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# Reductive Coupling and Loss of N<sub>2</sub> from Magnesium Diazomethane Derivatives

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#### Dedication ((optional))

**Abstract:** The reductive coupling of two diazomethanes is effected by reaction with  $[(NacNac^{Mes})Mg]_2$  affording the species  $[(NacNac^{Mes})Mg(N_2CPh_2)]_2$  **2** and  $[(NacNac^{Mes})Mg(N_2C(C_6H_4)_2)]_2$  **3**. These species containing N<sub>4</sub> linkages readily evolve the central N<sub>2</sub> at 50 and 75 °C to give the Mg-imide products  $[(NacNac^{Mes})Mg(NCPh_2)]_2$  **4** and  $[(NacNac^{Mes})Mg(NC(C_6H_4)_2)]_2$  **5**, respectively. The mechanism for the loss of N<sub>2</sub> is considered computationally. Compounds **2** and **3** react with O<sub>2</sub> to liberate the tetrazene (Ph<sub>2</sub>N<sub>2</sub>)<sub>2</sub> **6** and the hydrazine  $((C_6H_4)_2CN)_2$  **7** while reactions with Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> or Me<sub>3</sub>SiCl with **2** and **3** provide the related silyl imines **8** and **9**, respectively.

#### Introduction

Main group systems have garnered much attention in recent years, in part due to the growing body of evidence that these elements can in some instances behave in a fashion analogous to transition metals.<sup>[1]</sup> While Power described early examples of the irreversible reactions of Ge-Ge multiple bonds with H<sub>2</sub>,<sup>[2]</sup> species of the form ArSn=SnAr were also shown to react reversibly with ethylene.<sup>[3]</sup> Similarly, Bertrand demonstrated the irreversible reaction of singlet carbenes with H<sub>2</sub> and NH<sub>3</sub>,<sup>[4]</sup> while our group described frustrated Lewis pairs (FLPs), which react reversibly with H<sub>2</sub>.<sup>[5]</sup> In subsequent work, FLP chemistry has been exploited for metal-free reductions, other catalytic processes and the stoichiometric capture of a variety of other small molecules.<sup>[5-6]</sup>

While the breadth of reactivity of main group systems has grown dramatically in the last decade, notably absent from the substrates under consideration is dinitrogen. While early matrix isolation work had implied the interaction of  $N_2$  with boron-based species,<sup>[7]</sup> it has only been very recently that the first main group system capable of binding  $N_2$  was described by the Braunschweig group.<sup>[8]</sup> Seeking to develop main group-N<sub>2</sub> chemistry, we note that main group systems that evolve  $N_2$  are limited to reactions of azides. For example, the classic reaction<sup>[9]</sup> exploits Staudinger azides to generate phosphinimines. In some cases, the intermediate phosphazide derivatives have been intercepted.<sup>[10]</sup> Other main group azides<sup>[11]</sup> are isolable and lose N2 to give element-nitride derivatives. Similarly, photochemical reactions of azide precursors have been used in the synthesis of heavier main group-N fragments and shown to often prompt substituent migration to N.<sup>[12]</sup> Other main group species that evolve N2 are rare. The species Ph<sub>3</sub>PNNPPh<sub>3</sub> is reported to lose N<sub>2</sub> at 215 °C.<sup>[13]</sup> We and others have shown that reactions of diazomethanes with boranes effect

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carbene insertion into B-C bonds with loss of N<sub>2</sub>.<sup>[14]</sup> More recently, the use of a sterically demanding diazomethane has been used to intervene in such reactions allowing the interception of a diazomethane-borane adduct.<sup>[15]</sup> Nonetheless, this adduct is thermally unstable, above -35 °C, evolving N<sub>2</sub> to give a product formulated as the carbene-borane adduct.



Figure 1 (a) Reductive couplings of organic substrates induced by 1; (b) current report.

