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Molecular Manipulations of a Utility Nitrogen-Heterocyclic Carbene by Sodium Magnesiate Complexes and Transmetallation Chemistry with Gold Complexes

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Dedicated to Professor Dietmar Stalke on the occasion of his 60th birthday

Abstract: Expanding the scope and applications of anionic Nheterocyclic carbenes (NHCs), a novel series of magnesium NHC complexes is reported using a mixed-sodium-magnesium approach. Sequential reactivity of classical imidazol-2-ylidene carbene IPr with NaR and MgR₂ (R= CH₂SiMe₃) affords [(THF)₃Na(µ-IPr⁻)MgR₂(THF)] (2) $[IPr^- = :C{[N(2,6-iPr_2C_6H_3)]_2CHC]}$ containing an anionic NHC ligand, whereas surprisingly sodium magnesiate [NaMgR₃] fails to deprotonate IPr affording instead the redistribution coordination adduct [IPr₂Na₂MgR₄] (1). Compound 2 undergoes selective C2methylation when treated with MeOTf furnishing novel abnormal NHC complex [{alPr^{Me}MgR₂}₂] (3). Dissolving 3 in THF led to the dissociation of this complex into MgR₂ and alPr^{Me} with the latter isomerizing to the olefinic NHC IPr=CH2. The ability of 2 and 3 to transfer their anionic and abnormal NHC ligands respectively to Au(I) metal fragments has been investigated allowing the isolation and structural characterization of [RAu(µ-IPr⁻)MgR(THF)₂] (4) and [alPr^{Me}AuR] (5) respectively. In both cases transfer of an alkyl R group is observed. However while 3 can also transfer its abnormal NHC ligand to give 5, in 4 the anionic NHC still remains coordinated to Mg via its C4 position, whereas the {AuR} fragment occupies the C2 position previously filled by a donor-solvated {Na(THF)₃}⁺ cation.

Introduction

Since starting as mere laboratory curiosities and phosphine alternatives, N-heterocyclic carbenes (NHCs), in particular imidazol-2-ylidenes, have developed into rising stars of the chemical world. Their applications as versatile ligands are now widespread, spanning from transition metal catalysis,^[1] small molecule activation,^[2] organocatalysis,^[3] to stabilisation of low-valent main group complexes,^[4] to name just a few. A signature feature of these strong σ-donor ligands is their ability to be fine-tuned both sterically and electronically, which can be accomplished by modifying the substituents on their N atoms or their olefinic backbones.^[5] While typically, the carbene centre is

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sandwiched between the two nitrogen atoms (C2 position) enabling π-donation by both adjacent N-heteroatoms into the empty p_{π} orbital of the carbene, the expansion of their coordination chemistry have created a different type of NHC complex, where the imidazole ring binds to the metal centre through its backbone. These less stabilised carbenes, where there is only one N-atom adjacent to their carbenic carbon, have been termed as abnormal (or mesoionic) NHCs (commonly written as aNHCs).[6,7] Another important class of carbenes that has recently emerged and continues to thrive over the past few years is that of anionic NHCs, resulting from the metallation of the unsaturated backbone of the imidazol-2-ylidene ring.^[8,9] A key landmark in this field is Robinson's lithiation of IPr (IPr=1,3bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene) by "BuLi which affords a unique polymeric structure where the lithium atoms are connected by anionic NHC bridges through their normal C2 and C4 positions.^[9] Contrasting with this reactivity, moving to the diagonal neighbour of "BuLi in the periodic table, when "Bu2Mg is used, the deprotonation process is completely inhibited, affording instead a normal coordination adduct.^[10] Furthermore, there are several literature examples of structurally defined NHC complexes containing Mg amides, Grignard reagents and other dialkylmagnesium compounds.^[10-13] Nevertheless, highlighting the power of bimetallic alliances in s-block metal chemistry, our collaborative work with Mulvey and O'Hara has recently shown that by pairing Mg with Na within the same molecule it is actually possible to promote the magnesiation of IPr.^[14] Interestingly, these studies using heteroleptic magnesiates which combine the highly basic amido group TMP (TMP = 2,2,6,6tetramethylpiperidide) with butyl ligands, have revealed that that the regioselectivity of these reactions is finely controlled by the structure of the bimetallic base employed, enabling IPr to be metallated at its backbone, but also at the para position of one of its substituent aromatic arms. On the other hand, using tris(amido) sodium magnesiate [NaMg(HMDS)₃] (HMDS 1,1,1,3,3,3-hexamethyldisilazide), Hill has reported formation of coordination adducts, where two carbenes coordinate to Na, forming charge separated species [{NaIPr₂}+{Mg(HMDS)₃}-].^[15] Intrigued by these contrasting reactivities, and aiming to expand the scope and applications of anionic NHCs in s-block metal chemistry, here we report a novel series of magnesium compounds containing neutral, anionic and abnormal NHC ligands using a mixed-sodium-magnesium approach. The ability of some of these novel magnesium/magnesiate systems to act as transfer reagents towards transition metal complexes has

also been assessed by studying their reactivity towards Au(I) complexes.

