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Multi-Step, Self-Assembly of Heteroleptic Magnesium and Sodium-Magnesium Benzamidinate Complexes

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Abstract

Reaction of the magnesium bis(alkyl) Mg(CH₂SiMe₃)₂ and the sodium amide NaHMDS with benzonitrile yields the homometallic heteroleptic complex [PhC(NSiMe₃)₂Mg{μ-NC(CH₂SiMe₃)Ph}]₂ (1). It appears that at least six independent reactions must have occurred in this one-pot reaction to arrive at this mixed benzamidinate ketimido product. Two benzonitrile solvated derivatives of Mg(CH₂SiMe₃)₂ (5a and 5b) have been synthesised with 5a crystallographically characterized as a centrosymmetric (MgC)₂ cyclo dimer. When, the components of 5a are allowed to react for longer, partial addition of the Mg-alkyl unit across the C≡N triple bond occurs to yield a trimeric species (Me₃SiCH₂)₂Mg₃[μ-N≡C(CH₂SiMe₃)Ph]₄·2N≡CPh (6) with bridging ketimido groups and terminal alkyl groups. Finally, using the same starting materials as that which produced 1, but altering their order of addition, a magnesium bis(alkyl) unit is inserted into the Na-N bonds of a benzamidinate species to yield a new sodium magnesiate complex PhC(NSiMe₃)₂Mg(μ-CH₂SiMe₃)₂Na·2TMEDA (7). The formation of 7 represents a novel (insertion) route to mixed-metal species of this kind and is the first such
example to contain a bidentate terminal anion attached to the divalent metal center. All new species are characterized by $^1$H and $^{13}$C NMR spectroscopy and where appropriate by IR spectroscopy. The solid-state structures of complexes 1, 5a and 7 have also been determined and are disclosed within.

**Introduction**

The chemistry of heterometallic compounds containing at least one alkali-metal is currently at the forefront of organometallic research, primarily due to the unusual reactivity that these compounds can display which cannot be obtained by either of the homometallic derivatives. An early example of such chemistry was the discovery of the Lochmann-Schlosser superbases,$^1$ which contain both lithium (from BuLi) and potassium (from KOtBu) and display a greater deprotonating ability than either of these constituent parts. Recently, Knochel has reported on Turbo-Grignard $^2$ and Turbo-Hauser reagents,$^3$ whereby the presence of a lithium halide salt greatly increases the solubility and consequently the reactivity and selectivity of a variety of traditional Grignard (RMgCl) and Hauser (R$_2$NMgCl) reagents. Our interest in heterobimetallic chemistry stems from both a reactivity $^4$ and a structural perspective,$^5$ with knowledge of the latter helping to rationalize the trends of the former. We have recently added the benzamidinate $^6$ family of ligands, in particular the N, N’-disilylated derivative to our ongoing investigations. These bidentate, monoanionic ligands can easily be prepared as their alkali-metal salts from either the addition of an alkali-metal amide across a nitrile moiety (followed by a 1,3 sigmatropic shift of an organic unit) $^7$ or alternatively the addition of an alkali-metal aryl reagent across a carbodiimide $^8$ (scheme 1).
Scheme 1. Alternative synthetic methodologies to give alkali-metal benzamidinates.

Alkali-metal benzamidinates are particularly attractive since subtle changes, such as with the addition of various functional groups at different positions on the aromatic ring, can exert considerable effects on their structure and consequently on their reactivity. They are useful precursors to larger heteroatomic compounds such as substituted 1,3,5-triazines or bicyclic SN compounds as well as utilized as ligand transfer reagents to deliver main group and transition metal amidinate complexes.

Benzamidinate type complexes of the group IV metals have been comprehensively studied as catalysts for olefin polymerization, while other metal benzamidinates such as those of vanadium, nickel and yttrium have also been probed for catalytic activity. This ligand is attractive towards catalysis since it offers a similar level of steric protection to the cyclopentadienyl group but affords greater electrophilicity on the metal center as a consequence of being only a four-electron donor (as opposed to the six-electron donor Cp).