In targeting new systems that might evolve N<sub>2</sub> we noted strong reducing ability of the dimeric magnesium(I) the β-diketiminates, first reported by Jones and Stasch.<sup>[16]</sup> This reagent has proved highly reactive and affords unique reactivity (Figure 1a),<sup>[17]</sup> including the coupling of azides to give  $N_{6}$ fragments,<sup>[18]</sup> coupling of isocyanides<sup>[18c]</sup>, isocyanates<sup>[19]</sup> or nitriles,<sup>[18c]</sup> reversible 1,1-diphenylethylene,<sup>[20]</sup> the activation of C-F bonds,<sup>[21]</sup> and permits the construction of rare Mn-Mg bonds.<sup>[22]</sup> In this paper, we apply the reactivity of the Mg(I) species [(NacNac<sup>Mes</sup>)Mg]<sub>2</sub> 1 <sup>[23]</sup> (NacNac<sup>Mes</sup> = [(MesNCMe)<sub>2</sub>CH]<sup>-</sup>) to effect the reductive coupling of diazomethanes (Figure 1b), affording tetrazene-dianion complexes of Mg via N-N bond formation. The reactivity of these species is probed. The products of oxidation and mild thermolysis are characterized. In the latter case, facile loss of N2 affords magnesium-imide dimers,

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providing a rare example of isolable main group species, not derived from azides, that cleanly evolve  $N_2$  under mild conditions. The mechanism of this loss is considered.

#### **Results and Discussion**

In an initial reaction compound 1 was combined with two equivalents of Ph<sub>2</sub>CN<sub>2</sub> in toluene solution (Scheme 1). After 30 minutes, a dark purple solid 2 was isolated in 89% vield. The <sup>1</sup>H NMR data were consistent with the product being comprised of the reactants but gave little structural insight. Purple crystals of this product were grown by cooling a saturated pentane solution at -35 °C. A crystallographic study of 2 established the formulation as [(NacNacMes)Mg(N2CPh2)]2 (Figure 2a) in which electron transfer from Mg(I) to the diazomethane affords Mg(II) centers and a central [Ph<sub>2</sub>CN<sub>4</sub>CPh<sub>2</sub>]<sup>2-</sup> fragment. The pseudo tetrahedral Mg(II) centers are coordinated to the NacNac<sup>Mes</sup> ligand and to alternating nitrogen atoms of the N<sub>4</sub> linkage. The Mg-N distances for the NacNac<sup>Mes</sup> ligands were found to range from 2.006(3) Å to 2.025(3) Å, while the Mg-N to the reduced diazomethane are 2.178(4) Å, 2.010(4) Å, 2.139(4) and 2.024(5) Å. The corresponding N-Mg-N angles in the six and four member-rings were found to be 94.41(12)°, 96.54(12)° and 63.84(16)° and 64.51(16)°, respectively. The chelation in the MgN<sub>3</sub> rings give rise to transannular Mg-N distances of 2.588(5) Å and 2.551(4) Å. The exocycle Ph<sub>2</sub>C fragments give rise to C-N distances of 1.351(6) Å and 1.335(5) Å, while the adjacent N-N distances were found to be 1.316(6) Å and 1.327(6) Å with a central N-N distance of 1.454(6) Å. It is noteworthy that the central CN<sub>4</sub>C linkage is approximately coplanar suggestive of extended conjugation while the phenyl rings on either end are canted at angles of 27.7°, 52.5°, 33.2° and 43.6° with respective to the CN<sub>4</sub>C plane.

