC(O)OPh (0.072 g, 0.328 mmol) in toluene (*ca.* 5 mL) over 5 min. Initially yellow/brown following addition, the solution changed to a deep red wine colour after several minutes, and became deep red-brown on warming to ambient temperature. The reaction solution was then reduced *in vacuo* to *ca.* 15 mL and cooled to 8 ºC overnight, yielding red

blocks of **5** (yield 0.167 g, 47 %). M.p. > 260 ºC (decomp.); ^{1}H NMR (400 MHz, C_6D_6) δ = -0.30 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), -0.18 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), 0.69 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), 0.98 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), 1.21 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), 1.28 (virt. t, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 12H; CH(CH_3)$_2$), 1.54 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H; CH(CH_3)$_2$), 2.72-2.80 (2 x overlapping sept, 4H; CH(CH$_3$)$_2$), 3.562 (sept, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 2H; CH(CH$_3$)$_2$), 3.92 (sept, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 2H; CH(CH$_3$)$_2$), 5.06 (s, 1H; NCCH), 5.13 (s, 1H; NCCH), 6.72-6.84 (m, 3H; PhH), 6.92 (d, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 2H; PhH), 6.98-7.09 (m, 10H; Ar/PhH), 7.19-7.23 (m, 3H; ArH), 7.33-7.37 (m, 2H; PhH), 8.37-8.39 (m, 2H; PhH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ = 23.4 (2xCH(CH$_3$)$_2$), 23.5 (CH(CH$_3$)$_2$), 23.9 (CH(CH$_3$)$_2$), 24.3 (CH(CH$_3$)$_2$), 24.6 (CH(CH$_3$)$_2$), 24.8 (CH(CH$_3$)$_2$), 24.9 (CH(CH$_3$)$_2$), 25.1 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 26.8 (CH(CH$_3$)$_2$), 27.5 (CH(CH$_3$)$_2$), 29.1 (NCCH$_3$), 29.3 (NCCH$_3$), 94.9 (NCCH), 95.1 (NCCH), 118.8, 118.9, 123.6, 123.7, 124.1, 124.3, 125.5, 125.6, 128.5, 129.3, 129.9, 133.0, 142.0, 142.2, 143.1, 143.9, 145.0, 146.3, 146.7, 160.1 (ArC), 169.9 (NCCH), 170.0 (NCCH), 333.0 (PhCO); IR (ATR, Nujol); $\tilde{\upsilon}$(cm^{-1}) = 1594(w), 1519(m), 1460(m), 1432(s), 1397(s), 1311(s), 1176(m), 1098(m), 1020(s), 929(m), 791(s); EI/MS (70eV): *m/z* (%): 1081.8 (M^{+}, 7), 868.5 (M^{+}-MeCNDip, 10), 441.3 (^{Dip}NacnacMg^{+}, 20), 418.3 (^{Dip}NacnacH^{+}, 50), 202.1 (MeCNDip^{+}, 77); elemental analysis: calc. for $C_{71}H_{92}Mg_2N_4O_2$: C, 78.80%; H, 8.57%; N, 5.18%; found: C, 78.87%; H, 8.65%; Mg, N, 5.05%.

Thermal decomposition of compound 2, yielding compound 6. A solution of **2** (35 mg 0.04 mmol) in C_6D_6 (*ca.* 1 mL) was heated at 100 ºC for approx. 30 h in a sealed NMR tube equipped with a J. Young's stopper. The decomposition of **2** was followed via ^{1}H NMR spectroscopy. Upon completion, the solution was reduced under vacuum to *ca.* 0.3ml, then subjected to slow cooling from 50 ºC to 8 ºC overnight, yielding large, colourless crystals of the decomposition product **6**. (yield estimated by ^{1}H NMR spectroscopy *ca.* 96 %). M.p. 242-