We recently attempted to synthesise a bimetallic benzamidinate species through the reaction of the sodium silylamide NaHMDS and the magnesium bis-alkyl Mg(CH₂SiMe₃)₂ with benzonitrile in the presence of the chelating donor ligand TMEDA. To our surprise, we discovered that the resulting product was in fact a homometallic, heteroleptic Mg dimer which contained both benzamidinate ligands and also a bridging ketimido N=C(Ph)CH₂SiMe₃ moiety (scheme 2).
On closer inspection, we surmised that there must be at least six independent reactions occurring in this one-pot synthesis to arrive at the final isolated product. These reactions are summarized in scheme 3. In this communication, we report our systematic studies into the intermediate products en route to the synthesis of 1, along with an alternative synthetic strategy using the same starting materials to give a heterobimetallic sodium magnesiate complex.
Results and Discussion

Synthesis and characterization of complex 1

As shown in scheme 2, the reaction of NaHMDS (prepared \textit{in situ} by deprotonation of HMDS(H) with $^t$BuNa) and Mg(CH$_2$SiMe$_3$)$_2$ with benzonitrile in the presence of TMEDA furnished 1. The same product was also obtained when TMEDA was omitted from the reaction mixture showing that it does not play a significant role in the reaction. After filtration and recrystallization, a final yield of crystalline product of 45\% was obtained. The $^1$H NMR spectrum of 1 showed three resonances in the
aliphatic region. Integration of these peaks suggested that there were SiMe₃ and CH₂SiMe₃ groups present in a 2:1 ratio. The chemical shift of the CH₂ group (2.82 ppm) strongly hinted that it was no longer bound to an electropositive metal center like that in the starting material. The aromatic region displayed six different resonances, suggesting that two phenyl rings in different environments are present. This evidence was all corroborated by the ¹³C NMR spectrum (see experimental for complete assignment). The molecular structure (figure 1) elucidated by X-ray crystallographic studies proved complex 1 to exist as a homometallic Mg dimer. Pertinent bond parameters are displayed in table 1.

![Molecular structure of complex 1](image)

Figure 1. Molecular structure of [PhC(NSiMe₃)₂Mg{µ-NC(CH₂SiMe₃)Ph}]₂ (1) with selective atom labelling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level.
Table 1. Selected bond lengths (Å) and angles (°) for complex 1

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The structure of 1 is spirocyclic, with a central Mg₂N₂ ring and two outer MgN₂C rings formed by the bidentate N,N’-coordination of a benzamidinate moiety to the Mg center. This benzamidinate unit is more strongly bound to the Mg center in 1 (Mg-Nbenzamidinate = 2.067(1) – 2.089(1)Å) than that in the related benzonitrile solvated Mg-bis(benzamidinate) complex (2.109(3)-2.138(3) Å),¹⁶ possibly reflecting the difference between a four and five-coordinate Mg center. The four-membered rings adopt obviously different forms, with the central ring planar and almost square due to
the four similar (Mg-N) bonds, bringing the magnesium atoms to 2.965(6)Å from one another. Meanwhile, the MgN₂C rings are more heavily distorted as a consequence of the short C-N bonds on one side and the longer Mg-N bonds on the other. Both magnesium centers sit in a distorted tetrahedral environment as a consequence of the strain exerted by these distinct four-membered rings.

Transformed from a neutral nitrile PhC≡N to an anionic ketimido Ph(R)C= N via addition of the Mg-CH₂SiMe₃ unit across the triple bond, this ligand provides the nitrogen bridge of the central ring. Bond lengths within the CN units (1.268(2) and 1.269(2) Å) are consistent with this addition to give a C=N double bond. This addition of the Mg-alkyl unit across the C≡N triple bond is unexpected given that the closely related Mg bis-alkyl complex Mg[CH(SiMe₃)₂]₂ only gives the bis-solvated benzonitrile product even when the solution is stirred in neat benzonitrile or refluxed in toluene.¹⁷ Such a result may initially suggest that the presence of the NaHMDS/benzamidinate may play a crucial role in promoting such addition; however this supposition is later disproved by the preparation of addition product 6 (vide infra). The phenyl rings of the opposing co-planar CN double bonds lie in a trans conformation relative to each other.

**Synthesis and characterization of intermediates en route to 1**

The reactions of alkali-metal HMDS complexes with various nitriles to give amidinates (that is conversion of NaHMDS to 4 in scheme 3) have been comprehensively studied previously. For example, solvated complexes of MHMDS typically adopt structure 2a; that is dimeric species containing a central four-membered M₂N₂ ring. Lithium and sodium examples have been crystallographically characterized, with the nitrile bearing tBu,⁸,¹⁸ adamantyl ¹⁹ or o-EtPh ²⁰ groups. The
addition product 3 has never been isolated with an alkali-metal, presumably because it immediately converts to 4 via a 1,3 sigmatropic shift. However, Oakley has alluded to its synthesis, while the same ligand has been witnessed in a tantalum complex and a bimetallic titanium oxo structure. It should be noted at this juncture that in the former case the starting material was PhC(NSiMe₃)N(SiMe₃)₂ and in the latter re-migration of one of the trimethylsilyl groups had occurred from a Ti-benzamidinate complex upon insertion of O₂ (that is the starting material contained a typical benzamidinate moiety such as 4). In both cases, this η₁ ligation mode appears necessary for steric reasons.