The corresponding reaction of 1 reacted with 9-diazofluorene in toluene proceeds in a similar fashion after 30 minutes to give the dark golden solid 3 in 93% yield. Golden crystals of 3 were obtained by slow evaporation of a pentane solution at room temperature. The crystallographic study of 3 established the formulation as [(NacNac<sup>Mes</sup>)Mg(N<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>)]<sub>2</sub> (Figure 2b). The general structural features of 3 are analogous to 2, although 3 exhibits crystallographic C2 symmetry with Mg-N distances for the NacNac  $^{\rm Mes}$  ligands of 2.0133(18) Å and 2.0070(17) Å, Mg-N distances to the reduced diazomethane of 2.1076(17) Å and 2.0979(18) Å and N-Mg-N angles of 95.86(7)° and 63.02(6)° for the in the six and four member-rings respectively. The C-N distances of the central CN<sub>4</sub>C fragment in 3 was found to be 1.330(2) Å, with adjacent N-N distance of 1.328(2) Å and a central N-N distance of 1.418(3) Å. In contrast to 2, the central CN<sub>4</sub>C linkage is almost coplanar with the fluorenyl fragments as the interplanar angle between the CN<sub>4</sub>C fluorenyl group was found to be 7.17°. This further extends the conjugation in the central [((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CN<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> fragment accounts for the longer N-N distances adjacent the fluorenyl groups.

The formation of **2** and **3** is reminiscent of the N-N coupling of adamantly azides reported by Jones et al.<sup>[24]</sup> which afforded the species, [(NacNac<sup>Mes</sup>)Mg(N<sub>3</sub>Ad)]<sub>2</sub>. Holland and co-workers

have also reported the reductive coupling of azides from the reaction of (NacNac<sup>Mes</sup>)Fe(I) species with AdN<sub>3</sub>.<sup>[25]</sup> Reductive coupling of diazofluorene has been studied electrochemically and shown from chronoamperometric and coulometric gas-pressure studies to generate the dianion with the empirical formula [N<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>]<sup>2-,[26]</sup> however, the isolation of **2** and **3** represents the first isolation of derivatives of such N-N coupled diazomethanes to our knowledge.



Figure 2 POV-ray depictions of the structures of (a) 2 and (b) 3. Hydrogen atoms and solvent residue have been omitted for clarity. C: black, N: blue, Mg: brown.

Natural bond orbital (NBO) analysis<sup>[27]</sup> (M06-2X/TZVP//M06-2X/SVP)<sup>[28]</sup> reveals that the reductive coupling of diazomethanes forming 2 and 3 significantly weakens the terminal N-N bonds, supported by the much smaller Wiberg bond indices (WBIs) (2: 1.28 and 1.29; 3: 1.33 and 1.33) compared to the corresponding diazomethanes (Ph<sub>2</sub>CN<sub>2</sub>: 2.38; (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CN<sub>2</sub>: 2.41). The WBIs of the central N-N bonds in 2 and 3 are 1.03 and 1.08, respectively, while the Mg-N bonds show extremely small WBIs (maximum: 0.09). The  $C_2N_4$  units carry negative charges (2: -1.56; 3: -1.36), while the Mg atoms are very positively charged (2: 1.78 each; 3: 1.76 each). Interestingly, an inspection of the NBOs corresponding to the central C2N4Mg2 fragments of 2 suggest no Mg-N  $\sigma$ -bonds. Instead, the core N atoms contain two lone pairs of electrons and form  $\sigma\text{-bonds}$  with the adjacent N atoms (see SI). Collectively, the electronic structures of 2 and 3 feature is best described as being comprised of cationic [LMg]+ and anionic  $[C_2N_4]^{2-}$  units.