247 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 1.21 (s, 9H; C(C*H*$_3$)$_3$), 1.35 (s, 3H; ArC*H*$_3$), 1.40 (s, 3H; ArC*H*$_3$), 1.44 (s, 3H; ArC*H*$_3$), 1.48 (s, 3H; ArC*H*$_3$), 1.57 (s, 3H; ArC*H*$_3$), 1.83 (s, 3H; ArC*H*$_3$), 1.87 (s, 3H; ArC*H*$_3$), 1.97 (s, 3H; ArC*H*$_3$), 2.02 (s, 3H; ArC*H*$_3$), 2.24 (s, 3H; ArC*H*$_3$), 2.26-2.29 (dd, $^{2}J_{HA\text{-}HB}$ = 13.6 Hz, $^{3}J_{HA\text{-}H}$ = 1.60 Hz, 1H; ArC*H*$_A$H$_B$CH(O)Ph), 2.28 (s, 3H; ArC*H*$_3$), 2.36 (s, 6H; ArC*H*$_3$), 2.39 (s, 3H; ArC*H*$_3$), 2.42 (s, 3H; ArC*H*$_3$), 2.79-2.85 (dd, $^{2}J_{HB\text{-}HA}$ = 13.6 Hz, $^{3}J_{HB\text{-}H}$ = 10.8 Hz, 1H; ArCH$_A$*H*$_B$CH(O)Ph), 4.40-4.43 (dd, $^{3}J_{H\text{-}HA}$ = 1.6 Hz, $^{3}J_{H\text{-}HB}$ = 10.4 Hz, 1H; ArCH$_A$H$_B$C*H*(O)Ph), 4.83 (s, 1H; NacnacH), 4.87 (s, 1H; NacnacH), 6.46, (s, 1H; Ar*H*), 6.72 (s, 1H; Ar*H*), 6.88 (s, 1H; Ar*H*), 6.89 (s, 1H; Ar*H*), 6.94 (s, 2H; Ar*H*), 7.04 (s, 1H; Ar*H*), 7.09 (s, 1H; Ar*H*), 7.13-7.19 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100MHz, C_6D_6) δ = 16.9 (Ar*C*H$_3$), 17.5 (Ar*C*H$_3$), 17.6 (Ar*C*H$_3$), 17.9 (2xAr*C*H$_3$), 18.8 (Ar*C*H$_3$), 19.0 (Ar*C*H$_3$), 19.6 (Ar*C*H$_3$), 19.7 (2xAr*C*H$_3$), 20.7 (Ar*C*H$_3$), 21.7 (NCC*H*$_3$), 22.0 (NCC*H*$_3$), 22.7 (NCC*H*$_3$), 22.9 (NCC*H*$_3$), 32.6 (C(*C*H$_3$)$_3$), 45.1 (Ar*C*H$_2$CH(O)Ph), 66.0 (*C*(CH$_3$)$_3$), 77.0 (ArCH$_2$*C*H(O)Ph), 93.7 (NC*C*H) 94.7 (NC*C*H), 124.4, 125.0, 127.8, 128.1, 128.3, 128.5, 128.5, 128.6, 129.2, 129.3, 130.3, 130.5, 130.5, 130.7, 131.1, 131.1, 131.2, 131.4, 131.6, 132.9, 144.8, 145.3, 145.8, 146.0, 148.7 (Ar*C*, some signals obscured), 166.8 (N*C*CH), 167.0 (N*C*CH), 167.4 (N*C*CH), 167.9 (N*C*CH); IR (ATR. Nujol mull) $\tilde{\upsilon}$(cm^{-1}) = 1528(m), 1455(s), 1395(s), 1198(s), 1016(m), 853(s), 749(m), 702(m); EI/MS (70eV): *m/z* (%): 893.0 (M^{+}, 18), 819.9 (M^{+}-OBu^{t}, 28), 357.3 (^{Mes}NacnacMg^{+}, 100), 160.2 (MesNCMe^{+}, 92), 119.1 (Mes^{+}, 42); elemental analysis: calc. for $C_{57}H_{72}Mg_2N_4O_2$: C, 76.59%; H, 8.12%; N, 6.27%; found C, 76.47%; H, 8.05%; N, 6.15%.

[(^{Dip}Nacnac)Mg{(NBu^{t})$_2$(*cyclo*-CHCMe$_2$CH$_2$C-)}] 7. To a stirred solution of [(^{Dip}Nacnac)MgBu^{t}] (0.30 g, 0.601 mmol) in benzene (6 mL) at room temperature was added neat Bu^{t}NC (0.134 mL, 1.202 mmol). The colourless solution was then heated to 70 ºC for 1 hr before being cooled to room temperature, yielding a deep red solution. This was

