

# Alkali-Metal-Mediated Magnesiations of an NHC: Normal, Abnormal and “Paranormal” Reactivity in a Single Tritopic Molecule\*\*

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**Abstract:** The metalation reaction is currently in the midst of an extraordinary transformative period due largely to development of bimetallic metalating agents, which operate through metal-metal synergistic effects inaccessible to unimetal bases. Here the sodium alkylmagnesium amide  $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{nBu})_2]$ , a template base as its deprotonating action is dictated primarily by its 12-atom ring structure, is studied with the common NHC, IPr [1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene]. Remarkably, magnesiatio

of IPr occurs at the *para*-position of an aryl substituent, sodiation occurs at the abnormal C4 position and a dative bond occurs between normal C2 and sodium, all within a 20-atom ring structure that accommodates two  $\text{IPr}^{2-}$  dianions. Studies with different K-Mg and Na-Mg bimetallic bases have realized two other magnesiatio NHC structures containing two or three  $\text{IPr}^-$  monoanions bound to Mg via abnormal C4 sites. Synergistic in that magnesiatio can only work through alkali metal mediation, these reactions add magnesium to the small cartel of metals capable of directly metalating a NHC.

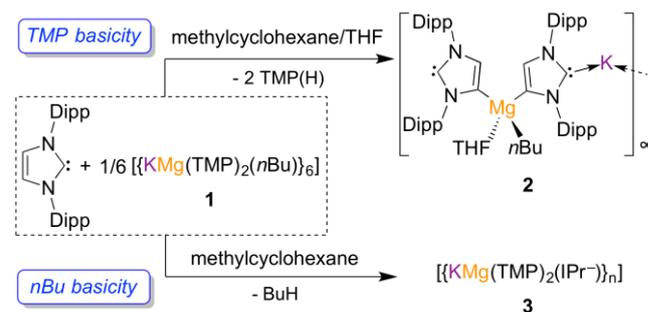
Chemists often find fascination in synergistic systems, especially if the cooperativity can be usefully exploited in a practical application. Such effects are prominent in synthetic organometallic chemistry where two metals are involved.<sup>[1]</sup> For example, elegant studies by Xi<sup>[2]</sup> show that close proximity of two Li centres in 1,4-dilithio-1,3-butadienes can promote intra- and inter-molecular reactions beyond the scope of monolithio systems. A core tool in synthesis, metalation has advanced greatly in recent times through cooperative effects delivered, not by dimetallo dianions, but by combinations of different metal monoanion components.<sup>[3]</sup> Knochel's salt-boosted organometallic reagents<sup>[4]</sup> typified by  $\text{TMPMgCl}\cdot\text{LiCl}$  (TMP = 2,2,6,6-tetramethylpiperidide), the use of which has recently been extended to continuous flow reactors,<sup>[5]</sup> are exemplars of these multicomponent metalators. LiTMP lithiations can also be rendered synergistic by pre-mixing the aromatic substrate with a

salt (e.g.,  $\text{MgCl}_2$ ) so that sensitive lithiated substrates can be transmetalated rapidly (in situ trapping) to a more stable, more synthetically pliable form.<sup>[6]</sup> Trans-metal-trapping with  $i\text{Bu}_2\text{Al}(\text{TMP})$  not only stabilises LiTMP lithiated substrates but can shift equilibrium reactions towards the wanted product.<sup>[7]</sup> Of special relevance in this work, *pre-inverse-crowns*<sup>[8]</sup> are two-metal macrocyclic complexes whose deprotonating action is governed more by their template structures than by the substituents on the aromatic substrates. Thus *pre-inverse-crown*  $[\text{Na}_4\text{Mg}_2(\text{TMP})_6(\text{nBu})_2]$  can dideprotonate *N,N*-dialkylanilines and *tert*-butylbenzene selectively at *meta-meta'* positions<sup>[9]</sup> in violation of directed *ortho*-metalation (DoM) principles.<sup>[10]</sup> Here, in reporting the first metalation study between *pre-inverse-crowns* and N-heterocyclic carbenes (NHCs), we describe the first directly magnesiatio NHCs in positions both expected and wholly unexpected.

