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Tris(carbene) Stabilization of Monomeric Magnesium Cations: A Neutral, Nontethered Ligand Approach

Akachukwu D. Obi, Jacob E. Walley, Nathan C. Frey, Yuen Onn Wong, Diane A. Dickie, Charles Edwin Webster,* and Robert J. Gilliard, Jr.*

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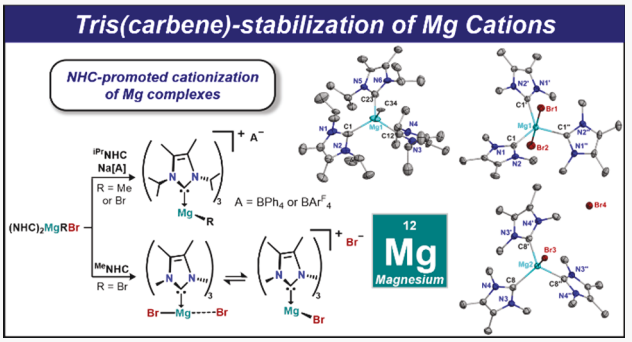
ABSTRACT: Herein, we describe the syntheses and structural characterization of bis(carbene)- and tris(carbene)-stabilized organomagnesium cations. The reaction of the N-heterocyclic carbene (NHC) stabilized Grignard reagent (^{iPr}NHC)$_2$Mg(Me)(Br) (**1**) and Na[BAr$^F_4$] (^{iPr}NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Ar^F = 3,5-bis(trifluoromethyl)phenyl) in chlorobenzene yields exclusively the bis(NHC)-stabilized dication [{(^{iPr}NHC)$_2$Mg}$_2$(μ-Me)$_2$][(BAr$^F_4$)$_2$] (**2**). If the reaction is performed in ethereal or nonpolar arene solvents, **2** undergoes Schlenk-type rearrangements to tris(NHC)-stabilized cations [(^{iPr}NHC)$_3$Mg(Me)][BAr$^F_4$] (**3**[**BAr$^F_4$**]) and [(^{iPr}NHC)$_3$Mg(Br)][BAr$^F_4$] (**4**[**BAr$^F_4$**]). These monomeric cations **3**[**A**] and **4**[**A**] (A = BAr$^F_4$, BPh$_4$) can be independently prepared as single pure products in high yields using common hydrocarbon solvents. The electronic influence of tris(carbene) stabilization is further evidenced by an NHC-mediated ionization of magnesium bromide in the absence of abstraction reagents. The reaction between the sterically unencumbered 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) ligand and (^{Me}NHC)$_2$MgBr$_2$ (**7**) resulted in two geometrically unique cations of the type [(^{Me}NHC)$_3$MgBr][Br]: complex **8a** bearing a weakly coordinating bromide anion resulting in a trigonal bipyramidal magnesium center, and complex **8b** bearing a noncoordinating bromide anion where the magnesium atom resides in a tetrahedral coordination environment. All isolated complexes were characterized by NMR spectroscopy and single-crystal X-ray diffraction, and their bonding was investigated by density functional theory (DFT).



INTRODUCTION

The study of alkaline-earth (Ae) metals in unusual coordination environments is currently experiencing a renaissance, attracting broad interest across the fields of chemical synthesis and catalysis.[1] Indeed, these elements were fairly recently discovered to facilitate stoichiometric and catalytic bond activations when the metal center resides in a low oxidation state or in a bonding situation that renders the metal electrophilic.[2] Due to the vital importance of electrostatic interactions between alkaline-earth metals and substrates,[3] a trend in utilizing charge separation to enhance the electrophilicity of the metal has emerged. The research groups of Harder and Hill have reported an array of β-diketiminate (NacNac)-stabilized cationic alkaline-earth complexes which formed stable, unsupported bonding interactions with a diverse array of arenes, terminal alkynes, silyl ethers, and phosphines.[4] Notably, these cations have been utilized as frustrated Lewis pair type reagents mediating two-electron dearomatization of benzene,[5] aromatization of cyclooctatetraene,[4d] and diverse reactivity at carbon−carbon multiple bonds.[4f,6]