A plethora of known examples of alkali-metal benzamidinate type structures 4 also populate the literature with a variety of Lewis donors. These include monomeric with the chelating donor TMEDA (4a), dimeric with L = THF, OEt₂ or NCC₆H₄R (R = H, p-Me, 4b) and even a trimeric structure with one molecule of donor NCC₆H₄R (R = H, p-Me, 4c).
Given these previous precedents, we turned our attention to the isolation of possible intermediates 5 and 6 in scheme 3. Lappert has previously reported solvates of the closely related bis-silyl species Mg[CH(SiMe3)2]2 with both diethyl ether and 2,6-dimethylphenylisonitrile. The former was crystallographically characterized as a monosolvated monomer with a three-coordinate metal center, while the latter was shown to contain two solvent ligands per magnesium. Despite stirring Mg[CH(SiMe3)2]2 in neat PhCN or refluxing the PhCN adduct in toluene the authors were unable to force the magnesium bis-alkyl to add across the C≡N triple bond. In our experimental work, one molar equivalent of PhCN was added to a white suspension of Mg(CH2SiMe3)2 in hexane solution. The solid immediately dissolved and gave a bright yellow solution. Sonication ensured a homogenous solution. Upon cooling the solution to -30°C a crop of colourless crystals of 5a had deposited which
were subjected to a $^1$H and $^{13}$C NMR spectroscopic analysis. The $^1$H NMR spectrum showed principal peaks at -0.79 and 0.51 ppm in the ratio 2:9, indicative of the CH$_2$SiMe$_3$ group bound to an electropositive metal center. Aromatic peaks were also evident suggesting a C$_6$H$_5$ fragment was present; overall integration showed that there were two CH$_2$SiMe$_3$ groups per Ph group, consistent with a monosolvated structure. The $^{13}$C NMR spectrum was consistent with the $^1$H data, the trimethylsilyl carbon atoms resonating at 4.5 ppm while the metal bound carbon atom was more shielded at -3.6 ppm. A single crystal of 5a was therefore analyzed by X-ray diffraction.

**Figure 2.** Molecular structure of mono-benzonitrile solvate [Mg(CH$_2$SiMe$_3$)$_2$·NCPh]$_2$ (5a) with selective atom labelling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level. Symmetry transformations used to generate equivalent atoms: 1-x, 1-y, 1-z. Selected bond lengths (Å) and angles (°): Mg(1)-C(10) 2.122(2), Mg(1)-C(20) 2.235(1), Mg(1)-C(20A) 2.322(2), Mg(1)-N(1) 2.157(2), N(1)-C(1) 1.136(2); C(10)-Mg(1)-C(20) 125.76(7), C(20)-Mg(1)-C(20A) 103.79(6), C(10)-Mg(1)-C(20A) 115.38(7), C(10)-Mg(1)-N(1) 112.56(6), C(20)-
Mg(1)-N(1) 97.63(6), C(20A)-Mg(1)-N(1) 96.72(6), Mg(1)-C(10)-Si(1) 120.34(9),
Mg(1)-C(20)-Mg(1A) 76.20(6), Mg(1)-C(20)-Si(2) 103.78(7), Mg(1A)-C(20)-Si(2) 165.27(9), Mg(1)-N(1)-C(1) 168.48(13).