NHC metalation (C-H to C-metal exchange) is a relatively recent development within the fast growing NHC literature.<sup>[11]</sup> Robinson made a seminal breakthrough in 2010 deprotonating IPr [1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] at its C4 (alkenic backbone) position with  $n\text{BuLi}$ <sup>[12]</sup> to open up an “abnormal” construction point for functionalization. Goicoechea subsequently synthesized the potassium congener of this lithium carbanionic NHC via metathesis with  $t\text{BuOK}$  to use in ligand transfer applications.<sup>[13]</sup> Bertrand achieved C4-functionalisation via a different approach by making imidazolium IPr cations with the C2 position blocked by E substituents [E = e.g.,  $\text{PhC}(\text{O})$ ,  $\text{PPh}_2$ ] that intramolecularly rearrange to C4-E species on deprotonation by  $\text{KHMDS}$ .<sup>[14]</sup> Both indirect (via Robinson's lithiated NHC and  $\text{Et}_2\text{Zn}$ )<sup>[15]</sup> and direct (via Hevia's sodium TMP-zincate reagent)<sup>[16]</sup> methods of zincating IPr at position C4 have also been reported. An unusual amido-directed lateral lithiation of a  $\text{CH}(\text{Me})_2$  wingtip on a Dipp (diisopropylphenyl) group in a 4-amido-NHC has recently been described by Braunstein *et al.*<sup>[17]</sup>

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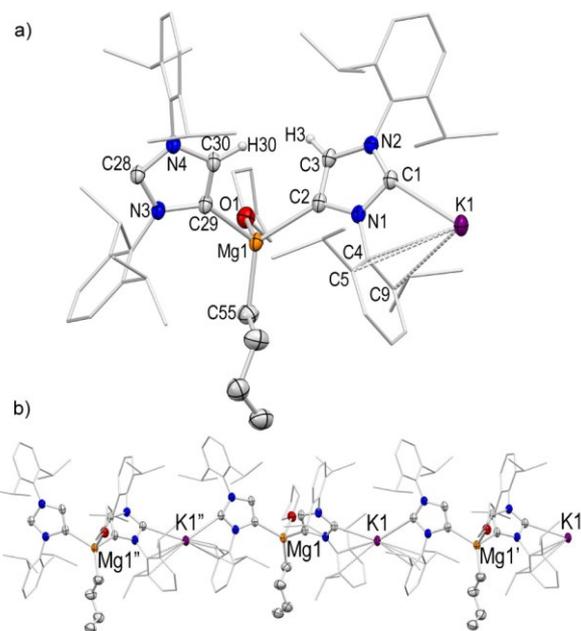
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**Scheme 1.** Solvent-dependent reactions of IPr with 1. Synthesis of  $[\{\text{KMg}(\text{IPr})_2(\text{nBu})(\text{THF})\}]_n$  2 and  $[\{\text{KMg}(\text{TMP})_2(\text{IPr})\}]_n$  3.