Compound 2 does not exhibit prolonged stability in benzene solution at room temperature, rather it shows a half-life of about

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4 days under these conditions. Quantitative conversion of 2 to a new species 4 was achieved in 12 h at 50 °C (Scheme 1). This transformation was evident from the color change from purple to yellow. Again, while NMR data fails to provide definitive structural information, yellow crystals of 4 were obtained by slow evaporation of a pentane solution at room temperature. The crystallographic data affirmed the formulation of 4 as [(NacNac<sup>Mes</sup>)Mg(NCPh<sub>2</sub>)]<sub>2</sub> (Figure 3a). This centrosymmetric dimer features two pseudo-tetrahedral Mg centers linked by two bridging Ph<sub>2</sub>C=N ligands The Mg-N distances for the NacNac ligands were found to be 2.064(1) Å and 2.084(1) Å while the bridging imide ligands gave rise to Mg-N distances of 2.097(1) Å and 2.077(1) Å. The chelate bite angle for the NacNac<sup>Mes</sup> ligand is 91.41(6)° while the N-Mg-N and Mg-N-Mg' angles for the N<sub>2</sub>Mg<sub>2</sub> were found to be 87.70(5)° and 91.73(7)° and 92.87(7)°, respectively. The C-N distance in the imide ligand are 1.260(3) Å and 1.273(3) Å, consistent with the C=N double bonds.



**Scheme 1** Reactions of **1** with diazomethanes and subsequent loss of  $N_2$ , L = NacNac<sup>Mes</sup>.

In contrast to **2**, compound **3** was stable in benzene solution at room temperature. However, on warming to 75 °C for 24 h (Scheme 1), the cyan color of **3** in toluene solution was replaced with pink. Pink crystals of a new species **5** were obtained by slow evaporation of a pentane solution at room temperature. Again, crystallographic data were acquired to confirm the formulation of **5** as  $[(NacNac^{Mes})Mg(NC(C_6H_4)_2)]_2$  (Figure 3b), analogous to those in **4**. However, the poorer quality crystallographic data precludes a detailed comparison of the metric parameters.

The formation of **4** and **5** clearly proceeds via loss of  $N_2$  from the precursors **2** and **3**, respectively. While the loss of  $N_2$  from an  $N_4$  species is perhaps not unexpected, this behaviour stands in contrast to conventional reactions of diazomethanes where loss of  $N_2$  affords, the transient carbene fragment. In the present cases the reductive coupling of these diazomethanes appears to labilize the central  $N_2$  unit. To probe the mechanism of this reaction, density functional theory (DFT) calculations were performed at the SMD-M06-2X/TZVP//M06-2X/SVP level of

theory<sup>[28b]</sup> using **1** with  $Ph_2CN_2$  (Figure 4). Initially, one-electron reduction of Ph<sub>2</sub>CN<sub>2</sub> by 1 gives a radical intermediate IN1 (0.7 kcal mol<sup>-1</sup>) that subsequently undergoes dimerization to provide 2 (-59.7 kcal mol<sup>-1</sup>). The loss of N<sub>2</sub> from 2 is computed to yield 4 in a highly exothermic concerted reaction (-78.2 kcal mol<sup>-1</sup>), proceeding via a transition state that represents an activation barrier of 33.1 kcal mol<sup>-1</sup>. This relatively high barrier is in line with the experimental observation that the conversion of 2 to 4 is extremely slow at room temperature, allowing for the isolation of the room-temperature-stable magnesium diazomethane derivative 2. In the present calculation, the rate limiting step is found to involve cleavage of an N-N bond alpha to the C=N bond generating a Mg-imide fragment coordinated to the remaining N<sub>3</sub> unit on the other Mg center. The subsequent loss of N<sub>2</sub> and subsequent dimerization give the Mg-imide 4 in a highly exothermic reaction.



**Figure 3** POV-ray depictions of the structures of (a) **4** and (b) **5**. Hydrogen atoms and solvent residue have been omitted for clarity. C: black, N: blue, Mg: brown.