When alkaline-earth metals bind to the anionic β-diketiminate framework, one electron is immediately consumed in bonding, leaving one terminal or bridging metal−organic unit. Thus, the formation of electrophilic cations via abstraction of an organic group affords an alkaline-earth center that is free of an exocyclic functional group (excluding weakly coordinating anions, Chart 1). In contrast, the use of L-type neutral ligands for the stabilization of cationic Ae complexes provides a well-defined functional group (e.g., CH_3^-) at the metal.[7] To this end, N-heterocyclic carbenes (NHCs) are particularly attractive as neutral ancillary ligands, due to their high donor strength, tunable sterics, and electronic flexibility.[8] However, despite being popular ligands in p-block and transition-metal chemistry, NHC s-block chemistry remains underexplored.[9] Thus, carbene-stabilized alkaline-earth cations are rare. This is mostly due to the fact that the solution-phase coordination chemistry of such species can be complex, where Schlenk-type ligand

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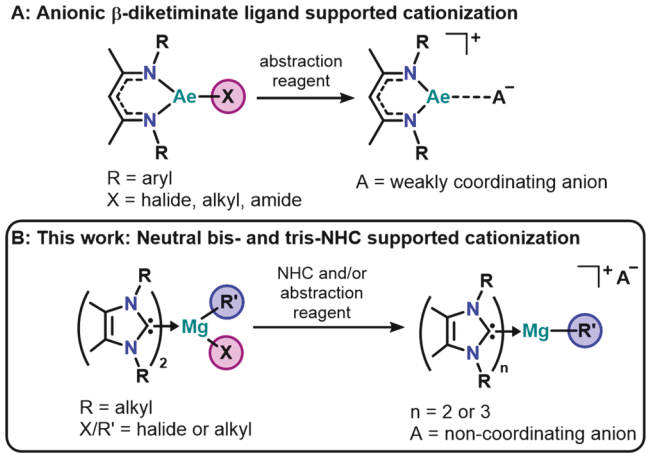
Chart 1. Bonding Comparison of Neutral and Anionic Ligand-Supported Alkaline-Earth Cations



redistributions and reversible solvent coordination are prominent, especially in their monodentate ligand supported adducts.[10] Nevertheless, recent remarkable advances in carbene-stabilized group 2 organometallics necessitate a reevaluation of the unique potential of NHCs for unusual transformations at these highly electropositive metal centers.[9d,11]

The utilization of NHCs in group 2 chemistry often requires sterically demanding *N*-aryl substitutions at the carbenes to induce kinetic stabilization around the metal center in a manner similar to NacNac-stabilized species. However, we recently initiated studies on the electronic influence of less sterically demanding NHCs on the structure and chemical properties of organoalkaline-earth reagents.[12] Employing a dual NHC coordination strategy with 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{iPr}NHC), we isolated the first carbene-stabilized terminal Grignard reagent (i.e., (^{iPr}NHC)$_2$MgMeBr (**1**)) along with a series of unsolvated monomeric magnesium alkyls and halides.[12a] This system resulted in persistent ligand coordination in contrast to dynamic solvent interaction observed in the mono-NHC-stabilized magnesium complexes.[7c,12a,13] We now report the syntheses and structural characterization of solvent-free organomagnesium cations stabilized by a nontethered multicarbene system. Notably, complexes **2**−**5** and **8** represent the first examples of cationic organomagnesium complexes benefiting from bis- and tris(carbene) stabilization.[14] Solvent-dependent ligand rearrangements from bis(NHC)- to tris(NHC)-stabilized cations are also observed. The electronic influence of multiple carbenes on magnesium halides is demonstrated in the carbene-mediated cationization of magnesium bromide in the absence of halide abstraction reagents, resulting in the remarkable isolation of geometrically unique Mg cations (**8a**,**b**) of the type [(^{Me}NHC)$_3$MgBr][Br] (^{Me}NHC = 1,3,4,5-tetramethylimidazol-2-ylidene).