In this work IPr was directly magnesiated by pre-inverse-crown  $[[\text{KMg}(\text{TMP})_2(n\text{Bu})]_6] \mathbf{1}$  in methylcyclohexane/THF to afford the bis-carbene magnesiate  $[[\text{KMg}(\text{IPr})_2(n\text{Bu})(\text{THF})]_n] \mathbf{2}$  (Scheme 1: where IPr is  $[\text{C}\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CHC}^-\}]$ ). Interestingly this is not a template metalation. When  $\mathbf{1}$  acts as a template base, for example towards naphthalene, its six Bu ligands are substituted by six naphthalenide anions (butane is expelled) with retention of its 24-atom  $(\text{KNMgN})_6$  ring architecture.<sup>[6]</sup> In contrast, in making  $\mathbf{2}$ , pre-inverse-crown  $\mathbf{1}$  acts formally as an amido dibase while retaining a Bu group. Dibasicity of  $\mathbf{1}$  can be inferred but the moderate yield of  $\mathbf{2}$  (absolute 20%; with respect to IPr, 40%) and the failure to increase the yield on adding more IPr suggests a redistribution process is more likely starting from putative  $[\text{KMg}(\text{IPr})(\text{TMP})(n\text{Bu})]$ , though the key point is, irrespective of  $\mathbf{1}$  being a mono- or di-amido base,  $n\text{Bu}$  is retained. Robinson and Goicoechea have reported related redistribution processes with anionic NHCs of Zn<sup>[15]</sup> and Mn<sup>[18]</sup> respectively. Crystalline  $\mathbf{2}$  was also fully characterized by NMR spectroscopy in  $[\text{D}_8]\text{THF}$  solution.<sup>[19]</sup> A 2:1 ratio for IPr and  $n\text{Bu}$  ligands is observed in the <sup>1</sup>H spectrum in agreement with the formulation of  $\mathbf{2}$ . The  $\text{CH}(\text{CH}_3)_2$  fragments of the Dipp groups resonate as two distinct sets of signals in the <sup>1</sup>H and <sup>13</sup>C spectra as a result of the symmetry loss in IPr due to the metallation in the backbone of the imidazole ring, which is also mirrored by a large downfield resonance at 156.4 ppm in the <sup>13</sup>C NMR spectrum for the Mg-C4 fragment (122.5 ppm in the free IPr). In addition, the resonance assigned to the carbenic-C2 is shifted upfield (214.1 ppm) compared to that observed in free IPr (221.1 ppm) reflecting the formation of an NHC-complex with potassium. A fluxional process at room temperature makes equivalent the dative  $\text{C2} \rightarrow \text{K}$  interaction on both IPr fragments explaining the single resonance for C2. More significantly, a unique broad singlet is observed for the two imidazole CH at 4.96 ppm, dramatically upfield to that in free IPr (7.20 ppm) and previous C4 metalated examples (range: 6.07–6.66 ppm).<sup>[12–13, 16]</sup> This unexpected shielding of the imidazole CH in  $\mathbf{2}$  correlates with the upfield resonances for the *para*- and *meta*-CH (at 6.43 and 6.86 ppm, respectively) of one of two inequivalent Dipp groups. This effect can be explained by a close intramolecular spatial proximity between the imidazole CH of one IPr and a Dipp ring from the second IPr moiety (and vice versa) which overall results in a mutual shielding by anisotropic effects. THF could be a factor in the lack of a template effect in the metalation as this lone pair donor can compete for metal coordination sites and deaggregate the  $(\text{KNMgN})_6$  24-atom ring structure. Significantly donor-solvated potassium magnesiate  $[(\text{PMDTA})\text{KMg}(\text{TMP})_2(\text{CH}_2\text{SiMe}_3)]$  is known to deprotonate aromatic substrates kinetically through TMP.<sup>[20]</sup> Crystalline  $\mathbf{2}$  exhibits as an infinite, zig-zag chain structure (Figure 1). Mg occupies a distorted tetrahedral ( $\text{C}_3\text{O}$ ) anionic site comprising two distinct C4-deprotonated IPr, one  $n\text{Bu}$  and one THF ligand. Alternating with anionic moieties along the chain, K<sup>+</sup> bridges two “normal” IPr sites (C1 and C28; mean bond length, 2.87 Å) and engages in longer  $\text{K}-\eta^3\text{C}_6$   $\pi$ -arene interactions with one Dipp substituent on each IPr at *ipso*, *ortho* and *meta* sites [length range: 3.029(2)–3.406(3) Å]. Repeating the reaction without THF (Scheme 1) gave an oily mixture from which a brown solid was extracted. Though this product could not be obtained as single crystals, NMR characterization in  $[\text{D}_8]\text{THF}$  solution<sup>[19]</sup> is consistent with a single compound of empirical formula  $[[\text{KMg}(\text{TMP})_2(\text{IPr})]_n] \mathbf{3}$ , where IPr is deprotonated at C4.<sup>[21]</sup> Most compelling, <sup>1</sup>H DOSY NMR<sup>[22]</sup> data of  $\mathbf{3}$  in  $[\text{D}_8]\text{THF}$  confirm a