The centrosymmetric structure of 5a (figure 2) adopts a dimeric conformation with a planar central Mg₂C₂ ring. This is in contrast to the structure of the closely related complex Mg[CH(SiMe₃)₂]₂·OEt₂ which is monomeric due to a combination of the bulkier bis(trimethylsilyl) groups and bulkier donor solvent. Distorted tetrahedral (>Mg = 96.72(6)° – 125.76(7)°), the magnesium centers of 5a are bonded to the two alkyl carbon atoms, the nitrogen atom of the donor nitrile with the coordination sphere completed by an interaction with one of the Mg bound carbon atoms of a second molecule. The Mg-C bonds vary considerably, the shortest being that to the terminal carbon C10 [2.122(2)Å]. This is only marginally shorter than the Mg-C bonds of the bis-silyl diethyl ether solvated monomer mentioned earlier [2.141(2)Å] and is longer than the terminal Mg-C bond in the mixed alkyl-alkoxy cubane [Mg(CH₂SiMe₃)(μ³-OCH₂SiMe₃)]₄ [mean = 2.092(3) Å]. The intermolecular Mg-C20A bridging interaction is unsurprisingly the longest at 2.322(2)Å and this interaction causes elongation of the intramolecular Mg-C20 bond to 2.235(1)Å. Angular values in the central ring are distorted, with the endocyclic angle at Mg [103.79(6)°] much greater than that at C [76.20(6)°]. This brings the two magnesium angles to a separation distance of only 2.813(1)Å, which is shorter than the Mg(I)-Mg(I) bonds in the species (L)MgMg(L) (L = [(Dipp)NC(NiPr₂)N(Dipp)]⁻ 2.8508(12)Å; {[(Dipp)NC(Me)]₂CH}⁻ 2.8457(8)Å; Dipp = 2,6-diisopropylphenyl) and also shorter than a series of dimeric tBuMg amides by approximately 0.1Å. Such a distance is comparable with a non-bonding Mg···Mg interaction in the cluster [Mg(THF)(μ-
C₆H₄)₄ [2.804(2)Å].³³ The intramolecular C10-Mg1-C20 angle [125.76(7)°] is considerably less than that in Lappert’s bis-silyl ether solvated monomer [148.45(10)°],¹⁷ reflecting both the change from a three-coordinate to a four-coordinate magnesium center and also the difference in steric bulk between the bis-silyl and mono-silyl ligands.

We also attempted to synthesise a bis-solvated monomer such as that seen for Mg[CH(SiMe₃)₂]₂¹⁷ by adding two molar equivalents of PhCN to our magnesium bis-alkyl reagent. After sonication, the resulting yellow hexane solution was immediately cooled to -30°C, depositing large yellow crystals. A ¹H NMR spectrum of this product (5b) had an identical pattern to that of 5a, with the chemical shifts of the resonances all within 0.03 ppm. However, integration of the peaks showed that there were three donor benzonitrile molecules for every two molecules of Mg bis-alkyl. The ¹³C NMR spectrum confirms unequivocally that no addition has taken place, with only a CN triple bond present as evidenced by the typical chemical shift for this functionality at 119.6 ppm. From these NMR data we tentatively suggest that 5b exists in solution as a tri-solvated dimer. We note here that both 5a and 5b display a sharp C≡N stretch in their IR spectra (at 2261 and 2263 cm⁻¹ respectively).

An attempt was also made to add Mg(CH₂SiMe₃)₂ across the triple bond of benzonitrile. Like in the synthesis of 5, the magnesium reagent was suspended in hexane and two equivalents of PhCN were added but this time the resulting yellow solution was allowed to stir overnight upon which time a pale yellow powder had precipitated. The mixture was briefly heated to re-dissolve the powder and cooled to -30°C resulting in the recrystallization of a yellow non-crystalline solid (6). Its ¹H NMR spectrum displayed four singlets in the aliphatic region. These resonances, in a
2:4:9:18 ratio, indicate that there are two distinct CH$_2$SiMe$_3$ environments, in a 1:2 ratio. The CH$_2$ resonances show considerably different shifts, with the smaller signal resonating at -1.01 ppm, suggesting it is bound to an electropositive metal center. The other peak is considerably less shielded at 2.66 ppm suggesting the Mg-CH$_2$ bond is no longer intact for this fragment. The aromatic environment displays six distinct resonances suggesting two different phenyl environments, again in a 2:1 ratio. The $^{13}$C spectrum concurs with the $^1$H spectrum, with four aliphatic resonances, the CH$_2$ resonances (as confirmed by DEPT-135) resonate at 38.6 and -5.5 ppm, agreeing with the earlier assertion that both metallated and non-metallated CH$_2$SiMe$_3$ fragments are present in 6. The aromatic region gives further clues to the identity of this product. The DEPT-135 spectrum allowed us to identify four of the ten peaks in the aromatic region as quaternary (two of the ten are hidden under the solvent). The chemical shifts of these suggest the presence of a benzonitrile ligand (110.2 and 118.9 ppm, cf. complex 5a; 108.6 and 119.9 ppm for the ipso and nitrile carbons respectively) and a (Ph)-CN double bond (148.4 and 175.9 ppm, cf. complex 1; 147.6 and 181.3 ppm). A C≡N stretch at 2261 cm$^{-1}$ in the IR spectrum proved the presence of donor PhCN. Taken together, this evidence allows us to propose a trinuclear structure of formula (Me$_3$SiCH$_2$)$_2$Mg$_5$[μ-N=C(CH$_2$SiMe$_3$)Ph]$_4$2N=CPh (figure 3) for complex 6.
Figure 3. Proposed structure of addition product 6.

