

Stoichiometrically-controlled reactivity and supramolecular storage of butylmagnesiato anions†

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Toluene is metallated by DABCO-activated disodium tetrabutylmagnesiato, but not by DABCO-activated monosodium tributylmagnesiato; this distinction is rationalised by DFT calculations on model systems, and the crystal structure of the main non-metallated product, which shows interstitial MgBu_4^{2-} dianions within a polycationic network, is reported.

Pioneered by Wittig more than fifty years ago,¹ alkali metal magnesium 'ate complexes constitute a broad class of compounds, which can be qualitatively formulated as "MMgR₃" or "M⁺(MgR₃)⁻". Though down the years reports of the structures of several such 'ates have added to the fascination of organo-alkali metal structural chemistry (work primarily associated with Weiss²), until recently the synthetic community had been apathetic towards utilising this class of compounds in chemical transformations. However the promise of these bimetallic reagents is now gradually coming to light through studies of their application in halogen- and hydrogen-metal exchange reactions,^{3,4} where in comparison to conventional monometallic reagents they can offer unusual regioselectivities and tolerate higher subambient temperatures. Amide-based 'ates "MMg(NR₂)₃" have also proved effective in polymetallation of arene and metallocene substrates, manifested in so called "inverse crown" macrocyclic products.⁵ Part of a broader study investigating the synergic chemistry of mixed alkali metal-magnesium compounds, this communication focuses on sodium magnesiates of the most important, synthetically useful "carbanion" "Bu⁻". We demonstrate how cocomplexation with Bu₂Mg can debilitate BuNa in its reactivity towards toluene and how changing the Na : Mg stoichiometry, and thereby the structure of the cocomplex, can dramatically alter the course of the reaction. In evidence we present the first structural characterisation of the tetrabutylmagnesiato dianion [$\{\text{Mg}(\text{Bu})_4\}^{2-}$], encapsulated within the interstices of a novel polycationic 3-dimensional network.

To begin the discussion, a fundamental of s-block organometallic chemistry needs to be stated: in general, organosodium compounds exhibit significantly higher carbanionic reactivities than their organomagnesium counterparts. This gradation can be demonstrated in practice by the ability of BuNa, suspended in hexane, to metallate toluene almost instantaneously at room temperature—a reaction that can be followed visually as bright orange "NaCH₂Ph" is produced—and the inability of Bu₂Mg to

do likewise even under forcing reflux conditions. But what if BuNa and Bu₂Mg are mixed together, does the mixture retain the individual reactivity characteristics of its two components? To seek an answer, we treated a stirred suspension of BuNa in hexane with an equimolar quantity of Bu₂Mg, at which point it was obvious to the eye that a new white precipitate had deposited.‡ Surprisingly this solid was found to be incapable of metallating toluene, when either suspended in hexane or dissolved in neat toluene. Such inactivity rules out unequivocally that the solid is unreacted BuNa and an NMR spectroscopic study confirmed that it was neither BuNa nor Bu₂Mg. Thus we propose that the solid is monosodium tributylmagnesiato "NaMgBu₃", **1**, a claimed but poorly characterised formulation employed previously in anionic polymerisations of isoprene and styrene.⁶ We have now characterised **1** spectroscopically (by NMR), but having as yet failed to obtain it in a pure crystalline form we decided to model it theoretically (*vide infra*). Aware that the lithium 'ates "LiMgBu₃" and "Li₂MgBu₄" are known, distinct compounds,⁴ we then examined a 2 : 1 BuNa : Bu₂Mg mixture which, by analogy, should afford disodium tetrabutylmagnesiato "Na₂MgBu₄", **2**. This mixture likewise produced a white solid‡ that proved to be inert towards toluene (metallation). Hence it can be reasoned that the second molar equivalent of BuNa cannot be free (otherwise toluene metallation would be facile) but does indeed cocomplex with **1** to generate a second cocomplex **2**. Furthermore there is a precedent for disodium tetraorganomagnesiates in the structurally authenticated aryl complex [$\{(\text{Na}.\text{PMDETA})^+\}_2(\text{MgPh}_4)^{2-}$].⁷

To compare the reactivities of the stoichiometric variants **1** and **2**, we tested each separately with the bicyclic diamine donor molecule DABCO [diazabicyclo(2,2,2)octane]. As a prelude, we performed a control reaction between BuNa, toluene, and DABCO in hexane: this was marked by a distinct colour change (colourless to orange), and the precipitation of orange "DABCO·NaCH₂Ph", which was characterised by ¹H and ¹³C NMR spectroscopy (ESI†). In contrast, no such colour change accompanied the corresponding reaction where **1** replaced BuNa, suggesting metallation had not occurred this time: instead, following addition of a few drops of THF, the pale yellow crystalline solid [$\{[\text{Na}_2(\text{DABCO})_3(\text{toluene})]^{2+}(\text{MgBu}_4)^{2-}\}_n$], **3**, was obtained.‡ Conversely, a mixture of **2**, toluene, and DABCO proved more akin to the BuNa control reaction, undergoing the same colour change and producing an orange precipitate. NMR analysis established the precipitate to be a mixture of "DABCO·NaCH₂Ph" (the major product) and **3**.