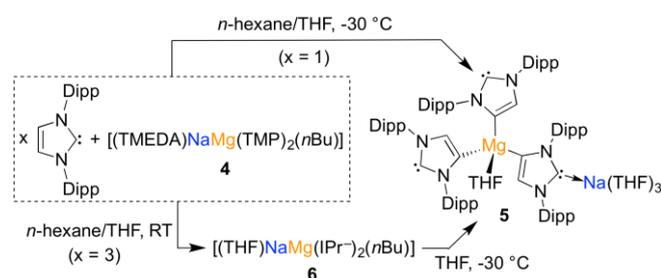
single monomeric version of  $\mathbf{3}$   $[[(\text{D}_8)\text{THF}]_3\text{KMg}(\text{IPr})(\text{TMP})_2]$ .<sup>[19]</sup> Significantly, this formulation is consistent with a template metalation through  $n\text{Bu}$  basicity (butane loss) matching other reactions of  $\mathbf{1}$  in non-donor media, which implies that here IPr acts as a C-H substrate as opposed to a donor since donor IPr synergic metalations usually show TMP basicity [TMP(H) loss] as evidenced by Hevia’s TMP-zincate study.<sup>[16]</sup>



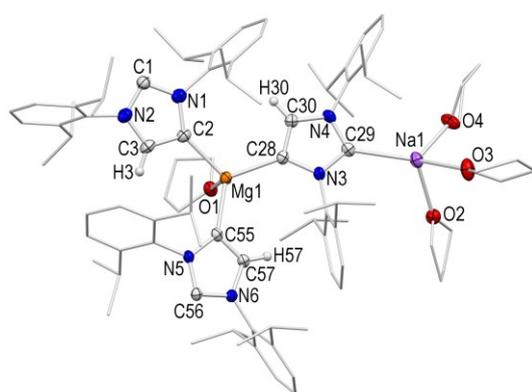
**Figure 1.** a) Molecular structure of  $[[\text{KMg}(\text{IPr})_2(n\text{Bu})(\text{THF})]_n] \mathbf{2}$ ,<sup>[23]</sup> showing the contents of the asymmetric unit, which corresponds to a single turn of the zig-zag chain. Displacement ellipsoids are displayed at 35% probability. Hydrogen atoms (except H3 and H30) and disordered components for  $n\text{Bu}$  and IPr groups are omitted for clarity. Dipp and THF groups are pictured as capped sticks for clarity. The dashed lines illustrate  $\text{K} \cdots \text{C}$  (aryl) contacts. b) Section of the extended framework structure showing atom connectivity between normal-C2 (C1 and C28) sites to K, and abnormal-C4 (C2 and C29) and the  $n\text{Bu}$  ligand to Mg.