Support for this proposed structure comes from a recently determined structure \(^{34}\) of the addition product obtained from the manganese(II) congener Mn(CH\(_2\)SiMe\(_3\))\(_2\) with benzophenone which shows a similar trinuclear metal motif with addition having occurred only in the ligands occupying bridging positions.

**Synthesis of heterometallic, heteroleptic complex 7**

Having proved that both starting materials [NaHMDS and Mg(CH\(_2\)SiMe\(_3\))\(_2\)] add separately across the triple bond of benzonitrile; and that the final product is homometallic; we decided to alter our synthetic strategy in the pursuit of a heterometallic complex. This involved allowing the NaHMDS to fully consume all of the PhCN starting material *prior* to adding the magnesium reagent. Thus, equimolar amounts of NaHMDS and PhCN were stirred in hexane for four hours to ensure complete conversion to the sodium benzamidinate \(^4\), at which point solid Mg(CH\(_2\)SiMe\(_3\))\(_2\) was introduced. There was no obvious reaction so a molar equivalent of TMEDA was added to aid the dissolution of the Mg species; the solution
immediately turned yellow. Cooling this solution in the freezer afforded a crop of yellow crystals which were characterized crystallographically (figure 4).

Figure 4. Molecular structure of PhC(NSiMe₃)₂Mg(μ-CH₂SiMe₃)₂Na·2TMEDA (7) with selective atom labelling. Hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability level. Only one of the independent molecules is shown for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for complex 7. Parameters for the second independent molecule are in parentheses.

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The molecular structure of 7 shows that it is heterobimetallic containing a benzamidinate anion bound terminally to magnesium, with two trimethylsilylmethyl groups bridging the group 2 metal to sodium. From this structure it can be envisaged that the Mg bis-alkyl has inserted into the Na-N bonds of the parent sodium benzamidinate to generate the spirocyclic sodium magnesiate complex. The reaction is summarized in scheme 4.
Disorder in the organic periphery of this structure makes a detailed discussion of such regions unwarranted. However, the important features of this structure include the long C-Na bonds (>3 Å), which leaves the sodium center exposed enough that it can coordinate two molecules of the bidentate Lewis donor TMEDA, giving it an overall distorted octahedral coordination sphere. The steric bulk around sodium caused by the TMEDA molecules appears to push the trimethylsilyl groups towards the phenyl ring, evidenced by the Mg-C-Si angles [116.5(2)-120.8(2)°] being smaller than the Na-C-Si angles [142.8(2)-155.7(2)°]. This seems to have a subsequent effect on the SiMe₃ groups of the benzamidinate component, with the C-N-Si angles again less obtuse [128.6(3)-130.4(3)°] than the Mg-N-Si angles [140.7(2)-142.1(1)°]. This trimethylsilyl displacement in the Mg-benzamidinate fragment, which is not witnessed in complex 1, may also be electronic in nature rather than purely steric since the tetrahedral environment of the magnesium results in the SiMe₃ groups lying perpendicular to one another. Like in the previously discussed structures, the strain induced by the four-membered rings cause the Mg atom to lie in a distorted tetrahedral environment.

The NMR spectra of complex 7 are in full agreement with the structure shown above. In each case, the metal bound CH₂ is shielded in the negative low frequency region (¹H -1.73, ¹³C -4.5 ppm), while the two distinct SiMe₃ environments are clearly resolved. The CH₂ and CH₃ groups of the TMEDA group are coincidental in the ¹H spectrum but are well separated in the ¹³C spectrum, as confirmed by a HSQC spectrum. Further, the ¹³C spectrum shows typical chemical shifts for the ipso and NCN carbon atoms of a benzamidinate ligand at 144.7 and 180.7 ppm (cf. complex 1, vide supra).
This structure of 7 essentially displays all the salient features of a bimetallic M(I)/M(II) synergic base; that is an alkali-metal bound neutral donor, two bridging anions and a terminal anion.\textsuperscript{4c} The synthesis of this sodium magnesiate complex represents a new pathway for the preparation of synergic bimetallics. To explain, the typical structure for this type of complex can be considered as being formed as a result of co-complexation of the starting materials, whereby the constituent parts maintain their original interactions in the final product (figure 5a).\textsuperscript{35} However, in the synthesis of 7, the Mg bis-alkyl unit has inserted into the Na-N bonds of the sodium benzamidinate (figure 5b), yielding a final product whose constituent parts are now partially fragmented. This structure clearly displays the stronger electrophilicity of the Mg(II) center since it preferentially binds to the bidentate anion.