Results and Discussion

Bimetallic Approaches for IPr metallation: Magnesiate versus Sequential Single-metal Reactivities

We started by investigating the reactivity of **IPr** with sodium magnesiate NaMgR₃ (R= CH₂SiMe₃). This ate was first developed by our group^[16] and has already shown great promise as an efficient precatalyst in hydroamination reactions of isocyanates and carbodiimides.^[17,18] Performing this reaction at room temperature in a hexane/benzene non-Lewis basic solvent mixture, using equimolar amounts of **IPr** and NaMgR₃ led to the isolation of sodium tetra(alkyl) magnesiate [**IPr**₂Na₂MgR₄] (1) as colourless crystals in a 13% yield (note that the maximum possible yield for this reaction is 50%, Scheme 1a). This can be regarded as a higher order magnesiate having a 2:1, instead 1:1, Na:Mg stoichiometry.^[19]



Scheme 1. Synthesis of 1 and 2.

X-ray crystallographic studies established the molecular structure of 1 to be a discrete contacted ion pair (CIP) structure (Figure 1). Isolation of 1 reveals that while NaMgR₃ does not seem basic enough to promote the deprotonation of IPr, the carbene must induce a redistribution process to the higher order magnesiate complex with the 2:1 Na/Mg ratio. Α tetracoordinated distorted tetrathedral Mg atom occupies the centre of the trinuclear bimetallic unit with four R-groups forming bridges with outer IPr-capped sodium atoms in an almost linear arrangement along C1...Na1...Mg1...Na2...C44 plane, evidenced by C1…Na1…Mg1 = 175.09(15)°, Na1…Mg1…Na2 = 176.32(9)° and Mg1···Na2···C44 = 171.17(16)° angles. The four Mg-C bond distances are almost identical, with an average value of 2.259 Å, being in excellent agreement with those reported for the related magnesiate complex [(SIMes₂Li₂MgR₄] resulting from the reaction of the saturated NHC SIMes (SIMes = 1,3-bis-(2,4,6trimethylphenyl)imidazolidin-2-ylidene) with a 2:1 mixture of LiR and MgR₂.^[20] Each Na exhibits a planar three-coordinate geometry made up by coordination to two alkyl groups and one IPr molecule.



Figure 1. Molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms except those on the imidazole ring have been omitted for clarity. The unit cell of **1** contains two crystallographically independent molecules with identical connectivity.

The Na-C_{carbene} distances (average 2.430 Å) are within the same range as those previously witnessed by Hill for $[{Na(IPr)_2}^+{Mg(HMDS)_3}^-]$ [2.439(6) and 2.452(2) Å]^[15] and noticeably shorter than the Na-C_{alkyl} bonds in **1** [range: 2.506(5)-2.568(6) Å]. The elongation of the latter can be rationalized considering the ancillary nature of these Na-C bonds when compared with the Mg-C bonds that anchor the magnesiate framework, to which the {Na(IPr)}⁺ fragments are affixed. [21]</sup>

 ^1H and ^{13}C NMR spectroscopic studies of 1 in in C_6D_6 solution are consistent with the retention of its structure in the solid state, displaying only one set of resonances for the Dipp and R groups. The persistence of **IPr** coordination to Na is best indicated by an informative resonance at 202.9 ppm in the ^{13}C NMR spectrum at a similar chemical shift to those previously found in other Na-NHC complexes. $^{[14,15,22,23]}$

While redistribution processes on magnesiate chemistry have been previously noted,^[24] this is as far as we can ascertain the first one induced by an N-heterocyclic carbene. Furthermore, previous attempts trying to prepare and isolate solvent free [Na₂MgR₄] had proved unsuccessful leading instead to the isolation of the relevant triorganomagnesiate [NaMgR₃] and NaR.^[16] Here, by introducing **IPr**, an alternative redistribution process on NaMgR₃ is activated, where a putative [**IPr**NaMgR₃] complex evolves into **1** and MgR₂. The lack of metallation of **IPr**, and its preference to act as a neutral donor instead, contrast with our previous studies using heteroleptic sodium magnesiates^[14] which combine TMP and Bu groups and seem to be more aligned with Hill's formation of coordination adducts when using [NaMg(HMDS)₃].^[15]

This prompted us to try a stepwise approach, by reacting sequentially the single components of NaMgR₃. This strategy relies on the ability of NaR to metallate the NHC to form a sodium anionic NHC which in turn can undergo transmetallation to a lower polarity metal fragment^[25] and it has been recently successfully applied by us for the synthesis of novel sodium ferrate^[21] and sodium gallate^[23] complexes containing anionic NHCs. Thus, by treating **IPr** with a molar equivalent of NaR followed by the addition of MgR₂ and THF, heteroleptic [(THF)₃Na(µ-**IPr**⁻)MgR₂(THF)]] (2) [**IPr**⁻ = :C{[N(2,6-

 $\mathit{i} Pr_2C_6H_3)]_2CHC]$ was obtained in a 58% isolated yield (Scheme 1b).]