RESULTS AND DISCUSSION

A Bis(N-heterocyclic carbene)-Stabilized Magnesium Dication. The bis-NHC Grignard reagent (^{iPr}NHC)$_2$MgMeBr (**1**)[12a] was treated with Na[BAr$^F_4$] (Ar^F = 3,5-bis(trifluoromethyl)phenyl) in chlorobenzene to afford compound **2** as a colorless solid in 63% yield (Scheme 1). The ^{1}H NMR spectrum of **2** in C_6D_5Br is consistent with two chemically equivalent ^{iPr}NHC ligands stabilizing a cationic Mg−Me fragment, where the characteristic carbene and methyl protons all resonate upfield of those of **1** (e.g., δ(Mg−CH_3) −1.02 ppm for **2** and −0.82 ppm for **1**).

The molecular structure of **2** was unambiguously determined by single-crystal X-ray diffraction, which revealed a dinuclear complex where the Mg atoms are each stabilized by two ^{iPr}NHC ligands and dissymmetrically bridged by their methyl substituents (Figure 1). The resulting dication is balanced by two

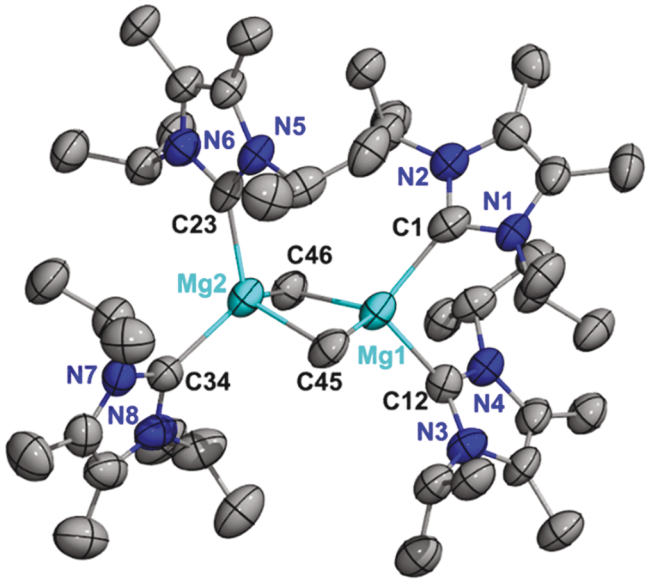
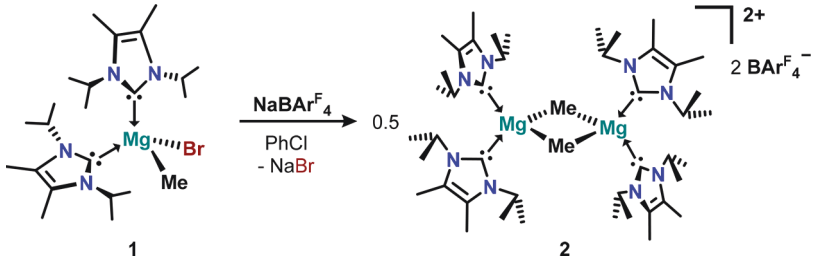


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability. H atoms, BAr$^F_4$ anions, and one cocrystallized chlorobenzene solvent molecule are omitted for clarity.

noncoordinating BAr$^F_4$ anions, indicating that the formation of the [Mg(μ-Me)]$_2^{2+}$ core (Mg···Mg 2.737(4) Å) is preferred over anion or arene solvent interactions. The ^{NHC}C−Mg bond distances (2.209(10)−2.233(12) Å) are slightly shortened from **1** (2.258(3) and 2.261(3) Å) and are in the range of reported examples.[12a−d,13] The Mg−(μ-Me) interactions (average

Scheme 1. Synthesis of a Bis(N-heterocyclic carbene)-Stabilized Magnesium Dication