Sodium magnesiate  $[(\text{TMEDA})\text{NaMg}(\text{TMP})_2(n\text{Bu})] \mathbf{4}$  reacted with IPr in a 1:1 stoichiometry in  $n$ -hexane and after a crystallisation process in  $n$ -hexane/THF produced the tris(mononionic) carbene  $[(\text{THF})_3\text{Na}(\mu\text{-IPr})\text{Mg}(\text{THF})(\text{IPr})_2] \mathbf{5}$  (Figure 2). Our NMR studies point to a complicated ligand redistribution process in forming  $\mathbf{5}$  (Scheme 2) when THF is present in the reaction media.<sup>[19]</sup> When  $\mathbf{4}$  was subjected to IPr in a 1:3 molar ratio in  $n$ -hexane a similar compound to  $\mathbf{2}$  of empirical formula  $[(\text{THF})\text{NaMg}(\text{IPr})_2(n\text{Bu})] \mathbf{6}$  (Scheme 2) was isolated and characterized by NMR spectroscopy. <sup>1</sup>H NMR data of  $\mathbf{6}$  in  $[\text{D}_8]\text{THF}$  solution show a singlet for the imidazole CH at 6.30 ppm, two discrete resonance sets for the Dipp groups and a characteristic  $\text{MgCH}_2$  signal at -1.25 ppm for the Bu group. Abnormal-C4 exhibits a resonance at 161.0 ppm in the <sup>13</sup>C spectrum, in agreement with that seen in  $\mathbf{2}$ . Similarly, the formation of crystalline  $\mathbf{5}$  was observed when  $\mathbf{6}$  was dissolved in  $n$ -hexane/THF, reinforcing the idea of a ligand-induced redistribution phenomena in forming  $\mathbf{5}$ . The discrete contacted ion pair structure of  $\mathbf{5}$  has a distorted tetrahedral tris(THF)-solvated Na<sup>+</sup> bound to carbenic “C2”  $[\text{Na1}-\text{C29}, 2.492(4) \text{ \AA}]$ , previously seen in zincate  $(\text{THF})_3\text{Na}[\text{C}\{\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CHCZn}(t\text{Bu})_2]$ .<sup>[16]</sup> However, the counter anion is unique exhibiting a distorted tetrahedral Mg, bound to one THF

molecule and the “C4” positions of three IPr<sup>-</sup> ligands and, two terminal and one bridging to Na. Homoleptic metal complexes containing three anionic NHC ligands are extremely rare.<sup>[25]</sup>

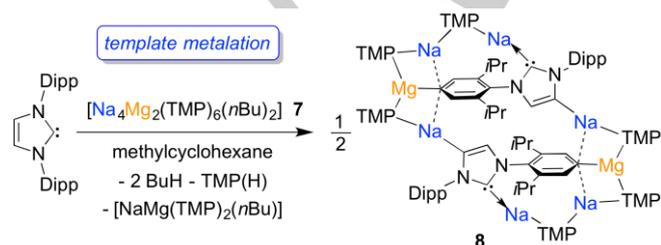


**Scheme 2.** Synthesis of [(THF)<sub>3</sub>Na( $\mu$ -IPr)Mg(THF)(IPr)<sub>2</sub>] **5** and [(THF)NaMg(IPr)<sub>2</sub>(*n*Bu)] **6**.

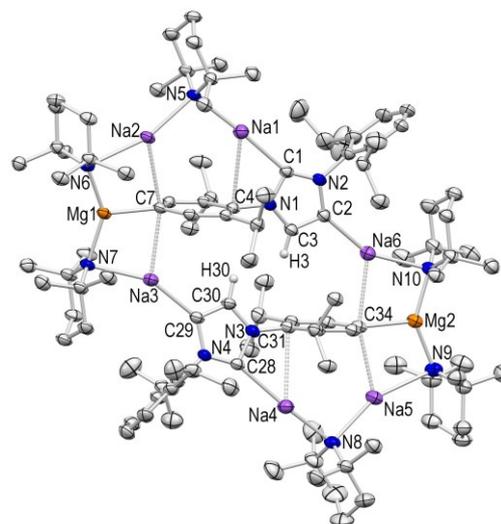


**Figure 2.** Molecular structure of [(THF)<sub>3</sub>Na( $\mu$ -IPr)Mg(THF)(IPr)<sub>2</sub>] **5**.<sup>[23]</sup> Displacement ellipsoids are displayed at 35% probability. Hydrogen atoms (except H3, H30 and H57) and disordered components for one THF molecule and one *i*Pr group are omitted for clarity. Dipp and THF groups are pictured as capped sticks for clarity.

