

PAPER

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13332Atom-economic access to cationic magnesium
complexes†Etienne V. Brouillet,  Scott A. Brown, Alan R. Kennedy,  Annabel Rae,
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Cationic alkaline-earth complexes attract interest for their enhanced Lewis acidity and reactivity compared with their neutral counterparts. Synthetic protocols to these complexes generally utilize expensive specialized reagents in reactions generating multiple by-products. We have studied a simple ligand transfer approach to these complexes using (NacNac)MgR and ER₃ (NacNac = β-diketiminato anion; E = group 13 element; R = aryl/amido anion) which demonstrates high atom economy, opening up the ability to target these species in a more sustainable manner. The success of this methodology is dependent on the identity of the group 13 element with the heavier elements facilitating faster ligand exchange. Furthermore, while this reaction is successful with aromatic ligands such as phenyl and pyrrolyl, the secondary amide piperidide (pip) fails to transfer, which we attribute to the stronger 3-centre-4-electron dimerization interaction of Al₂(pip)₆.

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Introduction

Interest in cationic alkaline-earth metal complexes has recently been growing on account of their high Lewis acidity, interesting reactivity and potential exploitation as sustainable-metal catalysts.¹ A common approach to their development is to incorporate a bulky bidentate β-diketiminato (BDI or NacNac) monoanion as the stabilizing ligand² due to their ease of synthesis, steric/electronic tunability, and the sizeable steric protection they can offer to the cationic metal centre. These ligands were already particularly prevalent in s-block chemistry in for example the stabilization of low-valent [(Mg(I), Ca(I)) or reactive hydrido-equipped alkaline-earth metal complexes,³ the stabilization of dihydropyridyl ligands and hydrogen-rich B/N ligands⁴ and the development of magnesium complexes for deprotonation or C–H/C–F bond activation and consequent stabilization of the resulting sensitive products.⁵ However, it is now established that these ligands are not as innocent as they were initially thought to be, with recent alkali-metal research in this area showing that NacNac is susceptible to attack at the backbone site⁶ on account of the HOMO being located at the C_γ position, which renders it nucleophilic.⁷

If such species are genuinely contenders to become sustainable reagents it is not enough for them to simply be accessible

but rather, they must be sustainably accessible *via* facile methodologies using inexpensive reagents, in high yields and with minimal or ideally no waste products. For example, some textbook examples of these complexes, [(NacNac)Mg]⁺ [X][−] were prepared on sub-mM scales by reaction of (NacNac)Mg*n*Bu with the specialized reagents [CPh₃]⁺ [X][−], resulting in elimination of Ph₃CH and 1-butene by-products ([X][−] = weakly coordinating anions [B(C₆F₅)₄][−] and [Al(OC(CF₃)₃)₄][−] Scheme 1a).⁸

Recently we have been interested in exploiting ligand exchange reactions as a means of delivering high atom economy in the synthesis of magnesium aluminate complexes with application as magnesium battery electrolytes and thus postulated that a similar approach may be beneficial here (Scheme 1b).⁹ We report now our findings, discussing both the advantages and limitations of this methodology.