Efforts to effect further reactivity of **2** and **3** were undertaken. Addition of H<sub>2</sub> led to no reaction at room temperature, while at elevated temperatures **2** and **3** underwent thermal conversions to **4** and **5** respectively. Exposure of **2** to atmospheric O<sub>2</sub> led to degradation and the formation of a mixture of products, although the tetrazene [Ph<sub>2</sub>CN<sub>4</sub>CPh<sub>2</sub>] **6** was isolated in 88 % yield. (Figure 5). Interestingly, the reaction of **6** with **1** regenerated **2**. It is noteworthy that Herbranson et al.<sup>[26]</sup> previously described the electrochemical oxidation of the dianion [((C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CN<sub>2</sub>)<sub>2</sub>]<sup>2</sup> gave the fluorenyl analogue of **6** which subsequently lost N<sub>2</sub> to give

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the hydrazine [(( $C_6H_4$ )<sub>2</sub>CN)<sub>2</sub>] **7**. The corresponding aerobic oxidation of **3** proceeded quickly to give **7** in 72% yield (Figure 5). The structures of **6** and **7** were confirmed crystallographically (Figure 6, 7). In addition, preliminary results showed that treatment of **2** with trimethylsilyl triflate (Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub>) or **3** with trimethylsilyl chloride (Me<sub>3</sub>SiCl) in C<sub>6</sub>D<sub>6</sub> afforded the corresponding silyl imines **8** (86 %) or **9** (57 %), respectively, along with some unidentified magnesium by-products (Figure 5).



Figure 4 (a) Computed reaction profile for conversion of 1 to 2 to 4 with loss of N<sub>2</sub>. (b) Optimized structures of key intermediate IN1 and transition state TS1.



Figure 6 POV-ray depictions of the structure of 6. Hydrogen atoms and solvent residue have been omitted for clarity. C: black, N: blue.



Figure 7 POV-ray depictions of the structure of 7. Hydrogen atoms have been omitted for clarity. C: black, N: blue.

In summary, the reactions of diazomethanes with the Mg(I) species 1 yield the formation of dianionic dimers of these diazomethane complexes of magnesium, 2 and 3. These systems represent the first unequivocal data demonstrating the reductive coupling of diazomethanes. Moreover, these species have shown to be precursors to Mg-imide species 4 and 5 via thermally induced loss of N2. The silyl imines 8 and 9 are derived from reactions of 4 and 5 with Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> or Me<sub>3</sub>SiCl, while in the presence of dry O2, 2 and 3 convert to a tetrazene 6 and a hydrazine 7, respectively. Apart from main group azide derivatives, these transformations provide rare examples of main group system that evolve N2. These findings suggest that new strategies to reversible main group N2-binding may emerge from sterically demanding systems that preclude dimeric products. Synthetic efforts to this end are on-going and will be reported in due course.

#### **Experimental Section**

General Remarks: All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N2. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (toluene, n-hexane and npentane) were prepared using an Innovative Technologies solvent purification system. Benzene was degassed and stored over molecular sieves (4 Å) for at least overnight prior to use. Deuterated benzene (C<sub>6</sub>D<sub>6</sub>) and chloroform (CDCl<sub>3</sub>) purchased from Cambridge Isotope Laboratories Inc. were degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification otherwise. [(NacNacMes)Mg]<sub>2</sub> **1**<sup>[18a]</sup>, unless indicated diazodiphenylmethane and 9-diazofluorene<sup>[29]</sup> were prepared according to literature procedures. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer or an Agilent DD2 600 MHz spectrometer. <sup>1</sup>H, <sup>13</sup>C{1H} NMR chemical shifts  $(\delta/ppm)$  are referenced to the residual solvent resonance of the deuterated solvent. Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyzer. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JMS-T100LC JOEL (DART).