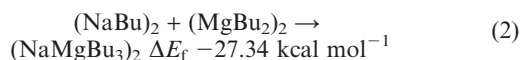
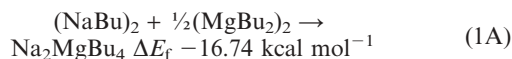
To attempt to rationalise these conflicting observations, we utilised DFT calculations.⁸ Geometry optimisations were

† Electronic supplementary information (ESI) available: Full experimental details and theoretical calculations. See <http://www.rsc.org/suppdata/cc/b416636a/>

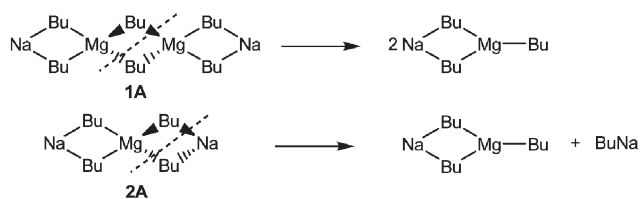
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performed using Gaussian 03. Exploratory *ab initio* calculations at the Hartree Fock (HF) level were performed, utilising the 6-31G* basis set. The resultant optimised geometries were subject to a frequency analysis and then refined further by density functional theory (DFT) calculations using the B3LYP functionals and the 6-311G** basis set. (Full details are presented in the ESI†). The theoretical structure of $(\text{Na}_2\text{MgBu}_4)$, **2A**, exhibits S_4 symmetry with Mg located in a tetrahedron of butyl groups, two opposing edges of which bridge to Na in a classical “Weiss” alkali metal magnesiate motif.² Maintaining the basic motif, but substituting the central Mg atom of **2A** by a $\text{Mg}(\mu\text{-Bu})_2\text{Mg}$ molecule gives dimeric $[(\text{NaMgBu}_3)_2]$, **1A**. Significantly, formation of both mixed-metal species from model homometallic constituents (eqns. (1), (1A) and (2)) is exothermic with energy gains of 49.15 and 16.74 kcal mol⁻¹ for **2A** (starting from monomeric and dimeric reactants, respectively) and 27.34 kcal mol⁻¹ for **1A**. This explains the absence of free BuNa in the reactions of **2** and **1** with toluene. Furthermore, the theoretical study exposes a rudimentary distinction between the ‘ate structures: **1A** can be cleaved symmetrically to release two molecules of ‘NaMgBu₃’ monomer, whereas **2A** can only be cleaved asymmetrically to release ‘NaMgBu₃’ and free BuNa (Scheme 1). This likewise explains the test reactions with DABCO, a strong donor expected to promote such cleavage (in the first instance), as only in the case of **2** can ‘DABCO·NaCH₂Ph’ be produced as free BuNa is required for toluene metallation. Clearly, DABCO ligation must promote further (secondary) reactions as the other expected product ‘NaMgBu₃’, common to both cleavage situations, does not rest as simply ‘DABCO·NaMgBu₃’, but ultimately forms sodium-rich **3** and presumably ‘MgBu₂’.



The crystal structure of **3** (Fig. 1)§ is made up of separated cationic $[\text{Na}_2(\text{DABCO})_3(\text{toluene})]^{2+}$ and anionic $(\text{MgBu}_4)^{2-}$ moieties. Each DABCO and toluene bridges two Na atoms in the former to construct a 3-dimensional coordination network (Fig. 2). The shortest circuits in the network involve six Na atoms in $[\text{Na}(\text{DABCO})_6]$ or $[\text{Na}_6(\text{DABCO})_4(\text{toluene})_2]$ rings. Both types of Na occupy a distorted tetrahedral environment comprising three N atoms from distinct DABCO ligands and the π -face of toluene. The $(\text{MgBu}_4)^{2-}$ dianions sit discretely in interstices within the polycationic network, but do not form any short contacts with it. This is the most innovative feature of **3** as it represents the first