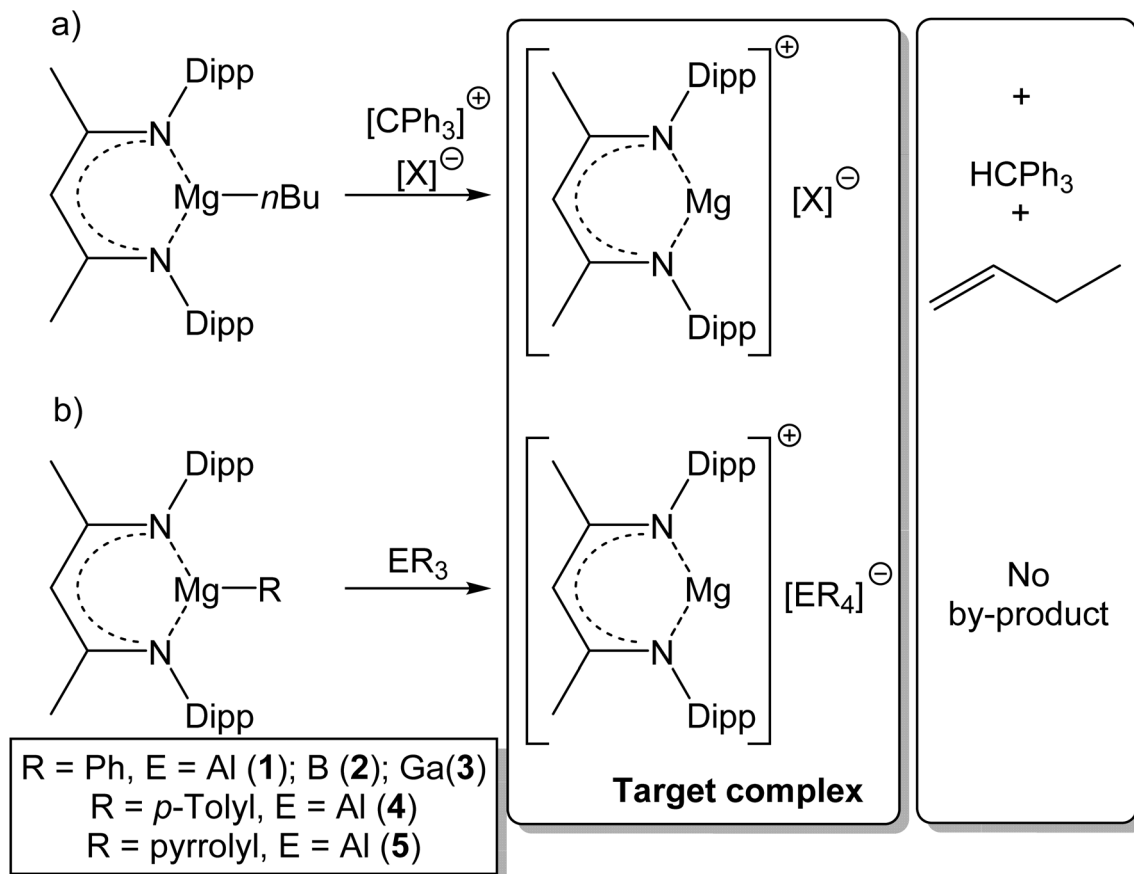
Results and discussion

We initiated this study by reacting (Dipp[−]NacNac)MgPh·THF (Dipp = 2,6-diisopropylphenyl, see Fig. S1–S3†)¹⁰ with the Lewis acid AlPh₃·OEt₂¹¹ in a 1 : 1 stoichiometric ratio in THF solution according to Scheme 1b. This was done on an NMR scale in a J. Youngs tube so that the reaction could be monitored using ²⁷Al NMR spectroscopy, exploiting the tetrahedral symmetry of the putative anion which should deliver a sharp and narrow resonance. This was realised in such a resonance at 133 ppm consistent with the emergence of the [AlPh₄][−] anion.¹² The broad nature of the AlPh₃ resonance meant that loss of starting material could not be adequately monitored

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Scheme 1 Synthetic methodologies employed to access NacNac supported cationic magnesium complexes: (a) previous work; (b) this work.

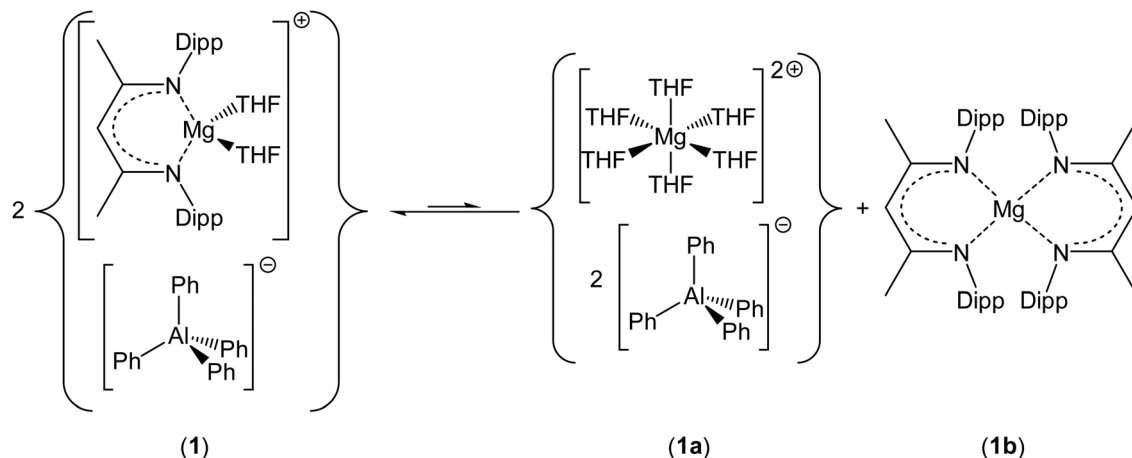
and so this study was supplemented with ^1H NMR data to determine when the reaction was complete. Although necessarily busy on account of converting one multi-proton containing species into another similar species, the area around 5 ppm in the ^1H NMR spectrum was informative as only the singlet of the NacNac γ -H resonates in this region. After two days at room temperature the ratio of reactant:product was nearing 50:50 and so heat was applied for a further week. However, this only improved the ratio to 40:60 after 2 days, suggesting either that the reaction has concluded, or was in equilibrium. This reaction was repeated on a millimolar scale in the hope that recrystallization of the target SSIP $[(^{\text{Dipp}}\text{NacNac})\text{Mg}]^+ [\text{AlPh}_4]^-$ (**1**, Scheme 2) would shift this equilibrium to the right. The product after attempted recrystallization from a hexane/THF mix was a yellow oil which contained only a few colourless crystals. Single crystal X-ray analysis revealed these to be the charge-separated complex $[\text{Mg} \cdot 6\text{THF}]^{2+} 2[\text{AlPh}_4]^-$ (**1a**, Fig. 1) which we believe is a minor Schlenk equilibrium¹³ product of the targeted complex **1**. However, its anionic moiety unequivocally confirms that ligand (phenyl) transfer from Mg to Al has occurred as intended, supporting the ^{27}Al NMR observations.

A ^1H NMR spectrum of the yellow oil in C_6D_6 solution was highly complicated, indicative of the presence of multiple

species. However, focusing on the 4.8–5.0 ppm region, where the NacNac backbone (γ) hydrogen atom resonates, this displayed four distinct resonances. The two smaller resonances at 4.88 and 4.86 ppm can be assigned to $^{\text{Dipp}}\text{NacNac}(\text{H})$ and $(^{\text{Dipp}}\text{NacNac})\text{MgPh}$ starting material respectively. The resonance at 4.97 ppm is tentatively assigned to $\text{Mg}[(^{\text{Dipp}}\text{NacNac})_2]$ (**1b**) by comparison with the spectrum of the pure compound reported by Harder to resonate at 5.01 ppm in the related NMR solvent $\text{C}_6\text{D}_5\text{CD}_3$.^{2a} The most intense resonance at 4.83 ppm is thus assigned to the desired cation in **1**. Further evidence came from the ^{27}Al NMR spectrum which again displayed a sharp singlet at 133 ppm diagnostic of the highly symmetrical tetraphenylaluminate anion.¹² We are confident that this resonance does not represent the crystallographically verified magnesium bisaluminate species **1a** as we have prepared this rationally (see ESI, Fig. S4–S6†) and it is too insoluble to display any resolvable resonances in C_6D_6 , with highly polar DMSO required to dissolve it sufficiently to record usable spectra.