The most extraordinary result came from subjecting IPr to pre-inverse-crown [Na<sub>4</sub>Mg<sub>2</sub>(TMP)<sub>6</sub>(*n*Bu)<sub>2</sub>] **7** in hydrocarbon media. An equimolar reaction (Scheme 3) produced the remarkable inverse crown [(Na<sub>3</sub>Mg(TMP)<sub>3</sub>(IPr<sup>2-</sup>))<sub>2</sub>] **8** (where IPr<sup>2-</sup> is [C{[N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-4)N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)]CHC<sup>-</sup>}) isolated in a high (crystalline) yield of 72% (with respect to IPr, quantitative conversion determined by NMR). Formation of an inverse crown, absence of *n*Bu in its formula, and the fact that the bulk solvent was donor free, collectively signal a template or at least partial template metalation. Byproducts of butane, TMP(H) and “NaMg(TMP)<sub>2</sub>(*n*Bu)” would balance the reaction equation.



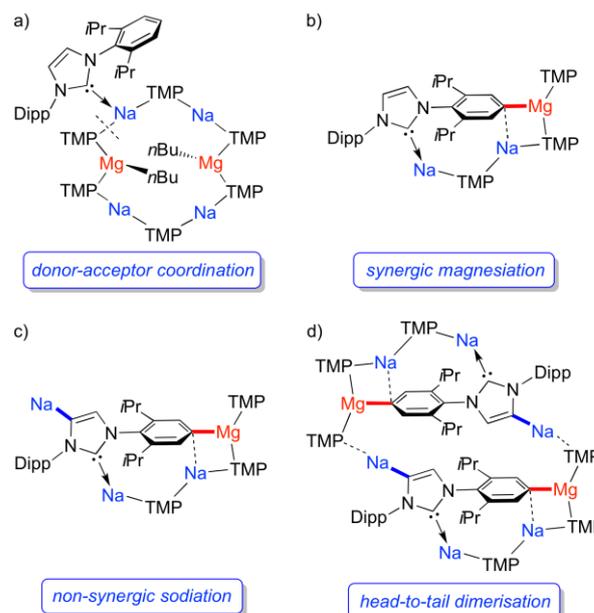
**Scheme 3.** Template metalation of IPr with [Na<sub>4</sub>Mg<sub>2</sub>(TMP)<sub>6</sub>(*n*Bu)<sub>2</sub>] **7**, formation of the inverse crown [(Na<sub>3</sub>Mg(TMP)<sub>3</sub>(IPr<sup>2-</sup>))<sub>2</sub>] **8**.



**Figure 3.** Molecular structure of inverse crown [(Na<sub>3</sub>Mg(TMP)<sub>3</sub>(IPr<sup>2-</sup>))<sub>2</sub>] **8**.<sup>[23]</sup> showing one of the two crystallographically independent molecules. Displacement ellipsoids are displayed at 35% probability. Hydrogen atoms (except H3 and H30) and methylcyclohexane molecules of crystallization are omitted for clarity. The dashed lines illustrate Na $\cdots$ C(aryl) contacts.