Figure 5a (top) Synthesis of typical bimetallic ate base by ‘co-complexation’ method and 5b (bottom) synthesis of bimetallic ate complex 7 by ‘insertion’.
The structure of 7 is also highly unusual in that it contains a bidentate anion bound to the M(II) in the terminal position. Very few bimetallic ate complexes contain a polydentate anion, while those that do generally have their polydentate anion bound to the M(I) as a consequence of an internal deprotonation of the ‘neutral’ donor. This has been demonstrated with both TMEDA and PMDETA molecules, each of which has been deprotonated in the $\alpha$-Me position, transforming them from neutral donors into polydentate anions.\(^{36}\) In such cases, this anion is not strictly terminal since the deprotonated CH\(_2\) moiety encroaches into the bridging position between the two metals.

**Conclusion**

We have shown that the seemingly simple reaction of a Mg bis-alkyl and an alkali-metal amide with benzonitrile is in fact far more complicated, with at least six separate reactions occurring in the one-pot synthesis to yield a homometallic heteroleptic dimer. Unlike its bulkier counterparts, Mg[CH\(_2\)(SiMe\(_3\))]\(_2\) is capable of adding across multiple bonds, although such addition can be inhibited at low temperature to yield simpler solvated complexes which are stoichiometry dependent. Further to this, the same starting materials can be used to provide a bimetallic ate complex simply by altering the conditions and the order of addition of the reagents. This novel sodium magnesiate complex 7 represents the first example of the ‘insertion’ route to potentially new mixed-metal bases and may have opened up a new general route to bases of this type.

**Experimental Section**
**General Procedures.** All reactions were carried out under a protective argon atmosphere using standard Schlenk techniques. Hexane was dried by refluxing over sodium benzophenone ketyl and was distilled under nitrogen prior to use. 1,1,1,3,3,3-hexamethyldisilazide [HMDS(H)] and N,N,N’,N’-tetramethylethylenediamine (TMEDA) were distilled over CaH₂ under nitrogen and stored over 4Å molecular sieves prior to use. Benzonitrile was stored over 4Å molecular sieves prior to use. Mg(CH₂SiMe₃)₂ was prepared by the literature method. NMR spectra were recorded on a Bruker AV400 MHz spectrometer (operating at 400.03 MHz for ¹H and 100.58 MHz for ¹³C) or a Bruker DRX 500 MHz spectrometer (operating at 500.13 MHz for ¹H and 125.76 MHz for ¹³C). All ¹³C NMR spectra were proton decoupled. IR spectra were collected on a Nikolet Impact 400D spectrometer. Satisfactory elemental analyses of 5b and 6 could not be obtained due to their high air- and moisture-sensitivity, while a minor impurity prevented satisfactory analysis of 7. ¹H NMR spectra of these compounds are included in the Supporting Information.

**X-ray crystallography.** All data were collected on an Oxford Diffraction Gemini S Diffractometer with Mo Kα radiation (λ = 0.71073 Å). Structures were refined using SHELXS-97, while refinements were carried out on F² against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program. All non-hydrogen atoms were refined using anisotropic thermal parameters.

Crystal data for 1: C₄₈H₇₈Mg₂N₆Si₆, M = 956.32, monoclinic, P2₁, a = 12.0416(2), b = 17.7556(3), c = 13.8627(2) Å, β = 97.955(1)°, V = 2935.40(8) Å³, Z = 2, T = 123K. 34216 reflections collected, 13562 were unique, R_m = 0.0195, R = 0.0322, R_w = 0.0795, GOF = 1.013, 578 refined parameters, max and min residual electron density = 0.354 and -0.200 e.Å⁻³.
Crystal data for 5a: C₁₅H₂₇MgNSi₂, M = 301.87, triclinic, P₁₁₁, a = 10.0894(8), b = 10.2655(6), c = 11.1908(7) Å, α = 63.035(6), β = 70.686(7), γ = 89.924(6)°, V = 959.57(14) Å³, Z = 2, T = 123K. 9464 reflections collected, 4281 were unique, R_int = 0.0177, R = 0.0335, R_w = 0.0935, GOF = 1.043, 178 refined parameters, max and min residual electron density = 0.337 and -0.406 e.Å⁻³.