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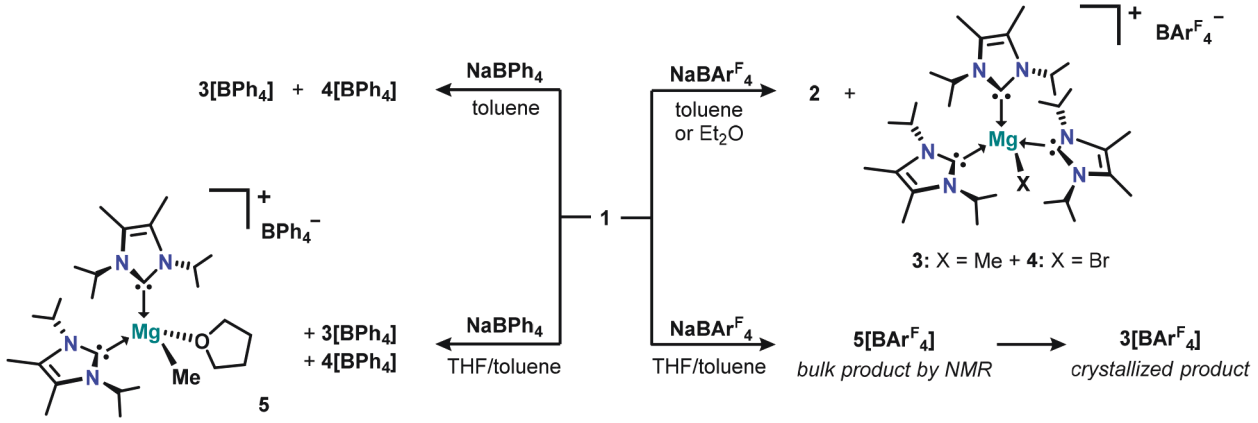
Scheme 2. Ligand Rearrangements of Bis(carbene) to Tris(carbene) Species: Solvent and Borate Anion Stabilization Effects



2.242(11) Å) are shorter than the terminal Mg−Me bond in **1** (2.277(5) Å), likely due to the dicationic nature of **2**. In contrast to similar homometallic organomagnesium complexes which feature planar dimers,[15] the $[Mg(\mu\text{-}Me)]_2^{2+}$ core in **2** exhibits a distorted metallacyclobutane "butterfly" configuration (Mg1−C46−Mg2 74.3(3)°, C45−Mg1−C46 102.7(4)°), where both Mg atoms lie slightly above the C46−Mg2−C45−Mg1 plane (torsion angle of 17.2(4)°) and the methyl groups slightly below. This rare distortion has been observed within an octamethyltrimagnesiate dianion.[16]

Ligand Rearrangements of Bis- to Tris(N-heterocyclic carbene)-Stabilized Magnesium Cations. The reaction between **1** and $Na[BAr^F_4]$ in toluene or diethyl ether yielded a mixture of **2** and the tris(NHC)-coordinated species $[(^{iPr}NHC)_3Mg(Me)][BAr^F_4]$ (**3**$[\mathbf{BAr^F_4}]$) and $[(^{iPr}NHC)_3Mg(Br)][BAr^F_4]$ (**4**$[\mathbf{BAr^F_4}]$) via Schlenk-type ligand rearrangements (Scheme 2). In notable contrast, the reaction of **1** and $Na[BPh_4]$ in toluene afforded exclusively the tris(carbene)-coordinated products **3**$[\mathbf{BPh_4}]$ and **4**$[\mathbf{BPh_4}]$. These observations suggest that the BAr^F_4 anions stabilize the formation of **2**, possibly due to intermediary $[Mg]^+\cdots F(BAr^F_4)$ contacts prior to dimerization to the dication. Similarly, the utilization of halogenated arene solvents may provide further halide-contact stabilization, as previously observed for cationic alkaline-earth complexes.[4a] Therefore, we expect that the combined stabilizing effects of the BAr^F_4 anion and chlorobenzene influenced the isolation of **2** as a pure product (Scheme 1).