Next, we decided to study the effect of the group 13 element upon the ligand transfer reaction and so turned our attention to the lighter congener BPh_3 . However, this corresponding reaction was found to be much slower than that with AlPh_3 . Consequently, we monitored this borane reaction at 60 °C in





Scheme 2 Proposed Schlenk equilibrium of heteroleptic complex **1** to give small quantities of homoleptic Mg complexes **1a** and **1b**.

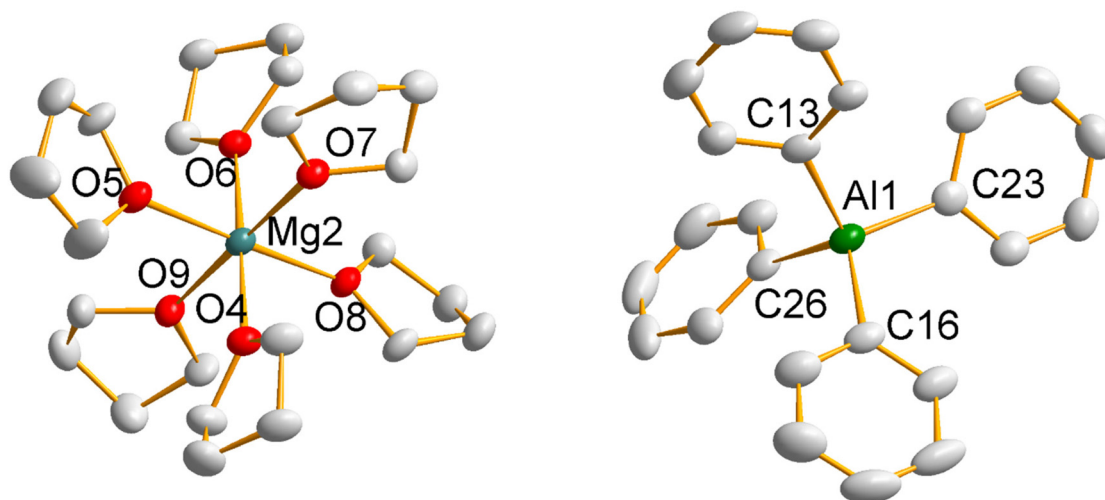


Fig. 1 Molecular structure of $[\text{Mg} \cdot 6\text{THF}]^{2+} 2[\text{AlPh}_4]^-$ (**1a**) with hydrogen atoms, minor disordered component of a THF backbone and one of the two aluminate anions omitted for clarity and with thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): Al–C, 2.006 (3)–2.015 (3), av. 2.011; Mg–O, 2.082 (2)–2.122 (2), av. 2.098; C–Al–C, 106.7 (1)–113.1 (1), av. 109.4; *cis* O–Mg–O, 88.78 (7)–90.81 (7), av. 90.00.

d_8 -THF by ^1H and ^{11}B NMR spectroscopy over a period of 8 days. The success of the reaction was evidenced again at the 5 ppm region of the ^1H NMR spectrum where loss of the resonance corresponding to the Nacnac γ -CH group of the starting material (4.91 ppm) was accompanied by downfield growth of the product resonance, $[(^{\text{Dipp}}\text{Nacnac})\text{Mg}]^+ [\text{BPh}_4]^-$ (**2**) at 5.11 ppm and a small resonance of $(^{\text{Dipp}}\text{Nacnac})_2\text{Mg}$ (5.00 ppm, Fig. 2 left, see Fig. S7 and S8† for full spectra) as seen previously in the alane reaction.

This result was mirrored by the ^{11}B NMR spectrum which showed gradual loss of the broad resonance of BPh_3 at 52.8 ppm and the growth of a sharp singlet of the $[\text{BPh}_4]^-$ anion at -6.6 ppm (Fig. 2, right).¹⁴ While this reaction was a success, the long timescale required to prepare the boron complex **2** versus aluminate **1** inspired us to pursue a gallium-centred Lewis acid. Triphenylgallium was therefore synthesised (see Fig. S9–S11†) and reacted with $^{\text{Dipp}}\text{NacnacMgPh}$ in d_8 -

THF. Fig. 3 shows the ^1H NMR spectra of both starting materials ($\text{GaPh}_3 \cdot \text{OEt}_2$ and $^{\text{Dipp}}\text{NacnacMgPh}$), followed by the reaction of both after 15 minutes (annotated in Fig. S12†). From these it can be seen by the lack of Mg–Ph peaks at approximately 6.6 ppm, that all of the starting $^{\text{Dipp}}\text{NacnacMgPh}$ has been consumed. New phenyl resonances can also be seen at 6.82, 6.91 and 7.57 ppm indicating the presence of a new M–Ph unit corresponding to the tetraphenylgallate anion of $[(^{\text{Dipp}}\text{Nacnac})\text{Mg}]^+ [\text{GaPh}_4]^-$ (**3**). Small resonances are still visible from the $\text{GaPh}_3 \cdot \text{OEt}_2$ starting material suggesting that this reactant was in slight excess in this reaction. It is clear from these observations that the reactivity increases as group 13 is descended.