Syntheses of 2: Toluene solution (1 mL) of  $Ph_2CN_2$  (40 mg, 0.21 mmol) was added to toluene solution (1 mL) of  $[(NacNacMes)Mg]_2$  1 (72 mg, 0.20 mmol), and the mixture was

stirred at room temperature for 30 minutes. The volatiles of the solution were removed under vacuum. The residue was added by 2 mL of n-pentane and the mixture was stored at -35 °C overnight. Dark purple solid separated out and was collected by removing the supernatant. The solid was washed with 2 mL of cold n-pentane and dried under vacuum to give 2 as a dark purple solid (90 mg). n-Pentane solutions were combined together and reduced to 0.5 mL. Crystallization from the npentane solution at -35 °C gave another crop of 2 (8 mg). Total yield of 2 is 89%. Single crystals of 2 were obtained by cooling a saturated n-pentane solution at -35 °C. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): 7.27 (br, 4H, Ar-H), 7.06 (m, 8H, Ar-H), 6.97 (t, <sup>4</sup>J<sub>H-H</sub> = 7.2 Hz, 2H, Ar-H), (t, <sup>4</sup>J<sub>H-H</sub> = 7.2 Hz, 2H, Ar-H), 6.84 (br, 4H, Ar-H), 6.77 (s, 4H, Ar-H), 6.76 (s, 4H, Ar-H), 4.95 (s, 2H, MeC(N)CH), 2.19 (s, 12H, CH<sub>3</sub>), 1.91 (s, 12H, CH<sub>3</sub>), 1.83 (s, 12H, CH<sub>3</sub>), 1.60 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): 168.8 (MeC(N)CH), 145.0, 142.4, 137.9, 133.1, 131.9, 131.8, 129.4, 129.2, 128.8, 128.7, 128.3, 126.8, 125.8, 124.4 (Ar-C and Ph<sub>2</sub>CN), 96.3 (MeC(N)CH), 23.1, 20.9, 19.7, 18.9 (CH<sub>3</sub>), 34.5, 22.7, 14.3 (npentane-C). Anal. Calcd for C<sub>72</sub>H<sub>78</sub>N<sub>8</sub>Mg<sub>2</sub>: C, 78.33; H, 7.12; N, 10.15. Found: C, 79.17; H, 6.93; N, 9.35.

Syntheses of 3: Toluene solution (1 mL) of 9-diazofluorene (40 mg, 0.21 mmol) was added to toluene solution (1 mL) of [(NacNacMes)Mg]<sub>2</sub> 1 (72 mg, 0.20 mmol), and the mixture was stirred at room temperature for 30 minutes. The volatiles of the solution were removed under vacuum. The residue was added by 2 mL of n-pentane and the mixture was stored at -35 °C overnight. A dark golden solid separated out and was collected by removing the supernatant. The solid was washed with 2 mL of cold n-pentane and dried under vacuum to give 3 as a dark golden solid (58 mg). n-Pentane solutions were combined together and reduced to 0.5 mL. Crystallization from evaporation of the n-pentane solution at room temperature gave another crop of 3 (44 mg). Total yield of 3 is 93%. Single crystals of 3 were obtained by slow evaporation of a n-pentane solution at room temperature. <sup>1</sup>H NMR (400 MHz, C6D6): 7.76 (dd, <sup>3</sup>J<sub>H-H</sub> = 11.6 Hz, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 4H, Ar-H), 7.39-7.18 (m, 10H, Ar-H), 7.15 (m, overlapped with C<sub>6</sub>D<sub>6</sub>, 2H, Ar-H), 6.50 (d, 4JH-H = 4.4 Hz, 8H, Ar-H), 5.15 (s, 2H, MeC(N)CH), 1.97 (s, 24H, CH<sub>3</sub>), 1.94 (s, 12H, CH<sub>3</sub>), 1.70 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): 169.6 (MeC(N)CH), 143.6, 137.5, 136.6, 135.4, 133.6, 131.5, 131.2, 131.1, 129.6, 129.3, 127.1, 126.4, 125.0, 124.1, 122.9, 120.3, 120.1, 117.4 (Ar-C and Fluorene-9C), 95.7 (MeC(N)CH), 22.9, 20.8, 19.6, 18.7 (CH<sub>3</sub>). Anal. Calcd for C<sub>72</sub>H<sub>74</sub>N<sub>8</sub>Mg<sub>2</sub>: C, 78.61; H, 6.78; N, 10.19. Found: C, 78.27; H, 6.88; N, 10.15.