Crystal data for 7: C₃₃H₇₇MgN₆NaSi₄, M = 717.67, monoclinic, P2₁, a = 14.2642(7), b = 14.0930(5), c = 23.4523(9) Å, β = 92.232(4)°, V = 4710.9(3) Å³, Z = 4, T = 123K. 31635 reflections collected, R_int = 0.0566, R = 0.0622, R_w = 0.1411, GOF = 0.918, 843 refined parameters, max and min residual electron density = 0.645 and -0.418 e.Å⁻³.

Synthesis of [PhC(NSiMe₃)₂Mg{μ-NC(CH₂SiMe₃)Ph}]₂ (1). HMDS(H) (0.21 mL, 1 mmol) was added to a stirring suspension of nBuNa (0.08 g, 1 mmol) in hexane (20 mL). After 1 h, Mg(CH₂SiMe₃)₂ (0.20 g, 1 mmol) was added as a solid, followed immediately by PhCN (0.20 mL, 2 mmol) giving a clear yellow solution. After stirring for 1 h, a white precipitate began to develop. The solution was filtered through Celite, reduced in volume to ca. 2 mL and cooled to -30°C to give 1 as bright yellow crystals (0.184 g, 45%). ¹H NMR (500.13 MHz, C₆D₆, 300 K): 0.00 (s, 36H, N-SiMe₃), 0.08 (s, 18H, CH₂SiMe₃), 2.82 (s, 4H, CH₂SiMe₃), 7.05 – 7.66 (m, 20H, aromatic). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 300K): -0.8 (CH₂SiMe₃), 2.1 (NSiMe₃), 39.6 (CH₂SiMe₃) 126.4, 126.6, 127.9, 128.3, 128.4, 128.8 (all aromatic C-H), 143.7, 147.6 (both aromatic ipso), 181.3 (C=N), 181.4 (N-C-N). Anal. Calcd for Mg₂N₆Si₆C₄₈H₇₈ (956.30): C, 60.29; H, 8.22; N, 8.79. Found: C, 59.36; H, 8.19; N, 8.76.

Synthesis of [Mg(CH₂SiMe₃)₂·NCP₈]₂ (5a). PhCN (0.1 mL, 1 mmol) was added to a suspension of Mg(CH₂SiMe₃)₂ (0.20 g, 1 mmol) in hexane (5 mL). This was sonicated until homogenous and immediately cooled to -30°C to give 5 as white crystals (0.251
g, 83%). $^1$H NMR (500.13 MHz, C$_6$D$_6$, 300 K): -0.79 (s, 4H, Mg-CH$_2$), 0.51 (s, 18H, SiMe$_3$), 6.57 (t, 2H, $^2$J$_{H,H} = 8$ Hz, meta C-H), 6.78 (t, 1H, $^2$J$_{H,H} = 8$ Hz, para C-H), 7.04 (d, 2H, $^2$J$_{H,H} = 7$ Hz, ortho C-H). $^{13}$C $^1$H NMR (100.59 MHz, C$_6$D$_6$, 300K): -3.6 (Mg-CH$_2$), 4.5 (SiMe$_3$), 108.6 (ipso), 120.0 (CN), 129.2 (meta), 132.6 (ortho), 134.3 (para). IR (Nujol, cm$^{-1}$): $\nu$ 2261 (C≡N). Anal. Calcd for Mg$_2$N$_2$Si$_4$C$_{30}$H$_{54}$ (603.72): C, 59.68; H, 9.01; N, 4.64. Found: C, 57.70; H, 8.76; N, 4.70.

**Synthesis of [Mg(CH$_2$SiMe$_3$)$_2$]·3NCPh (5b).** The synthesis of 5b was identical to that of 5a but twice as much PhCN (0.2 mL, 2mmol) was added. The resulting product was obtained as yellow crystals (0.261 g, 74%). $^1$H NMR (500.13 MHz, C$_6$D$_6$, 300 K): -0.78 (s, 8H, Mg-CH$_2$), 0.53 (s, 36H, SiMe$_3$), 6.58 (t, 6H, $^2$J$_{H,H} = 8$ Hz, meta C-H), 6.78 (t, 3H, $^2$J$_{H,H} = 8$ Hz, para C-H), 7.01 (d, 6H, $^2$J$_{H,H} = 7$ Hz, ortho C-H). $^{13}$C $^1$H NMR (100.59 MHz, C$_6$D$_6$, 300K): -4.0 (Mg-CH$_2$), 4.6 (SiMe$_3$), 109.7 (ipso), 119.6 (CN), 129.0 (meta), 132.5 (ortho), 133.7 (para). IR (Nujol, cm$^{-1}$): $\nu$ 2263 (C≡N).