Returning to an aluminium-centred Lewis acid, we probed the effect of modifying the electronics of the transferred ligand. Specifically, *p*-tolyl was chosen since modification at the *para*-position is unlikely to sterically prohibit the coordi-



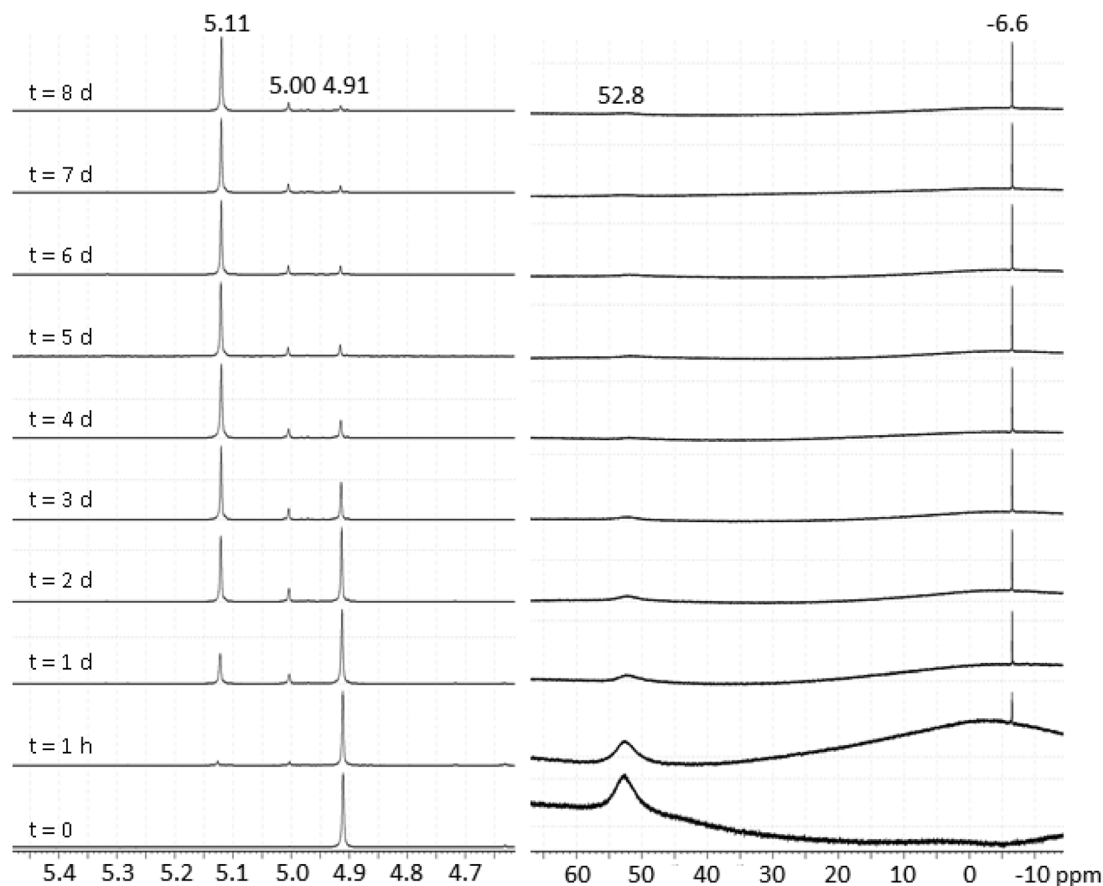


Fig. 2 Section of ^1H (left) and ^{11}B NMR spectra (right) of NMR scale reaction of $^{\text{Dipp}}\text{NacNacMgPh}$ and BPh_3 in $\text{d}_8\text{-THF}$ showing the region diagnostic of the $\text{C}_\gamma\text{-H}$ of the $^{\text{Dipp}}\text{NacNac}$ species; all values in ppm.

nation of four ligands around the aluminium centre as desired in the product. The starting materials $(^{\text{Dipp}}\text{NacNac})\text{Mg}(p\text{-Tol})\cdot\text{THF}$ and $\text{Al}(p\text{-Tol})_3\cdot\text{OEt}_2$ were prepared in an analogous manner to the original aryl substituents (see Fig. S13–S19†). NMR spectroscopic monitoring in $\text{d}_8\text{-THF}$ showed that the reaction to yield $[(^{\text{Dipp}}\text{NacNac})\text{Mg}]^+[\text{Al}(p\text{-Tol})_4]^-$ (**4**) was considerably slower than that of the original phenyl transfer reaction. Specifically, the growth of a sharp singlet in the ^{27}Al NMR spectrum at 133 ppm took much longer, and ^1H monitoring (specifically focusing on the emergence of the new resonance at 5.09 ppm in comparison to the original NacNac resonance at 4.90 ppm, see Fig. S20 and S21†) informed that only 10% conversion had occurred after 56 hours at room temperature. Heating at 60 °C for a week failed to make further change to this ratio, while variable temperature NMR studies gave no indication of an equilibrium between starting materials and products. With such a poor conversion, it seemed unwise to scale up and pursue a fractional crystallization of the product and so at this stage we turned to an alternative class of ligand, switching from aryl ligand transfer to (secondary) amido ligand transfer. Keeping with a six-membered cyclic ligand, we utilized the piperidine (NC_5H_{10} , pip) ligand for this task. $[(^{\text{Dipp}}\text{NacNac})\text{Mg}(\text{pip})]_2$ was prepared according to literature procedures,¹⁵ while $[\text{Al}(\text{pip})_3]_2$ was prepared *via* salt metathesis