Scheme 1

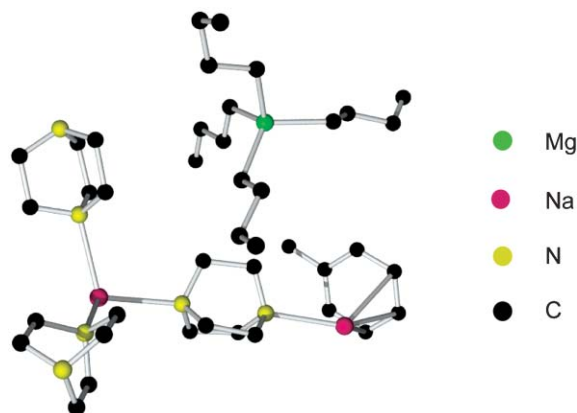


Fig. 1 Repeating unit of **3**. Disorder components and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mg(1)–C(1) 2.009(6), Mg(1)–C(13) 2.010(7), Mg(1)–C(9) 2.042(7), Na(1)–N(5) 2.542(4), Na(1)–N(1) 2.535(4), Na(1)–N(3) 2.567(4), Na(2)–N(2) 2.456(4), C(1)–Mg(1)–C(13) 106.4(2), C(1)–Mg(1)–C(9) 113.7(3), C(13)–Mg(1)–C(9) 107.5(3), N(5)–Na(1)–N(1) 105.10(15), N(5)–Na(1)–N(3) 100.74(14), N(1)–Na(1)–N(3) 109.23(14). For atom labelling scheme refer to .cif file.

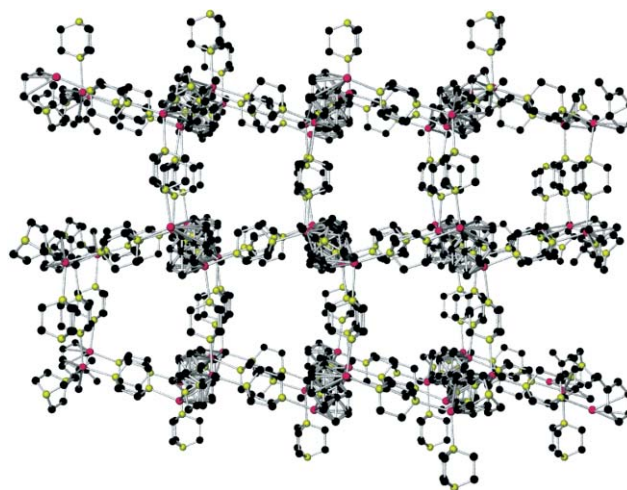


Fig. 2 Section of the three-dimensional network of **3**.

example of a discrete molecular tetraorganomagnesiate anion stored within a supramolecular framework. In contrast, alkali metal magnesiates commonly adopt contact ion-pair structures with M–C–Mg bridges.² Such supramolecular storage of discrete molecules could promote anion activation (or deactivation) with respect to the reactivity of conventional organomagnesiate compounds. Future work will address this intriguing possibility.

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Notes and references

‡ All reactions were carried out under a protective argon atmosphere.

Synthesis of $[[\text{Na}_2(\text{DABCO})_3(\text{toluene})]^{2+}(\text{MgBu}_4)^{2-}]$ (3**)** BuNa (0.4 g, 5 mmol) was suspended in hexane (10 mL). Then Bu_2Mg (5 mL of a 1 M solution in heptane, 5 mmol) was added to produce a white precipitate. A solution of DABCO (0.84 g, 7.5 mmol) in toluene (2 mL) was then introduced. The mixture was stirred at room temperature for 15 min affording a pale yellow suspension. THF (ca. 2 mL) was added until all of the solid dissolved. Placed in the freezer at -28°C , the resulting solution deposited yellow crystals (yield of first batch, 0.32 g, 18%). ^1H NMR (400 MHz, 25°C , d^8 -THF): 7.17–7.06 (m, 5H, C_6H_5 , toluene), 2.64 (s, 36H, CH_2 , DABCO), 2.27 (s, 3H, CH_3 , toluene), 1.34 [m (broad), 8H, CH_2 , Bu], 1.19 (m, 8H, CH_2 , Bu), 0.80 (t, 12H, CH_3 , Bu), -0.46 [m (broad), 8H, Mg– CH_2 , Bu]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, 25°C , d^8 -THF): 128.75, 128.02, 125.12, 122.47 (C_6H_5 , toluene), 47.54 (CH_2 , DABCO), 31.56 (CH_2 , Bu), 30.25 (broad, CH_2 , Bu), 23.41 (CH_3 , toluene), 14.09 (CH_3 , Bu), Mg– CH_2 signal not detected.

§ Crystal data for **3**: $\text{C}_{41}\text{H}_{80}\text{MgN}_6\text{Na}_2$, $M_r = 727.40$, orthorhombic, space group *Pbca*, $a = 19.637(1)$, $b = 20.2159(7)$, $c = 22.113(1)$ Å, $V = 8778.3(8)$ Å³, $Z = 8$, $\lambda = 0.71073$ Å, $\mu = 0.094$ mm⁻¹, $T = 150$ K; 10172 reflections, 5355 unique, $R_{\text{int}} = 0.0687$; final refinement to convergence on F^2 gave $R = 0.0703$ (F , 3094 obs. data only) and $R_w = 0.1959$ (F^2 , all data), GOF = 1.020. Disorder of the butyl and toluene moieties (modeled

over two sites with equal occupancies) had an adverse impact on the quality of the data collection and refinement. CCDC reference number 225283. See <http://www.rsc.org/suppdata/cc/b4/b416636a/> for crystallographic data in .cif or other electronic format.

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