Figure 3 shows the discrete structure of one of two crystallographically unique molecules of **8**. Inverse crowns are defined by an outer polymeric cationic ring charge balanced by an inner anionic moiety.<sup>[26]</sup> Each dimer of **8** displays a 20-atom [(NaMgNNaCNCNa)<sub>2</sub>]<sup>2+</sup> ring that encapsulates two IPr<sup>2-</sup> dianions but since one each of their negatively charged atoms (C2 and C29) lies within the ring wall the inner cavity carries only a 2- charge through C7 and C34 of Dipp substituents. Thus the number of inner carbanion sites matches the number of outer ring Mg atoms (through C7-Mg1; C34-Mg2), which is a signature feature of inverse crowns.<sup>[26]</sup> From a NHC perspective, IPr datively binds to Na via its normal “C2” position (C1-Na1, C28-Na4), is metalated by a second Na at its abnormal “C4” (C2-Na6, C29-Na3) the ones nearest the intact Dipp groups, and by Mg at the *para* (“paranormal”) position of the other Dipp groups (C7-Mg1, C34-Mg2). Among many unique features, **8** represents the first crystallographically characterised sodium anionic carbene, whereas the simple C4-sodiated Na<sup>+</sup>IPr<sup>-</sup> exists as an insoluble, presumably polymeric solid.<sup>[19]</sup> Based on well-established metalation patterns a pathway of intermediates leading to **8** can be proposed (Scheme 4). Being an excellent  $\sigma$ -donor, IPr would initially coordinate to the more exposed acceptor Na in the pre-inverse-crown leading to template cleavage. Complexes of type [(donor)NaMg(TMP)<sub>2</sub>(*n*Bu)] are common.<sup>[24]</sup> Pre-inverse-crowns invariably magnesiate via *n*Bu basicity so part of the template attached to “C2” through Na could execute the *para*-aryl magnesiation.<sup>[27]</sup> However, given the extended length of emergent IPr with respect to substituted benzene substrates, this magnesiation is likely to be accompanied by template fragmentation as its 12-atom ring would be too small to circumnavigate IPr. Hemi-inverse-crown “Na<sub>2</sub>Mg(TMP)<sub>3</sub>(IPr<sup>-</sup>)” could result, stabilising the anionic carbene by both a *para*-aryl C-Mg and normal C2 $\rightarrow$ Na bond. A test reaction between [Na<sub>4</sub>Mg<sub>2</sub>(TMP)<sub>6</sub>(*n*Bu)<sub>2</sub>] **7** and IPr in a 1:2 stoichiometry showed that the metallation could not be stopped at the hemi-inverse-crown “Na<sub>2</sub>Mg(TMP)<sub>3</sub>(IPr<sup>-</sup>)” but proceeded to form **8** as observed by NMR, implying a cascade reaction operates.<sup>[19]</sup> Related motifs are known when sodium TMP-magnesiates