of lithium piperidide with AlCl_3 in a 3 : 1 ratio in diethyl ether. Crucially, the presence of Lewis donor ether as the reaction medium did not break this up into monomeric $\text{AlR}_3\cdot\text{OEt}_2$ as was seen with the triarylaluminium complexes studied earlier, but rather recrystallisation from Et_2O or THF yielded dimeric unsolvated $[\text{Al}(\text{pip})_3]_2$.¹⁶ This was also witnessed by Smith *et al.* who prepared this dimer by direct deprotonation of piperidine with alane in THF, with the product remaining dimeric even in solution.¹⁷ The reaction of these two substrates in THF showed no evidence of ligand transfer with NMR analysis demonstrating only starting material. This may be due to the persistent dimeric nature of the neutral aluminium starting material which contains stronger 3-centre 4-electron dimerizing interactions which inhibits its ability to act as a ligand acceptor from the magnesium complex.

Consequently, given the relative success of phenyl transfer, we next studied the aromatic amide pyrrole, from the basis that its nitrogen lone pair would be unavailable for Lewis pair donation on account of it contributing to the aromaticity of the anion. Thus, a THF solution of $\text{Al}(\text{pyr})_3\cdot\text{OEt}_2$ (pyr = pyrrolyl, $\text{C}_4\text{H}_4\text{N}^-$) was introduced to a THF solution of $(^{\text{Dipp}}\text{NacNac})\text{Mg}(\text{pyr})\cdot\text{THF}$ (see Fig. S22–S27†) and this mixture was stirred at room temperature for two hours. Removing solvent under reduced pressure and attempting to re-dissolve the residue in



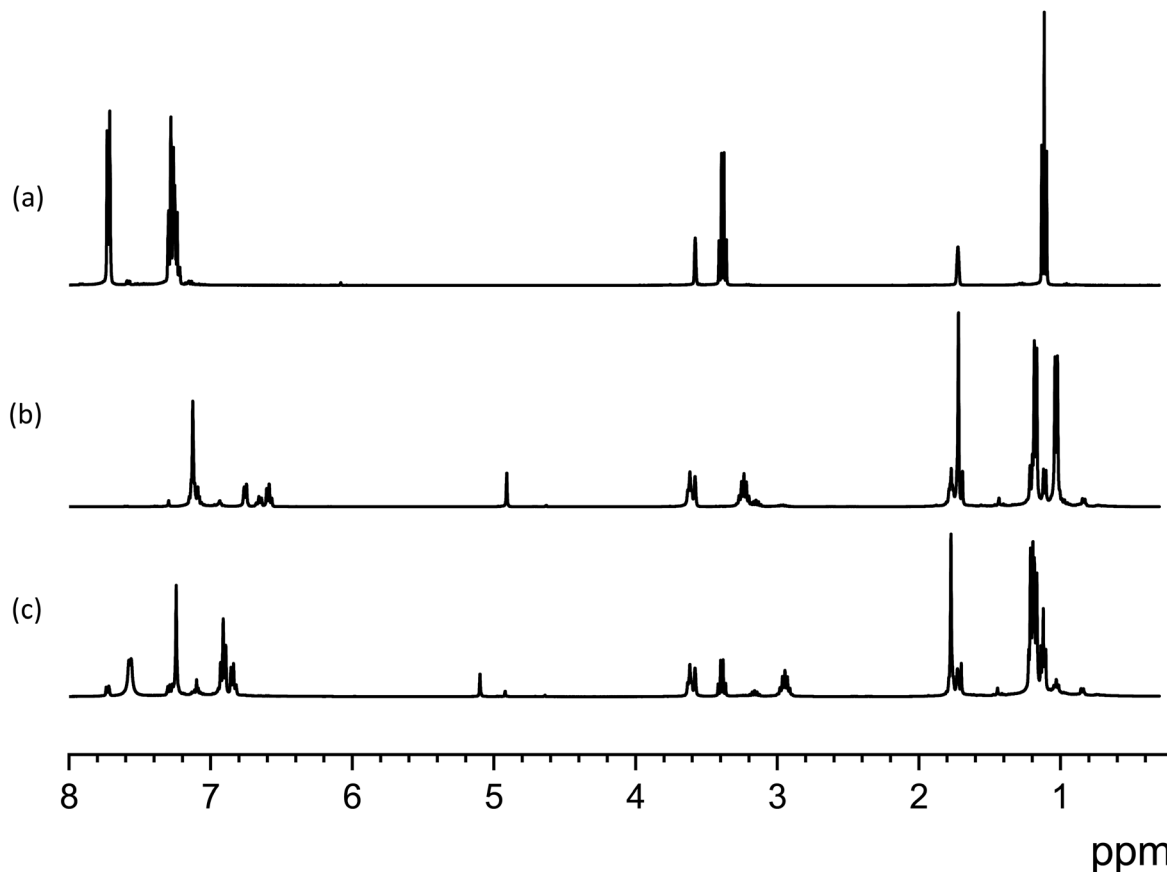


Fig. 3 ^1H NMR spectra of (a) $\text{GaPh}_3\cdot\text{OEt}_2$, (b) $^{\text{Dipp}}\text{NacNacMgPh}$ and (c) the reaction between $\text{GaPh}_3\cdot\text{OEt}_2$ and $^{\text{Dipp}}\text{NacNacMgPh}$ to yield **3** in d_8 -THF after 15 minutes.