**Syntheses of 4**: Toluene solution (1 mL) of **2** (16.6 mg, 0.015 mmol) stood at 50 °C for 12 hours. The volatiles of the solution were removed under vacuum to give **4** as a yellow solid (16.0 mg, 99%) without further purification. Single crystals of **4** were obtained by slow evaporation of a n-pentane solution at room temperature. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 8.27-5.75 (m/br, overlapped with C<sub>6</sub>D<sub>6</sub>, 28H, Ar-H), 4.88 (s, 2H, MeC(N)CH), 2.31 (s, 12H, CH<sub>3</sub>), 1.66 (br, 24H, CH<sub>3</sub>), 1.40 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): 167.7 (MeC(N)CH), 147.3, 132.4 (br), 132.2, 129.7 (br), 128.2 (Ar-C and Ph<sub>2</sub>CN), 97.3 (MeC(N)CH), 23.5,

21.2, 19.8 (br) (CH\_3). Anal. Calcd for  $C_{72}H_{78}N_6Mg_2$ : C, 80.37; H, 7.31; N, 7.81. Found: C, 79.19; H, 7.36; N, 7.56.

**Syntheses of 5**: Toluene solution (1 mL) of **3** (16.5 mg, 0.015 mmol) stood at 75 °C for 24 hours. The volatiles of the solution were removed under vacuum to give **5** as a pale pink solid (15.9 mg, 99%) without further purification. Single crystals of **5** were obtained by slow evaporation of a n-pentane solution with drops of toluene at room temperature. <sup>1</sup>H NMR (400 MHz, C6D6): 7.45 (d,  ${}^{3}J_{H+H} = 7.2$  Hz, 4H, Ar-H), 7.26 (t,  ${}^{3}J_{H+H} = 7.2$  Hz, 4H, Ar-H), 7.16 (m, overlapped with C<sub>6</sub>D<sub>6</sub>, Ar-H), 6.46 (s, 8H, Ar-H), 5.17 (s, 2H, MeC(N)CH), 2.18 (s, 12H, CH<sub>3</sub>), 1.79 (br, 24H, CH3), 1.52 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): 168.3 (MeC(N)CH), 146.5, 143.4, 137.3 (br), 132.4, 131.6, 131.0 (br), 129.5, 123.3 (br), 119.1 (br) (Ar-C and Fluorene-9C), 95.2 (MeC(N)CH), 23.3, 21.3, 19.4 (CH<sub>3</sub>), 34.5, 22.7, 14.3 (n-pentane-C). Anal. Calcd for C<sub>72</sub>H<sub>74</sub>N<sub>6</sub>Mg<sub>2</sub>: C, 80.67; H, 6.96; N, 7.84. Found: C, 78.88; H, 7.27; N, 7.53.

Syntheses of 6: Toluene solution (0.6 mL) of 2 (16.6 mg, 0.015 mmol) was sealed in a J-Young NMR tube and frozen in liquid nitrogen. The N<sub>2</sub> atmosphere was removed under vacuum and and replaced with 2.0 atm O<sub>2</sub>and the solution was warmed to room temperature. The volatiles of the solution were removed under vacuum. The residue was washed by n-pentane (2 mL x 2) and dried under vacuum to give **6** as a pale yellow solid (5.1 mg, 88%). Single crystals of **6** were obtained by slow evaporation of a bzenzene solution at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.73 (m, 4H, Ph-H), 7.50-7.32 (m, 12H, Ph-H), 7.23 (m, 4H, Ph-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 169.8 (C=N), 137.2, 134.8, 131.6, 130.3, 130.1, 129.9, 128.4, 128.1 (Ph-C).