deprotonate heterocyclic substrates such as tetrahydrothiophene leading to C-Mg and dative heteroatom (e.g. S-Na bonds).<sup>[28]</sup> In theory the byproducts could be “NaMg(TMP)<sub>2</sub>(*n*Bu)” and NaTMP or alternatively “NaMg(TMP)<sub>3</sub>” and *n*BuNa or a mixture of both pairs. Conventional Group 1 bases target abnormal “C4” sites (recall Robinson’s *n*BuLi reaction) so NaTMP or *n*BuNa could effect a second deprotonation at “C4” (i.e., C2 and C29 in **7**) to generate dianionic IPr<sup>2-</sup>. Since *n*Bu is attached to Mg in the template, NaTMP seems the more logical candidate for this sodiation, a choice reinforced by a control reaction between NaTMP and IPr which on Me<sub>3</sub>SiCl quenching gave near-quantitative Me<sub>3</sub>Si incorporation at “C4”.<sup>[19]</sup> Head-to-tail dimerization through N10-Na6 and N7-Na3 bonds involving TMP would complete the structure of **8**. A notable metric feature of **8** is that the N5-Na1-C1 and N8-Na4-C28 bond angles involving normal “C2” atoms (mean, 174.4°) approach linearity, whereas N10-Na6-C2 and N7-Na3-C29 involving abnormal “C4” are distinctly bent (mean, 154.3°). Aside from bridging two TMP N atoms, Na2, Na3, Na5 and Na6 interact with paranormal magnesiated C7 and C34 (mean length 2.74 Å), while bridging TMP N and carbene “C2” atoms, Na1 and Na4 engage in longer contacts with Dipp *ipso* C4/C31 atoms (mean length, 2.92 Å). Mg atoms have distorted trigonal planar (N<sub>2</sub>C) coordinations. NMR characterisation of **8** in [D<sub>12</sub>]cyclohexane solution<sup>[19]</sup> revealed a singlet at 6.41 ppm in the <sup>1</sup>H spectrum for the remaining imidazole CH, slightly upfield to that of free IPr (6.87 ppm), and an extraordinary downfield resonance for sodiated C4 in the <sup>13</sup>C spectrum (170.4 ppm in **8** cf. 121.6 ppm in free IPr). A resonance for the carbenic C2 at 200.2 ppm in the <sup>13</sup>C spectrum confirms the dative C2→Na bond in **8**. Reflecting not only the loss of symmetry in the IPr<sup>2-</sup> moiety but also the metalation in the *para* position of one Dipp group, two distinct sets of resonances are present for the Dipp groups in the <sup>1</sup>H and <sup>13</sup>C spectra. Two different signals are seen at 2.79 and 2.91 ppm for the CH of the *i*Pr groups in the <sup>1</sup>H spectrum, and more informative, a unique downfield singlet at 7.67 ppm appears for the two equivalent *meta*-CH of the metalated Dipp aromatic ring (non-metalated aromatic CH of the Dipp group, 7.00-7.12 ppm). Also, the paranormal magnesiated Dipp C exhibits an extreme downfield resonance in the <sup>13</sup>C spectrum (167.3 ppm in **8** cf. typical Dipp resonances of 122.8-146.7 ppm).



**Scheme 4.** Proposed four key stages (a-d) in the formation of new inverse crown **8**, starting from IPr and [Na<sub>4</sub>Mg<sub>2</sub>(TMP)<sub>6</sub>(*n*Bu)<sub>2</sub>] **7**.

In summary, while this study set out to introduce Mg to the cartel of metals that can directly metalate a NHC, an aim duly realized in both predictable and unpredictable ways, it has taken on greater significance with recognition that pre-inverse-crown template bases can undergo remarkable reactions with mismatched substrates, sterically incompatible with the ring template.

## Experimental Section

Full experimental details and copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra are included in the Supporting Information. CCDC 1417920 (**2**), 1417921 (**5**) and 1417922 (**8**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Keywords:** alkali metals • inverse crowns • magnesium • metalation • N-heterocyclic carbenes

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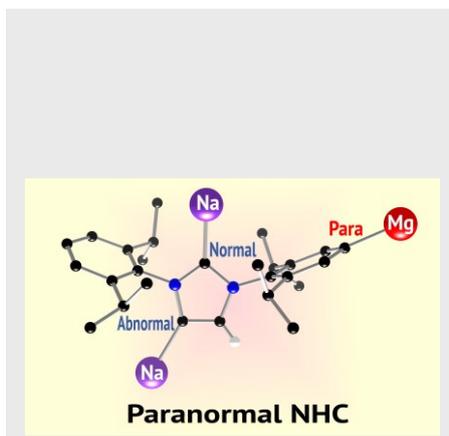
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**Paranormal NHC:** When a NHC encounters a pre-inverse-crown template base, an extraordinary multiple event occurs generating a dative C-Na bond at the normal C2 position, sodiation at the abnormal C4 position and magnesiation at the *para*-position of a Dipp substituent on N.



Antonio J. Martínez-Martínez, M. Ángeles Fuentes, Alberto Hernández-Gómez, Eva Hevia, Alan R. Kennedy, Robert E. Mulvey\* and Charles T. O'Hara

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**Alkali-Metal-Mediated Magnesiations of an NHC: Normal, Abnormal and “Paranormal” Reactivity in a Single Tritopic Molecule\*\***

Layout 2:

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