X-ray crystallisation analysis established a CIP structure of 2, however, this time the carbene has been incorporated as an anionic ligand simultaneously employing its C2 and C4 coordination sites. Witnessing the indirect magnesiation process, the Mg-centre is coordinated to the abnormal C4 position of IPr, preserving its two alkyl groups and completing its coordination sphere via a single molecule of THF, whilst the tris(THF)solvated Na-ion is bound to the normal C2 position (Figure 2). The Na-C_{carbene} (*i.e.* C1 in Fig 2) bond distance of 2.468(3) Å is comparable, but on the shorter end to previously reported Na-C bond distances in related bimetallic complexes containing a {Na(THF)₃}⁺ fragment bonded to the C2-site of an anionic IPr ligand, such as Na/Zn (2.501(3)Å),[26] Na/Fe (2.510(4)Å)[22] and Na/Ga (2.530(3)Å).^[23] The Mg-C4 (*i.e.* C2 in Fig 2) distance of 2.210(3) Å is only slightly elongated in comparison to the Mg-Calkyl bonds (average 2.182 Å) and within the same range to those found in the previous two examples of magnesiation of IPr using mixed TMP/Bu sodium magnesiates.^[14]



Figure 2. Molecular structure of **2** with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms except that on the imidazole ring and minor disorder in one molecule of THF have been omitted for clarity.

NMR studies of **2** in in d₈-THF solutions show that the CH(CH₃)₂ fragments of the Dipp groups resonate as two distinct sets of signals in the ¹H and ¹³C NMR spectra as a result of the symmetry loss in **IPr**. The symmetry loss, as a result of the metallation in the backbone of the imidazole ring, is also mirrored by a large downfield resonance at δ = 163.9 ppm in the ¹³C NMR spectrum for the Mg-C4 group (versus δ = 112.3 ppm in the free **IPr**). In addition, the resonance assigned to the carbenic C2 is at 200.2 ppm supporting the C2 coordination of the anionic NHC to Na.^[14,15,22,23]

Interestingly **2** is stable in solution without undergoing any redistribution process which contrast with previous examples of magnesiation using mixed metal systems where putative intermediate (THF)₃Na[(μ -IPr⁻)Mg(TMP)₂] is postulated to be formed but rapidly evolves to [(THF)₃Na(μ -IPr⁻)Mg(THF)(IPr⁻)₂] which has be isolated and structurally defined.^[14]

Accessing an abnormal NHC-Mg complex via electrophilic interception

Within main group chemistry, the number of complexes containing abnormal (or mesoionic) carbenes remains very limited, and for Mg the first examples containing this type of ligands were only reported in 2016 by Ghadwall.^[27] This method relies on the deprotonation of a C2-functionalised imidazolium salt using a Grignard reagent which affords [alPr^{Ph}Mgl₂·OEt₂] (alPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4ylidene) which can then further undergo salt-metathesis and give the [alPr^{Ph}·Mg(HMDS)₂] complex. Our previous attempt to access alPr·MgR₂ by employing thermally induced isomerization of its normal analogue (i.e. IPr·MgR₂),^[28] a methodology that has been successful for complexes of Ga,^[28] Fe,^[29] B^[2a] or Al^[30] and seems to be driven by the steric relief around the metal center, did not work even under forcing reaction conditions (72h at 100°C). Having successfully isolated anionic NHC complex 2 we next pondered, if it could undergo selective electrophilic interception to render the relevant neutral aNHC-Mg complex, as this approach has already shown promising potential for other main group elements including B,[31] Ga[22,27, 32] and Zn.[33] To explore this possibility sodium magnesiate 2 was treated with a molar equivalent of Me₃SiCl in toluene at -30 °C. Exchange of toluene in vacuo to a THF/hexane mixture led to isolation of free carbene IPr^{™s} in 61% yield (Scheme 2a), identified by comparison of its ¹H and ¹³C NMR data to literature data.^[34]



Scheme 2. Electrophilic interception of 2 with a) Me₃SiCl affording free IPr^{TMS} and b) MeOTf affording aNHC-Mg complex 3.

Surprisingly, in this reaction, despite the formation of this normal NHC ligands which could potentially coordinate to Mg to form an adduct (as observed for IPrMgR₂), here MgR₂ remains in solution, presumably forming a soluble donor-acceptor complex with THF. Formation of IPr^{TMS} contrasts sharply with the reactivity described for the related mixed K/Ga complex [(THF)₃K(µ-IPr-)GaR₃],^[23] which comprises the same anionic NHC, bridging between {K(THF)₃}⁺ and GaR₃ through its C2 and C4 positions respectively. Interestingly in this complex, silvlation is observed at the C2 site, furnishing a neutral abnormal NHC gallium complex, where the Ga-C4 bond is preserved. Since the steric demands for both systems are similar, the different outcome of these reactions can be attributed to the significant polarization of the C4-Mg bond in 2 rendering it susceptible to electrophilic interception. Consistent with this interpretation, preferred C4-silylation has also been observed by Robinson for the reaction of lithiated IPr to afford IPr^{TMS}.^[9] Complementing these experimental studies, natural bond orbital (NBO) analysis of 2 indicates that most of the positive charge is carried primarily by the metals, showing significant dicationic character for the Mg atom (calculated natural charge of Mg, +1.64). Furthermore, as shown in Figure 3, the three highest occupied molecular orbitals

HOMO, HOMO-1 and HOMO-2 calculated for **2** correspond to the polarized Mg-C bonding orbitals of the alkyl groups and the C4 of the anionic **IPr** ligand.



Figure 3. Calculated molecular orbitals HOMO, HOMO-1 and HOMO-2 of sodium magnesiate 2.