hexane, gave a cloudy solution. This was filtered and cooled to $-20\text{ }^\circ\text{C}$ to give colourless crystals of the desired product, $[(^{\text{Dipp}}\text{NacNac})\text{Mg}\cdot 2\text{THF}]^+ [\text{Al}(\text{pyr})_4]^-$ (**5**) in a 50% crystalline yield (Fig. 4), although NMR analysis suggests that the solution yield is much higher (*vide infra*). Gratifyingly, this product confirms that high atom economy has been achieved here as we have simply transferred a pyrrolyl anion from Mg to Al with loss of Al-coordinated Et_2O to form the desired charge-separated magnesium aluminate complex.

To the best of our knowledge the anionic moiety, $[\text{Al}(\text{pyr})_4]^-$ has never been reported before although tetrahedral tetra(cyclic-amido)aluminate structures such as $[\text{Al}(1,4\text{-dihydropyridyl})_4]^-$ ¹⁸ and calix[4]pyrrole aluminates¹⁹ have appeared in the literature. The cationic moiety of **5** comprises a four-coordinate magnesium centre coordinated by the two nitrogen atoms of the NacNac ligand and two THF molecules. There is asymmetry in the coordination of the two THF molecules such that the Mg centre is heavily distorted from tetrahedral with one THF molecule lying almost in the plane of the NacNac ligand and the other lying perpendicular to it. This has been witnessed previously in neutral ether-solvated $(^{\text{Dipp}}\text{NacNac})\text{MgR}$ complexes ($\text{R} = \text{Ph}$,¹⁰ C_6F_5 ,^{5b} $\text{C}_6\text{F}_4\text{CF}_3$ ^{5b}). Despite being in markedly different environments, these THF

molecules display very similar O–Mg bond lengths [1.987(2) and 1.991(2) Å respectively]. These values are intermediate between the O–Mg values in $(^{\text{Dipp}}\text{NacNac})\text{MgOtBu}\cdot 2\text{THF}$ [2.048(2) and 1.844(2) to neutral THF and anionic $^-\text{OtBu}$ respectively]²⁰ demonstrating the increased Lewis acidity of the magnesium in its cationic form.

The veracity of this structure was supported in solution by ^1H , ^{13}C and ^{27}Al NMR spectroscopy (Fig. S28–S30†). For example, the symmetric aluminate anion is represented by a sharp singlet in the ^{27}Al NMR spectrum at 98.1 ppm. The ^1H and ^{13}C NMR spectra are as anticipated, with the CH backbone resonance of **5** at 4.71 ppm coming very close to that assigned to the similar complex **1** (4.83 ppm). However, despite multiple attempts we were never able to obtain a purity higher than 80%, with the remaining 20% of material being the starting material, $(^{\text{Dipp}}\text{NacNac})\text{Mg}(\text{pyr})\cdot\text{THF}$. Efforts to increase purity included multiple fractional recrystallizations, rapidly precipitating the product out of solution, longer reaction times in different solvents and including an excess of $\text{Al}(\text{pyr})_3$ to ensure complete reaction of the Mg starting material, but all proved unsuccessful. It is perhaps unsurprising that this starting material co-crystallizes with the desired product given the similarities in their



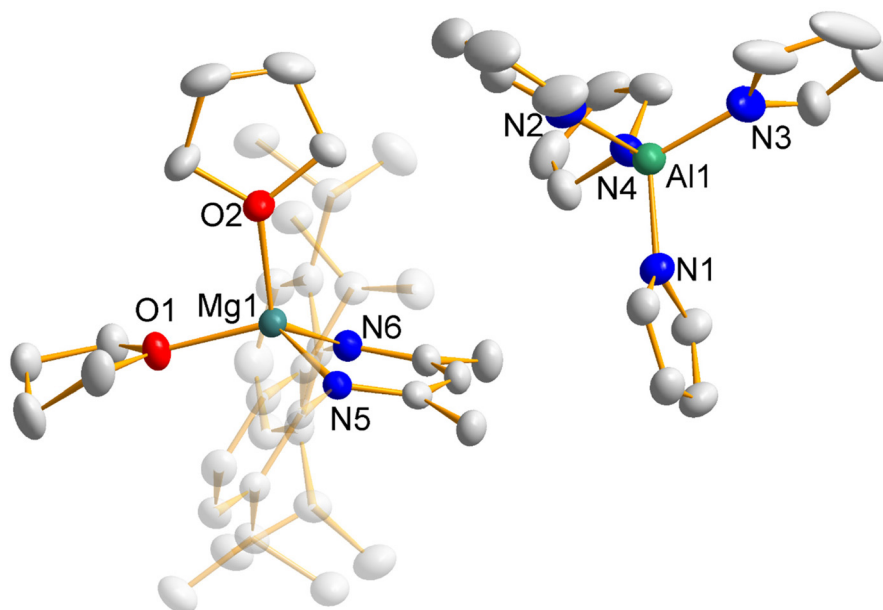


Fig. 4 Ion pair structure of $[(\text{DIPPNacNac})\text{Mg-2THF}]^+ [\text{Al}(\text{pyr})_4]^-$ (**5**) with hydrogen atoms and minor disordered component of a THF backbone omitted for clarity and with thermal ellipsoids drawn at 50% probability. Selected bond lengths (Å) and angles (°): Al–N, 1.842(2)–1.861(2) av. 1.851; Mg1–N5, 2.024(2); Mg1–N6, 2.006(2); Mg1–O1, 1.991(2); Mg1–O2, 1.987(2); N–Al–N, 107.5(1)–111.7(1) av. 109.4; N5–Mg1–N6, 96.31(7); O1–Mg1–O2, 99.33(7); N5–Mg1–O1, 120.17(7); N5–Mg1–O2, 112.46(7); N6–Mg1–O1, 113.72(7); N6–Mg1–O2, 115.99(7).