concentrated *in vacuo* to *ca.* 2 mL, resulting in a fine precipitate. The mixture was subsequently heated to re-dissolve the precipitate and cooled gradually from 80 ºC to 8 ºC overnight, yielding a mass of pale yellow crystals (yield 0.17 g, 43 %). M.p. = 188-189 ºC; ^{1}H NMR (500 MHz, C_6D_6) δ = 0.83 (s, 9H; C(CH_3)$_3$), 0.87 (s, 9H; C(CH_3)$_3$), 1.17-1.42 (overlapping m, 30H; CH_2C(CH_3)$_2$), CH(CH_3)$_2$), 1.61 (s, 3H; NCCH_3), 1.68 (s, 3H; NCCH_3), 2.17-2.26 (m, 2H; CH_2(CN)), 3.24 (sept, $^{3}J_{H\text{-}H}$ = 7 Hz, 1H; CH(CH_3)$_2$), 3.38-3.44 (2xsept, 2H; CH(CH_3)$_2$), 3.49 (sept, $^{3}J_{H\text{-}H}$ = 6.5 Hz, 1H; CH(CH_3)$_2$), 4.38 (s, 1H; CH(NBu^t)), 4.91 (s, 1H; NCCH), 7.14-7.18 (m, 6H; ArH); ^{13}C{^{1}H} NMR (100MHz, C_6D_6) δ = 20.3 (CHC(CH$_3$)$_2$), 24.4, 24.6, 24.7, 25.0, 25.1, 25.2, 25.5, 25.7 (CH(CH$_3$)$_2$), 28.0 (CHNC(CH$_3$)$_3$), 28.3, 28.5, 28.6, 28.7 (CH(CH_3)$_2$), 30.0, 30.4 (NCCH$_3$), 33.0 (CNC(CH$_3$)$_3$), 36.9 (CHC(CH_3)$_2$), 47.3 (CH$_2$CN), 49.5 (CHNBu^t), 54.9 (CNC(CH_3)$_3$), 80.4 (CHNC(CH_3)$_3$), 96.8 (NCCH), 123.4, 123.5, 123.9, 124.2, 124.3, 125.0, 125.1, 142.1, 142.4, 142.5, 143.1, 146.7 (ArC), 168.6 (2xNCCH), 187.9 (C=NBu^t); IR (ATR, Nujol); $\tilde{\upsilon}$(cm^{-1}) = 1661(m), 1536(w), 1513(m), 1458(m), 1432(m), 1399(s), 1364(s), 1308(s), 1258(m), 1205(m), 1170(s), 1015(m), 922(m), 789(s), 753(s); EI/MS (70eV): *m/z* (%): 663.6 (M$^+$-H, 22), 649.7 (M$^+$-Me, 37), 609.9 (M$^+$-Bu^t, 25), 441.4 (LMg$^+$, 100), 202.2 (DippNCMe$^+$, 63), 57.1 (Bu^{t+}, 33). A reproducible microanalysis could not be obtained for this compound as it consistently crystallized with small amounts (*ca.* 5%) of protonated ligand, ^{Dip}NacnacH, which could not be separated by repeated fractional crystallizations.

Crystallography. Crystals of **1**-**4**, **6** and **7** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either an Oxford Gemini Ultra diffractometer using a graphite monochromator with Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.5418 Å) radiation, or the MX1 beamline of the Australian Synchrotron (λ = 0.7108 Å). The software package Blu-Ice[23] was used for synchrotron data acquisition, while

the program XDS[24] was employed for synchrotron data reduction. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[25]) using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model).

Table S1, which contains crystal data, details of data collections and refinement for all compounds, can be found in the Supporting Information. CCDC 1558983-1558988 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.

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Accessing Stable Magnesium Acyl Compounds: Reductive Cleavage of Esters by Magnesium(I) Dimers

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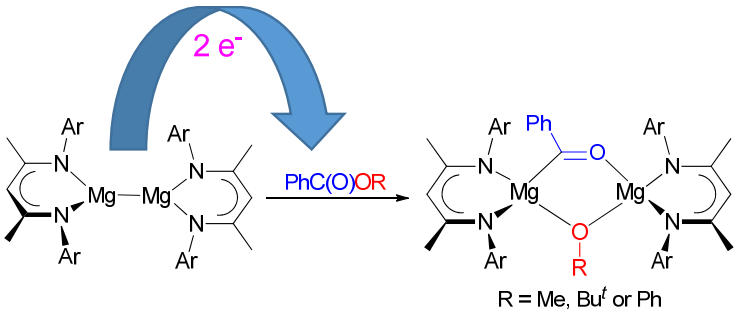

Stable s-block acyls. The first isolable s-block metal acyl complexes are readily synthesized *via* the reductive cleavage of esters using magnesium(I) dimers (see picture). Spectroscopic, crystallographic and computational data suggest that the nature of the bonding within the magnesium bound acyl fragments lies somewhere between umpolung acyl and oxo-carbene in character.