Contrasting with this C4 selectivity, when 2 is treated with the strong methylating agent MeOTf, an electrophile that has previously being successfully used for several mixed-metal anionic NHC complexes, [22,28,33] novel neutral abnormal complex $[{alPr^{Me}MgR_2}_2]$ (3) (alPr^{Me} = 1,3-bis(2,6-diisopropylphenyl)-2methyl-imidazol-4-ylidene) is formed in a 30 % isolated yield (Scheme 2b). It should be noted that this reaction needs to be carried out at -78 °C in toluene in order to control selectivity and stability of 3 (vide infra) and that the concomitant precipitation of a solid (presumably NaOTf) is also observed. Resulting from the selective C2-methylation of 2, complex 3 exhibits a dimeric structure in the solid state (Figure 4), with a central {Mg₂R₄} core, where the Mg centres are connected by two alkyl bridges and complete their coordination spheres by bonding terminally to the emergent abnormal NHC ligand. The bond length of the newly formed C2-C_{Me} (i.e. C1-C28 in Figure 4) is consistent with the single bond while that of Mg-C4 (i.e. C2 in Figure 4) bond length of 2.2363(13) Å is only slightly elongated compared to that found in the anionic variant 2 (2.211(3) Å).



Figure 4. Molecular structure of 3 with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms except those on imidazole scaffold and newly installed methyl group have been omitted for clarity. Symmetry operator: -x+2, -y+2, -z.

The dimeric structure of **3** contrasts with that reported by Robertson and Mulvey for the normal **IPr** adduct of MgR_2 ,^[11] which is restricted to a monomeric architecture with a three-

coordinate Mg center, exhibiting a Mg- $C_{carbene}$ bond distance of 2.267(3) Å. This different aggregation can be attributed to reduced steric demands of the *a*NHC ligand.

Reflecting the formation of a neutral aNHC complex, the ¹³C NMR spectrum of 3 in C₆D₆ shows a resonance at 143.5 ppm for the C4 attached to Mg (vs 163.9 ppm in anionic NHC complex 2) whereas the C-atom that has undergone methylation (originally C2 carbenic position in 2 resonates significantly upfield at 165.1 ppm in comparison to that observed for 2 (at 200.2 ppm).[35] During the spectroscopic characterization of 3 it became apparent that this complex was not stable in deuterated THF, with rapid conversion of the alPr^{Me} ligand to a new species, which displayed two distinct new resonances in the ¹H NMR spectrum at 2.40 and 5.85 ppm and a symmetrical imidazole ring. Comparison of ¹H and ¹³C NMR data was consistent with the formation of olefinic NHC IPr=CH₂ previously reported by Rivard^[36] and Robinson.^[37] In contrast, this decomposition pathway was extremely slow when 3 was dissolved in noncoordinating solvents such as hexane, toluene and benzene.[38] Formation of 4 can be rationalized assuming that in THF solutions, 3 undergoes de-cocomplexation with alPr^{Me} being replaced by the Lewis donor solvent [(i) in Scheme 3].



Scheme 3. Decomposition pathway of 3 in THF: i) THF-induced ligand dissociation; ii) isomerization of aNHC to NHO; iii) deuterium labelling experiment.

The preferred coordination of THF over an NHC ligand to the MgR₂ fragment has already been observed for **IPr^{TMS}** (*vide supra*). Related to the strength of the Mg-C_{NHC} bonds in Mg complexes, Mulvey and Robertson have also noted that in certain cases, such as for **IPr**·Mg^{*T*}Bu(TMP), the steric clash induces the dissociation of the NHC adduct in its constituting reagents even in non-coordinating C₆D₆ solutions.^[10] As a non-coordinated entity, **alPr^{Me}** can be expected to be highly unstable and "tautomerises" to olefinic carbene **IPr=CH**₂ [(*ii*) in Scheme 3]. Rivard has labelled complexes of this type N-heterocyclic olefins (NHOs).^[39] DFT calculations showed that this isomerization from *a*NHC to NHO is actually energetically favoured by 18.8 kcalmol⁻

¹. Supporting this interpretation, deuterium labeling of the Me group attached at the C2 position of 3 (synthesized by reacting 2 with $[D_3]$ -MeOTf formed $IPr^D=CD_2$ where deuterium have been incorporated at the C4 position of the imidazole ring and the methylene fragment [see (iii) in Scheme 3, Figure S7]. Building on our previous mechanistic studies on the isomerization of IPr to alPr in Ga complexes,^[28] and considering that aNHCs have been found to be stronger bases than their normal counterparts^[7] we can envisage that the formation of IPr=CH₂ occurs by the generation of free \textit{alPr}^{Me} that can intermolecularly deprotonate the Me group which binds to the C2 atom of another imidazole ring. Notably, highlighting again the similarities between 2 and Robinson's lithiated IPr complex,^[9] when the latter is reacted with methyl iodide, it affords IPr=CH2 in almost quantitative yields.[37] However, on this occasion the formation of an intermediate abnormal NHC complex (like 3) could not be detected. It should also be noted that contrasting with the lability of the alPr^{Me} component in complex 3 in THF solution, complex 2 where {MgR₂} is attached to the C4 position of an anionic NHC is perfectly stable in this donor solvent and does not undergo anv side reactions.

Assessing Transmetallation behaviours towards Au complexes

Our previous explorations of the reactivity of sodium zincates containing anionic NHCs have shown they can be excellent transfer agents to transition metal complexes, in particular gold systems, enabling the isolation of a novel complex where the anionic NHC connects two different Au centres (see complex I in Scheme 4) as the result of a dual transmetallation process.^[26]



Scheme 4. Comparison of reactivity of anionic NHC-containing sodium zincate and sodium magnesiate reagents towards gold(I) compounds.