structures, as a five-membered anion (pyrrolyl) is ultimately replaced with a neutral five-membered ligand (THF). Finally, we determined the Lewis acidity of the Mg cation in **5** via the Gutmann–Beckett method²¹ by addition of a small amount of $\text{Et}_3\text{P}=\text{O}$ to the NMR sample followed by recording of the ^{31}P NMR chemical shift. This methodology provides an Acceptor Number for the Lewis acid on a scale of 0–100. Complex **5** gave a chemical shift of 70.8 ppm for an Acceptor Number of 65.9, which is comparable for the same Mg cation paired with a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion (72.8 ppm; AN 70.3)^{1a} despite lack of fluorination of the aryl substituents.

also a factor in the outcome as no reaction was seen using tris-piperidyl aluminium, which dimerizes *via* 3-centre 4-electron bonding (even in the presence of Lewis basic ethers), whereas tris-pyrrolyl aluminium, whose nitrogen lone pair forms part of the aromatic manifold of the ring, proceeds smoothly and in good yield.

Whilst this ligand transfer methodology is not a general approach to cationic magnesium complexes, it does represent a viable potential route and its cost-effectiveness and atom-economy means that it is worthy of consideration on a case-by-case basis, bearing the above limitations in mind.

Conclusion

In this study, we have demonstrated that β -diketiminato supported magnesium cationic complexes can be prepared in an atom economical way by ligand transfer of a monodentate anion from Mg to a group 13 Lewis acid. While this approach represents a valuable and potentially highly useful methodology since it utilises only cheap and easy to prepare starting materials, there are also some limitations to the approach that must be considered. Schlenk equilibria may be a factor as the desired final products are heteroleptic magnesium complexes of general formula $[(\text{NacNac})\text{Mg}]^+ [\text{ER}_4]^-$. The identity of the central group 13 element of the Lewis acid influences the rate of the reaction as demonstrated using EPH_3 (E = B, Al, Ga), whereby the ligand transfer reaction proceeds faster as the group is descended. The aggregation state of the Lewis acid is

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- (a) J. Pahl, S. Brand, H. Elsen and S. Harder, *Chem. Commun.*, 2018, **54**, 8685–8688; (b) S. Brand, H. Elsen, J. Langer, W. A. Donaubauer, F. Hampel and S. Harder, *Angew. Chem., Int. Ed.*, 2018, **57**, 14169–14173; (c) L. Garcia, M. D. Anker, M. F. Mahon, L. Maron and M. S. Hill, *Dalton*