Syntheses of 7: Benzene solution (0.6 mL) of 3 (16.5 mg, 0.015 mmol) was sealed in a J-Young NMR tube and frozen by liquid nitrogen. The N<sub>2</sub> atmosphere was removed under vacuum and and replaced with 2.0 atm O<sub>2</sub> and the solution warmed to room temperature. The volatiles of the solution were removed under vacuum. The residue was added by a few drops of toluene and washed by n-hexane (2 mL x 2) and dried under vacuum to give 7 as a pale orange solid (3.8 mg, 72%). Single crystals of 7 were obtained by slow evaporation of a bzenzene solution at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.20 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, Ar-H), 8.07 (d, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, Ar-H), 7.59 (d, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 4H, Ar-H), 7.48 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, Ar-H), 7.43 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, Ar-H), 7.36 (t,  ${}^{3}J_{H-H}$  = 7.6 Hz, 2H, Ar-H), 7.24 (t,  ${}^{3}J_{H-H}$ = 7.6 Hz, 2H, Ar-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 165.5 (C=N), 143.4, 142.6, 136.3, 133.1, 133.0, 132.7, 131.6, 128.8, 128.7, 124.9, 120.4, 120.3 (Ar-C). MS (DART) [M+1] C<sub>26</sub>H<sub>17</sub>N<sub>2</sub><sup>+</sup> calc. 357.13917 m/z, found 357.14016 m/z.

**Syntheses of 8**: A C<sub>6</sub>D<sub>6</sub> solution (0.6 mL) of **2** (16.6 mg, 0.015 mmol), Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> (8.0 mg, 0.036 mmol) and diphenylmethane (22.7 mg, 0.135 mmol) was sealed in a NMR tube and the solution stood at room temperature for 1 hour. The <sup>1</sup>H NMR spectrum of the reaction solution was recorded and the yield of **8** (86%) was referenced to diphenylmethane. The generation of **8** was confirmed by HRMS: (DART) [M+1]  $C_{16}H_{20}NSi^+$  calc. 254.13650 m/z, found 254.13738 m/z.

**Syntheses of 9**: A  $C_6D_6$  solution (0.6 mL) of **3** (16.5 mg, 0.015 mmol), Me<sub>3</sub>SiCl (6.5 mg, 0.06 mmol) and diphenylmethane (22.7 mg, 0.135 mmol) was sealed in a NMR tube and the solution stood at 50 °C for 36 hour. The <sup>1</sup>H NMR spectrum of the reaction solution was recorded and the yield of **9** (57%) was referenced to diphenylmethane. The generation of **9** was confirmed by HRMS: (DART) [M+1]  $C_{16}H_{18}NSi^+$  calc. 252.12085 m/z, found 252.12089 m/z.

**Crystallographic Details** Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). The structures were solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.[S3]

**Computational Details** Calculations were carried out with the Gaussian 09 package.<sup>[28b]</sup> Geometry optimizations were performed with the M06-2X functional.<sup>[30]</sup> The SVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC) calculations to determine two corresponding minima.

The single-point energy calculations were performed at the M06-2X/TZVP level of theory for solution-phase. The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with toluene, while Bondi radii<sup>[31]</sup> were chosen as the atomic radii to define the molecular cavity. The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298K. Natural bond orbital (NBO) calculations were carried out using NBO 6.0 program<sup>[27]</sup> at the M06-2X/TZVP//M06-2X/SVP level of theory. Optimized structures were visualized by the CYLview program.<sup>[32]</sup>

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## **Entry for the Table of Contents**

## FULL PAPER

#### Reductive Coupling and Loss of N<sub>2</sub> from Magnesium Diazomethane Derivatives

Reactions of diazomethanes with  $[(NacNac^{Mes})Mg]_2$  effects reductive coupling to give the complexes  $[(NacNac^{Mes})Mg)$  $(N_2CR_2)]_2$ . On warming these species cleanly evolve N<sub>2</sub> to give Mg-imide products.



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