This complex is a rare example of an anionic NHC complex bridging between two different transition metal centres.^[40] Interestingly, previous work by Meyer has identified the formation of anionic NHC complexes between two Pd centres as a self-deactivation process in (allyl)PdNHC complexes.^[40c] Since initial reactivity studies are consistent with a large polarization of the Mg-C4 bond in **2**, we next pondered if it could also undergo transmetallation reactions towards Au(I) complexes. Thus, sodium magnesiate **2** was reacted with an equimolar amount of [Au(CI)(SMe₂)] in toluene at -70 °C which afforded the novel

mixed Mg/Au bimetallic complex $[RAu(\mu-IPr^-)MgR(THF)_2]$ (4) in 40 % yield (Scheme 4).

crystallographic studies of 4 confirmed X-rav that transmetallation had indeed taken place. However, instead of transferring the anionic IPr ligand to Au, 2 selectively transfers one of its anionic alkyl R groups, with the subsequent precipitation of NaCl (Figure 5). This creates a coordination vacancy in the C2 position of the anionic carbene (originally bound to Na) which can in turn replace the labile SMe₂ ligand on Au to furnish 4 (Scheme 4). This reactivity departs from that previously discussed for Na/Zn systems where the alkyl groups remain coordinated to Zn and are not involved in the transmetallation process.^[26] It also differs from Tamm's studies on the reactivity of [(PPh₃)AuCl] with an anionic lithium carbene containing a borate moiety on its imidazole backbone.[41] In this case a neutral mononuclear gold species is obtained, resulting from the single exchange of the C2 position of Li (which is eliminated as LiCl) and the {Au(PPh₃)}⁺ cation, keeping the borate part of the NHC intact.



Figure 5. Molecular structure of 4 with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

A close inspection on the geometrical parameters of 4 revealed that the Au-C_{NHC} bond distance [i.e Au-C1, 2.022(10) Å] is notably elongated when compared to those in other Au(I) complexes containing neutral NHC ligands such as IPrAuCI [1.942(3)Å]^[42] or that one found for digold complex I^[26] (Scheme 4) which also contains an anionic IPr ligand coordinated to one Au via its C2 position [1.975(5)Å]. However, it compares well with those reported for Au(I) complexes which contain an anionic NHC with a weakly coordinating borate at the C4 position such as in [(PPh₃)Au(μ -IPr⁻)B(C₆F₅)₃] [Au-C_{NHC} bond distances of 2.037(2) Å].^[41] For this family of compounds, the negative charge on the anionic NHC ligand is presumed to be located on the C4 (abnormal) position bonded to the borane moiety. In addition, comparing the Mg-C bonds in 4 with those observed in 2, both Mg-C_{alkyl} and Mg-C_{NHC} are notably shorter [2.127(11) and 2.143(10) Å in 4 vs 2.211(3) and 2.182 Å in 2 respectively], which is consistent with the magnesiate constitution of 2 as opposed to 4 which can best be envisaged as a coordination adduct between {(THF)2RMgIPr-} and AuR. Regarding its spectroscopic characterization using ¹H and ¹³C multinuclear NMR spectroscopy, two informative resonances in the ¹³C NMR spectrum of 4 in d₈-THF were observed at 155.6 and 199.4 ppm which can be assigned to the C4-Mg and C2-Au fragments respectively. Reflecting the changes in the Mg coordination

sphere, the C4-Mg resonance in **4** is significantly shifted upfield compared to the same resonance in the related sodium magnesiate **2** observed at 163.9 ppm; whereas the one for the carbenic C appears at a similar chemical shift to those previously described in the literature for normal NHC-Au complexes in deuterated THF solution.^[43] Building on the studies on electrophilic interception of **2** to render aNHC Mg complex **3**, we next probed the reactivity of **4** towards MeOTf. However, despite several attempts the reaction proved to be unselective yielding in solution a complex mixture of species that could not be identified by ¹H NMR spectroscopy. As an alternative method, we next pondered whether **3** could transfer its *a*NHC ligand to Au. Thus, [Au(CI)(PPh₃)] was added to an *in situ* prepared solution of **3** in toluene, affording gold complex [*a*IPr^{Me}AuR] (**5**) in 56% yield (Scheme 5).



Scheme 5. Stepwise synthesis of 5 from sodium magnesiate 2.

Interestingly, the neutral aNHC complex **3** induces a double transmetallation reaction, with carbene **aIPr**^{Me} replacing PPh₃ as a neutral donor but also with the substitution of Cl by a monosilyl group. X-ray crystallographic studies established the molecular structure of **5** (Figure 6), with Au in an almost linear geometry (C_{alkyl}-Au-C_{NHC} bond angle, 178.74(16)°]. The Au-C_{carbene} bond length of 2.036(3) Å falls within the range observed previously for other aNHC-Au complexes^[7,43] and it is slightly shorter than the Au-C_{alkyl} bond length [2.054(3) Å].



Figure 6. Molecular structure of **5** with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms except those on newly installed methyl group have been omitted for clarity.