- Trans.*, 2018, **47**, 12684–12693; (d) A. Friedrich, J. Pahl, H. Elsen and S. Harder, *Dalton Trans.*, 2019, **48**, 5560–5568; (e) J. Pahl, A. Friedrich, H. Elsen and S. Harder, *Organometallics*, 2018, **37**, 2901–2909; (f) K. Thum, A. Friedrich, J. Pahl, H. Elsen, J. Langer and S. Harder, *Chem. – Eur. J.*, 2021, **27**, 2513–2522.
- 2 (a) S. Harder, *Organometallics*, 2002, **21**, 3782–3787; (b) S. P. Sarish, S. Nembenna, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2011, **44**, 157–170; (c) L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031–3066.
- 3 (a) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754–1757; (b) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. – Eur. J.*, 2010, **16**, 938–955; (c) T. X. Gentner, B. Rösch, G. Ballmann, J. Langer, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 607–611; (d) A. S. S. Wilson, M. S. Hill and M. F. Mahon, *Organometallics*, 2019, **38**, 351–360; (e) H. Elsen, J. Langer, M. Wiesinger and S. Harder, *Organometallics*, 2020, **39**, 4238–4246.
- 4 (a) M. S. Hill, D. J. MacDougall and M. F. Mahon, *Dalton Trans.*, 2010, **39**, 11129–11131; (b) D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem. – Eur. J.*, 2010, **16**, 8508–8515; (c) M. S. Hill, M. Hodgson, D. J. Liptrot and M. F. Mahon, *Dalton Trans.*, 2011, **40**, 7783–7790; (d) M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon and C. Weetman, *Dalton Trans.*, 2011, **40**, 12500–12509; (e) J. Intemann, M. Lutz and S. Harder, *Organometallics*, 2014, **33**, 5722–5729; (f) P. Bellham, M. D. Anker, M. S. Hill, G. Kociok-Köhn and M. F. Mahon, *Dalton Trans.*, 2016, **45**, 13969–13978; (g) C. Weetman, M. S. Hill and M. F. Mahon, *Polyhedron*, 2016, **103**, 115–120; (h) C. Weetman, M. S. Hill and M. F. Mahon, *Chem. – Eur. J.*, 2016, **22**, 7158–7162; (i) J. Spielmann, D. F.-J. Piesik and S. Harder, *Chem. – Eur. J.*, 2010, **16**, 8307–8318; (j) C. Jones, S. J. Bonyhady, S. Nembenna and A. Stasch, *Eur. J. Inorg. Chem.*, 2012, 2596–2601.
- 5 (a) S. E. Baillie, V. L. Blair, T. D. Bradley, W. Clegg, J. Cowan, R. W. Harrington, A. Hernan-Gomez, A. R. Kennedy, Z. Livingstone and E. Hevia, *Chem. Sci.*, 2013, **4**, 1895–1905; (b) C. Bakewell, A. J. P. White and M. R. Crimmin, *J. Am. Chem. Soc.*, 2016, **138**, 12763–12766; (c) L. Davin, R. McLellan, A. Hernan-Gomez, W. Clegg, A. R. Kennedy, M. Mertens, I. A. Stepek and E. Hevia, *Chem. Commun.*, 2017, **53**, 3653–3656; (d) L. Davin, R. McLellan, A. R. Kennedy and E. Hevia, *Chem. Commun.*, 2017, **53**, 11650–11653; (e) C. Bakewell, B. J. Ward, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2018, **9**, 2348–2356; (f) M. Garçon, A. J. P. White and M. R. Crimmin, *Chem. Commun.*, 2018, **54**, 12326–12328; (g) L. Davin, W. Clegg, A. R. Kennedy, M. R. Probert, R. McLellan and E. Hevia, *Chem. – Eur. J.*, 2018, **24**, 14830–14835.
- 6 (a) R. M. Gauld, R. McLellan, A. R. Kennedy, J. Barker, J. Reid and R. E. Mulvey, *Chem. – Eur. J.*, 2019, **25**, 14728–14734; (b) C. Camp and J. Arnold, *Dalton Trans.*, 2016, **45**, 14462–14498; (c) F. A. LeBlanc, A. Berkefeld, W. E. Piers and M. Parvez, *Organometallics*, 2012, **31**, 810–818; (d) J. R. Lynch, A. R. Kennedy, J. Barker, J. Reid and R. E. Mulvey, *Helv. Chim. Acta*, 2022, **105**, e202200082.
- 7 (a) D. W. Randall, S. D. George, P. L. Holland, B. Hedman, K. O. Hodgson, W. B. Tolman and E. I. Solomon, *J. Am. Chem. Soc.*, 2000, **122**, 11632–11648; (b) W. Ren, S. Zhang, Z. Xu and X. Ma, *Dalton Trans.*, 2019, **48**, 3109–3115.
- 8 A. Friedrich, J. Eyselein, J. Langer and S. Harder, *Organometallics*, 2021, **40**, 448–457.
- 9 S. A. Brown, S. A. Cussen, R. Kennard, S. Marchesini, J. J. Pryke, A. Rae, S. D. Robertson, R. N. Samajdar and A. J. Wain, *Chem. Commun.*, 2022, **58**, 12070–12073.
- 10 A. P. Dove, V. C. Gibson, P. Hormnirun, E. L. Marshall, J. A. Segal, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2003, 3088–3097.
- 11 S. Kriek, H. Görls and M. Westerhausen, *Organometallics*, 2008, **27**, 5052–5057.
- 12 O. Mizrahi, N. Amir, E. Pollak, O. Chusid, V. Marks, H. Gottlieb, L. Larush, E. Zinigrad and D. Aurbach, *J. Electrochem. Soc.*, 2008, **155**, A103–A109.
- 13 (a) W. Schlenk and W. Schlenk Jr., *Chem. Ber.*, 1929, **62**, 920–924; (b) D. Seyferth, *Organometallics*, 2009, **28**, 1598–1605; (c) R. M. Peltzer, O. Eisenstein, A. Nova and M. Cascella, *J. Phys. Chem. B*, 2017, **121**, 4226–4237; (d) P. Rinke, H. Görls and R. Kretschmer, *Inorg. Chem.*, 2021, **60**, 5310–5321.
- 14 B. Wrackmeyer, *Z. Nat. B.*, 2015, **70**, 421–424.
- 15 L. J. Bole, L. Davin, A. R. Kennedy, R. McLellan and E. Hevia, *Chem. Commun.*, 2019, **55**, 4339–4342.
- 16 L. Sandig-Predzymirska, J. Ortmeyer, J. Wagler, E. Brendler, F. Habermann, M. Anders, M. Felderhoff and F. Mertens, *Dalton Trans.*, 2020, **49**, 17689–17698.
- 17 M. A. Andrianarison, M. C. Ellerby, I. B. Gorrell, P. B. Hitchcock, J. D. Smith and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1996, 211–217.
- 18 (a) P. T. Lansbury and J. O. Peterson, *J. Am. Chem. Soc.*, 1963, **85**, 2236–2242; (b) K. Hensen, A. Lemke, T. Stumpf, M. Bolte, H. Fleischer, C. R. Pulham, R. O. Gould and S. Harris, *Inorg. Chem.*, 1999, **38**, 4700–4704.
- 19 (a) F. Ebner, H. Wadepohl and L. Greb, *J. Am. Chem. Soc.*, 2019, **141**, 18009–18012; (b) F. Ebner, L. M. Sigmund and L. Greb, *Angew. Chem., Int. Ed.*, 2020, **59**, 17118–17124; (c) F. Ebner, P. Mainik and L. Greb, *Chem. – Eur. J.*, 2021, **27**, 5120–5124.
- 20 M. H. Chisholm, J. C. Huffman and K. Phomphrai, *J. Chem. Soc., Dalton Trans.*, 2001, 222–224.
- 21 (a) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235–1257; (b) M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polymer*, 1996, **37**, 4629–4631; (c) P. Erdmann and L. Greb, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114550.