**Synthesis of (Me$_3$SiCH$_2$)$_2$Mg$_3$[µ-N=C(CH$_2$SiMe$_3$)Ph]$_4$·2N≡CPh (6).** PhCN (0.2 mL, 2 mmol) was added to a stirring suspension of Mg(CH$_2$SiMe$_3$)$_2$ (0.20 g, 1 mmol) in hexane (5 mL). After stirring for 4 h, a yellow precipitate had developed. This was gently heated to redissolve the solid and cooled to -30°C to give 6 as a pale yellow powder (0.283 g, 70%). $^1$H NMR (500.13 MHz, C$_6$D$_6$, 300 K): -1.01 (s, 4H, Mg-CH$_2$), 0.02 (s, 36H, Mg-CH$_2$SiMe$_3$), 0.46, (s, 18H, SiMe$_3$), 2.66 (s, 8H, CH$_2$-SiMe$_3$), 6.72 (t, 4H, $^2$J$_{H,H} = 8$ Hz, donor meta C-H), 6.85 (t, 2H, $^2$J$_{H,H} = 8$ Hz, donor para C-H), 7.05 (t, 4H, $^2$J$_{H,H} = 7$ Hz, para C-H), 7.18 (d, 4H, $^2$J$_{H,H} = 7$ Hz, ortho C-H), 7.25 (t, 8H, $^2$J$_{H,H} = 8$ Hz, meta C-H), 7.51 (d, 8H, $^2$J$_{H,H} = 7$ Hz, ortho C-H). $^{13}$C $^1$H NMR (100.59 MHz, C$_6$D$_6$, 300K): -5.5 (Mg-CH$_2$), -0.5 (SiMe$_3$), 5.2 (Mg-CH$_2$-SiMe$_3$), 38.6 (CH$_2$-SiMe$_3$), 110.2 (donor ipso), 118.9 (donor CN), 127.0 (ortho), 129.1 (donor...
meta), 132.5 (donor ortho), 133.8 (donor para), 148.4 (ipso), 175.94 (C=N). IR (Nujol, cm$^{-1}$): v 2261 (C≡N).

**Synthesis of PhC(NSiMe$_3$)$_2$Mg(μ-CH$_2$SiMe$_3$)$_2$Na·2TMEDA (7).** HMDS(H) (0.21 mL, 1 mmol) was added to a stirring suspension of nBuNa (0.08 g, 1 mmol) in hexane (20 mL). After 1 h, PhCN (0.1 mL, 1 mmol) was added to give a clear, colourless solution. After 4 h, Mg(CH$_2$SiMe$_3$)$_2$ (0.20 g, 1 mmol) was added as a solid, followed immediately by TMEDA (0.30 mL, 2 mmol), resulting in a clear yellow solution. The solution was reduced in volume to ca. 3 mL and cooled to -30°C to give 7 as bright yellow crystals (0.364 g, 51%). $^1$H NMR (400.13 MHz, C$_6$D$_6$, 300 K): -1.73 (s, 4H, CH$_2$), 0.18 (s, 18H, N-SiMe$_3$), 0.48 (s, 18H, CH$_2$-SiMe$_3$), 1.93 (s, 32H, TMEDA CH$_2$ and CH$_3$), 7.05-7.13 (m, 3H, meta and para C-H), 7.43 (d, 2H, $^2$$J_{H,H} = 7$ Hz, ortho C-H). $^{13}$C($^1$H) NMR (100.59 MHz, C$_6$D$_6$, 300K): -4.5 (CH$_2$), 2.8 (N-SiMe$_3$), 4.7 (CH$_2$-SiMe$_3$), 45.7 (TMEDA Me), 57.4 (TMEDA CH$_2$), 126.5 (ortho), 127.1 (para), 127.6 (meta), 144.7 (ipso), 180.7 (N-C-N).

**Acknowledgment.** We are indebted to the UK EPSRC (through grant awards: EP/F063733/1 and EP/D076889/1) and the Royal Society (through a Wolfson merit award to REM) for generously sponsoring this research programme.

**Supporting Information Available:** NMR spectra of 5a, 6 and 7, CIF files for 1, 5a and 7. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).

**References**


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A seemingly simple reaction of a sodium amide and magnesium bis-alkyl with benzonitrile is proved to be more complex in practice giving a homometallic heteroleptic Mg dimer. Intermediates to this unexpected product are isolated and characterized; while the order of addition of reagents is altered to yield a sodium magnesiate via a novel ‘insertion’ route.