In addition, the ¹³C NMR spectrum of **5** displayed a diagnostic signal at 141.7 ppm for the carbenic position which is within the range of chemical shifts previously reported for Au *a*NHC complexes.^[44]

Isolation of **5** has disclosed a new method to access *a*NHC Au complexes which employs an anionic NHC as the source of the carbene ligand. Previous examples described in the literature involved the use of 2,4-functionalized imidazolium salts, which

can be subsequently deprotonated by a Group 1 metal base or Ag₂O in the presence of a Au precursor.^[7,45,46] In addition, Hashmi has reported a versatile synthesis of a range of abnormal NHC-Gold(I) complexes prepared by [3+2] cycloaddition of azomethine ylides to isonitrile gold(I) complexes which affords air- and light-stable crystalline solids.^[47]

Conclusions

Exploring bimetallic approaches for metallation of IPr, two novel NHC-stabilized sodium magnesiates have been structurally characterized: higher order tetraorganomagnesiate $[IPr_2Na_2MgR_4]$ (1) (R = CH₂SiMe₃) arising from an NHC-induced redistribution process; and [(THF)₃Na(µ-IPr-)MgR₂(THF)] (2), which contains an anionic NHC. Contrasting with our previous work on TMP-based sodium magnesiates, here the lower order variant NaMgR₃ is not powerful enough to deprotonate the imidazole backbone of IPr. However, highlighting the potential of sequential reactivity in mixed-metal chemistry, by treating IPr with NaR followed by addition of MgR₂ complex 2 is obtained, where a {MgR₂(THF)} fragment coordinates to the C4 position of the anionic NHC, while the C2 site is occupied by a {Na(THF)₃}+ cation.

Studies on the reactivity of 2 with electrophiles showed that while Me₃SiCl reacts preferentially with the C4 position of the anionic carbene to give normal IPr^{TMS} which contains a SiMe₃ substituent at its imidazole backbone, MeOTf induces selective C2-methylation of anionic IPr in 2 to form novel abnormal Mg [{**alPr^{Me}MgR**₂}₂] aNHC complex (3), which was crystallographically characterised. Interestingly these studies also revealed the preference of MgR₂ to coordinate to the hard Lewis donor solvent THF over softer, neutral normal and abnormal NHCs. In the case of 3, this preference translates in the dissociation of the carbene adduct, releasing IPr^{Me} which converts into the olefinic NHO compound IPr=CH2. Advancing the understanding on the formation of olefinic carbenes, this work demonstrates the involvement of an aNHC metal complex as a key intermediate.

In addition, by assessing the ability of 2 and 3 to transfer their anionic and abnormal NHC ligands respectively to gold(I) complexes we have isolated and structurally characterised complexes 4 and 5 which in both cases contain an alkyl CH₂SiMe₃ bound to Au. Showing a remarkably distinct reactivity, 2 only transfers one of its alkyl groups from Mg to [Au(SMe₂)Cl], with the retention of the Mg-C4 bond to anionic IPr. This ligand transfer occurs with the concomitant precipitation of NaCl, which in creating a coordination vacancy at the normal C2 position of the anionic NHC, allows its filling by the newly generated {Au(CH₂SiMe₃)} fragment. Contrastingly **3** transfers both alkyl and aNHC ligands to [Au(PPh₃)Cl] furnishing 6 and unveiling a new synthetic approach to access abnormal Au NHC complexes. Collectively this work not only advances the synthesis of anionic and abnormal NHC Mg complexes, but also provides novel reactivity insights on how these compounds can be exploited in transmetallation reactions to access unique NHC complexes of transition metals, as well as revealing key aspects of their

stability towards dissociation in donor solvents and the role of ${\bf 3}$ in forming NHOs.

Experimental Section

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. n-Hexane, THF and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. Na(CH₂SiMe₃),^[48] [AuCl(PPh₃)],^[49] IPr,^[50] and $[NaMg(CH_2SiMe_3)_3]^{[16]}$ were synthesized as described in the literature. [AuCl(SMe₂)] and TfOMe were purchased from Sigma Aldrich Chemicals, and used as received. Mg(CH₂SiMe₃)₂ was prepared from the Grignard reagent (Me₃SiCH₂)MgCl by manipulation of the Schlenk equilibrium via the dioxane precipitation method. The resultant off-white solid was purified via sublimation at 175°C (10-2 Torr) to furnish pure Mg(CH₂SiMe₃)₂. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H, 155.50 MHz for ⁷Li, and 100.62 MHz for $^{13}\text{C}\{^1\text{H}\}$. Elemental analyses were obtained using a Perkin-Elmer 2400 elemental analyzer. Crystallographic data were measured at 123(2) K on Oxford Diffraction diffractometers^[51] with Mo $K\alpha(\lambda = 0.71073 \text{ Å})$ or Cu $K\alpha(\lambda = 1.5418 \text{ Å})$ radiation. Structures were refined to convergence on F² and against all independent reflections by the full-matrix least squares method using the SHELXL-97 program.^[52] Copies of NMR spectra of compounds 1-5 are included in the Supporting Information. CCDC 1838641-1838645 contain the supplementary crystallographic data of 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.

Synthesis of [IPr2Na2MgR4] (1) To a suspension of NaCH2SiMe3 (0.055 g, 0.5 mmol) in hexane (10 mL) Mg(CH₂SiMe₃)₂ (0.1 g, 0.5 mmol) was added and the suspension stirred for 1 hour. Benzene (15 mL) was then added giving an almost clear solution followed by IPr (0.20 g, 0.5 mmol) giving a straw solution. All the volatiles were removed under vacuo and hexane (5 mL) was added which gave a clear solution on gentle heating. Storage in the freezer (-28 °C) overnight produced a crop of crystals which was isolated (0.04 g, 13%). ¹H NMR (400.13 MHz, 298 K, C₆D₆) δ (ppm) -1.91 (s, 8H, CH₂SiMe₃), 0.20 (s, 36H, CH₂SiMe₃), 1.02 (24H, d, J = 6.8 Hz, CH(CH₃)₂), 1.26 (24H, d, J = 6.8 Hz, CH(CH₃)₂), 2.58 (8H, m, CH(CH₃)₂), 6.41 (4H, s, NCHCHN), 7.10 (8H, d, J = 7.8 Hz, Ar-H), 7.27 (4H, t, J = 7.8 Hz, Ar-H). ¹³C {¹H} NMR (100.62 MHz, 298 K, C₆D₆) δ (ppm) -3.0 (CH₂SiMe₃), 4.8 (CH₂SiMe₃), 24.3 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 122.7 (NCHCHN), 124.4 (ArCH), 130.5 (ArCH), 136.3 (ArC), 145.5 (ArC), 202.9 (NCN). Despite several attempts due to the extremely air sensitive nature of this compound, no satisfactory elemental analysis could be obtained.

Synthesis of [(THF)₃Na(μ-IPr)MgR₂(THF)] (2) To a suspension of **IPr** (1.40 g, 3.6 mmol) in hexane (40 mL) was added NaR (0.44 g, 4 mmol) and stirred for 1 hour, after which MgR₂ (0.79 g, 4 mmol) was added and the suspension stirred overnight. THF was added dropwise (11 mL) and the clear solution transferred to the freezer which overnight deposited a crop of colourless crystals (1.86 g, 58%). ¹H NMR (400.03 MHz, 298 K, d₈-THF) δ (ppm) -2.11 (s, 4H, CH₂SiMe₃), 0.23 (s, 18H, CH₂SiMe₃), 1.10 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.13 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.17 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.24 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.78 (m, 12H, THF), 2.96 (m, 2H, CH(CH₃)₂), 3.09 (m, 2H, CH(CH₃)₂), 3.62 (m, 12H, THF), 6.56 (s, 1H, NC*H*CN), 7.10-7.23 (overlapping m, 6H, ArC*H*), ¹³C (¹H) NMR (100.62 MHz, 298 K, d₈-THF) δ (ppm) -5.9 (CH₂SiMe₃), 5.2 (CH₂SiMe₃), 24.1 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 25.3 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 26.4 (THF), 28.6 (CH(CH₃)₂), 68.2 (THF), 123.5 (ArCH), 123.8 (ArCH), 127.3 (ArCH), 128.4 (ArCH), 131.2 (NCHCN), 141.1 (ArC),

145.7 (ArC), 146.9 (ArC), 147.3 (ArC), 163.9 (NCHCN), 200.2 (NCN). Anal Calcd for $C_{51}H_{89}MgN_2NaO_4Si_2$: C, 68.23; H, 9.99., N 3.12. Found: C, 67.90, H, 10.03, N 3.56.

Synthesis of [{alPr^{Me}MgR₂}₂] (3) MeOTf (0.07 g, 0.45 mmol) dissolved in 5 mL of toluene was added to a toluene (30 mL) solution of compound 2 at -70°C. The pale yellow solution was stirred for 30 min allowing reaching room temperature, and the resulting orange suspension was filtered. Toluene was removed under vacuum affording red oil, to which hexane (2 mL) was added precipitating a white solid. Finally, compound 3 (0.08 g, 30%) was isolated by filtration and washing with hexane (3 x 2 mL) at 0 °C. ¹H NMR (400 MHz, C₆D₆): δ-1.24 (s, 4H, CH₂SiMe₃), 0.36 (s, 18H, CH₂SiMe₃), 0.89 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 0.92 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.05 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.34 (d, J = 6.8 Hz, 6H, CH(CH_3)_2) 1.37 (s, 3H, NCCH_3), 2.32 (m, 2H, CH(CH_3)_2), 2.53 (m, 2H, CH(CH₃)₂), 6.93 (s, 1H, NCHCN), 6.96 (d, J = 8 Hz, 2H, Ar-H), 7.07 (d, J = 8 Hz, 2H, Ar-H), 7.13 (t, J = 8 Hz, 1H, Ar-H), 7.21 (t, J = 8 Hz, 1H, Ar-H). ¹³C{¹H} NMR (125 MHz, C₆D₆): δ-4.6 (CH₂SiMe₃), 5.0 (CH₂SiMe₃), 10.3 (NCCH₃), 23.4 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 124.7 (ArCH), 130.6 (ArCH), 131.1 (ArCH), 131.2 (NCHCN), 135.1 (ArC), 143.5 (NCHCN), 144.8 (ArC), 145.6 (ArC), 165.1 (NCN). Anal Calcd for C36H60MgN2Si2: C, 71.90; H, 10.06., N 4.66. Found: C, 70.80, H, 9.97, N 5.13.

Following a similar procedure, to a toluene (30 mL) solution of compound **2** at -70°C [D₃]MeOTf (0.07 g, 0.45 mmol) dissolved in 5 mL of toluene was added. The resulting solution was stirred while warming to room temperature. After 2 hours an aliquot of the toluene solution was analyzed by ²H-NMR spectroscopy (Figure S7).

Compound [{RAu(µ-IPr-)MgR(THF)2] (4) To a toluene (10 mL) solution of compound 2 (0.45 g, 0.5 mmol) at -70 °C was added (Me₂S)AuCl (0.15 g, 0. 5 mmol) followed by addition of 10 mL of THF. After 30 min stirring allowing reaching room temperature the solvent of the resulting light red solution was removed under vacuum and the residue was extracted with toluene (2 x 10 mL). All the volatiles were removed in vacuo affording an oily residue which was dissolved in a mixture of THF (2 mL), hexane (5 mL) and transferred to the freezer (-30 °C). A crop of colourless crystals was deposited overnight (0.18 g, 40%).¹H NMR (400 MHz, [D₈]THF): δ -1.85 (s, 2H, MgCH₂SiMe₃), -0.68 (s, 2H, AuCH₂SiMe₃), -0.47 (s, 9H, MgCH₂SiMe₃), -0.14 (s, 9H, AuCH₂SiMe₃), 1.16 (d, J = 6.8 Hz, 6H, $CH(CH_{3})_{2}$), 1.20 (d, J = 6.8 Hz, 6H, $CH(CH_{3})_{2}$), 1.32 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.37 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.77 (m, 4H, THF), 2.78 (m, 2H, CH(CH3)2), 2.87 (m, 2H, CH(CH3)2), 3.62 (m, 4H, THF), 6.70 (s, 1H, NCHCN), 7.21 (dd, ³J = 8 Hz, ⁴J = 2.4 Hz, 4H, Ar-H), 7.32 (m, 2H, Ar-H). ¹³C{¹H} NMR (125 MHz, [D₈]THF): δ -.8.8 (MgCH₂SiMe₃), 3.7 (MgCH₂SiMe₃), 4.4 (AuCH₂SiMe₃), 4.9 (AuCH₂SiMe₃), 24.3 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 24.8 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 26.3 (THF), 29.0 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 68.2 (THF), 123.9 (ArCH), 124.0 (ArCH), 128.8 (ArCH), 129.3 (ArCH), 131.3 (NCHCN), 137.6 (ArC), 142.4 (ArC), 155.6 (NCHCN), 199.5 (NCN). Anal Calcd for 146.7 (ArC), C₃₉H₆₅AuMgN₂OSi₂: C, 54.76; H, 7.66; N, 3.27. Found: C, 54.07, H, 7.91; N. 3.16.

Synthesis of [alPr^{Me}AuR] (5) MeOTf (0.07 g, 0.45 mmol) dissolved in 5 mL of toluene was added to a toluene (10 mL) solution of compound 2 (0.45 g, 0.5 mmol) at -70°C. The pale yellow solution was stirred for 10 min at that temperature, then [AuCl(PPh₃)] (0.24 g, 0.5 mmol) and 10 mL of THF were added. After 1h stirring allowing the solution to warm to room temperature the solvent was removed under vacuum and the residue was extracted with toluene (10 mL). The solution was concentrated to 1 mL which was combined with 5 mL of hexane and transferred to the freezer (-70 °C). A crop of colourless crystals was deposited overnight (0.18 g, 56%).¹H NMR (400 MHz, C₆D₆): δ 0.33 (s, 9H, CH₂SiMe₃), 0.54 (s, 2H, CH₂SiMe₃), 0.92 (d, J = 6.8 Hz, 6H,

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CH(CH₃)₂), 0.93 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.04 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.38 (s, 3H, NCCH₃), 1.60 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 2.35 (m, 2H, CH(CH₃)₂), 2.68 (m, 2H, CH(CH₃)₂), 6.54 (s, 1H, NCHCN), 6.92 (d, J = 8 Hz, 2H, Ar-H), 7.15 (t, J = 8 Hz, 1H, Ar-H), 7.18 (m, 2H, Ar-H), 7.32 (t, J = 8 Hz, 1H, Ar-H). $^{13}C{^{1H}}$ NMR (125 MHz, C₆D₆): δ 4.4 (CH₂SiMe₃), 6.5 (CH₂SiMe₃), 10.5 (NCCH₃), 23.3 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 29.0 (CH(CH₃)₂), 124.5 (ArCH), 124.6 (ArCH), 126.6 (NCHCN), 130.5 (ArCH), 131.0 (ArCH), 131.3 (ArC), 135.3 (ArC), 141.7 (NCHCN), 145.1 (ArC), 145.6 (ArC), 180.7 (NCN). Anal Calcd for C₃₂H₄₉AuN₂Si: C, 55.96 H, 7.19; N, 4.08. Found: C, 55.99, H, 7.48; N, 3.82

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Normal or abnormal, it's still gold! Novel NHC stabilised Au(I) alkyl complexes have been accessed via a transmetallation approach based on a mixed Na/Mg platform containing an anionic NHC as a precursor

A. Hernán-Gómez, M. Uzelac, S. E. Baillie, D. R. Armstrong, A. R. Kennedy, M. Á. Fuentes, and E. Hevia*

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Molecular Manipulations of a Utility Nitrogen-Heterocyclic Carbene by Sodium Magnesiate Complexes and Transmetallation Chemistry with Gold Complexes