We further investigated the influence of THF solvation on the isolation of these cations. The reaction between **1** and $Na[BPh_4]$ in THF or a toluene/THF mixture yielded a complex mixture of products, including $[(THF)(^{iPr}NHC)_2Mg(Me)][BPh_4]$ (**5**$[\mathbf{BPh_4}]$) and the tris(NHC) species **3**$[\mathbf{BPh_4}]$ and **4**$[\mathbf{BPh_4}]$ as observed by NMR. Recrystallization of this mixture in bromobenzene/hexanes yielded colorless crystals identified by X-ray diffraction as the expected monomeric structure, which also included $[(^{iPr}NHC)_2(THF)Mg(Br)][BPh_4]$ in 4% population (Figure 2). Notably, the bulk solid recovered from the reaction between **1** and $Na[BAr^F_4]$ in THF was spectroscopically determined to be the single species **5**$[\mathbf{BAr^F_4}]$. However, **5**$[\mathbf{BAr^F_4}]$ rearranges and crystallizes from a concentrated THF/toluene mixture as the tris(NHC) species **3**$[\mathbf{BAr^F_4}]$ over 2 days at room temperature.

Gas-phase DFT (ωB97X-D/BS1) suggests a thermodynamic preference for the formation of **3** (−55.1 kcal/mol relative to **1**) over the bis(NHC) complexes **2** (−40.3 kcal/mol) and **5** (−41.4 kcal/mol, Figure S25). In contrast, the inclusion of solvation models for toluene resulted in a preference for **5** (−80.0 kcal/mol) over **3** (−33.1 kcal/mol), highlighting the observed stabilization of THF-coordinated bis(NHC) cations in the solvent. In addition to the dynamic THF coordination observed, the rearrangements in **5** are perhaps unsurprising, as coordinating solvents play a significant role in Schlenk-type ligand redistributions.[17] Therefore, we targeted the solvent-free tris(NHC)-stabilized cations as single products using common hydrocarbon solvents.

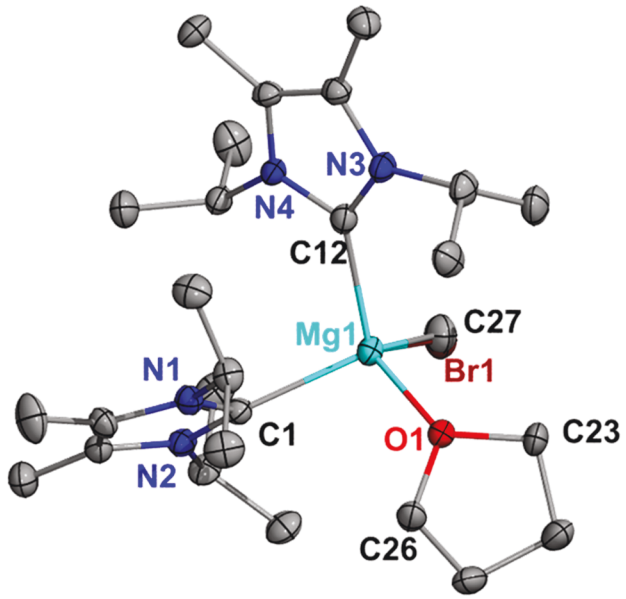


Figure 2. X-ray structure of **5**$[\mathbf{BPh_4}]$ including 4% cocrystallized $[(^{iPr}NHC)_2(THF)Mg(Br)][BPh_4]$. Thermal ellipsoids are shown at 50% probability. H atoms and the BPh_4 anion are omitted for clarity. Selected bond distances and angles are shown in Table 1.

Direct Syntheses and Structural Analyses of Tris(N-heterocyclic carbene)-Stabilized Magnesium Cations. Colorless crystalline solids of complexes **3** and **4** were isolated in 49−80% yields by combining $(^{iPr}NHC)_2Mg(X)(Br)$ (**1**, X = Me; **6**, X = Br),[12a] ^{iPr}NHC, and $Na[BAr^F_4]$ or $Na[BPh_4]$ in toluene (Scheme 3). Evidence of donor-rich metal centers can be found in higher-field resonances of the carbene methine protons (δ 4.72 for **3**$[\mathbf{BAr^F_4}]$ and δ 4.73 for **3**$[\mathbf{BPh_4}]$ in C_6D_6) with respect to **1** (δ 5.62). The nearly identical methine resonances in **3** are similarly observed for **4** (δ 4.90 for both **4**$[\mathbf{BAr^F_4}]$ and **4**$[\mathbf{BPh_4}]$ in CD_2Cl_2). This suggests that the

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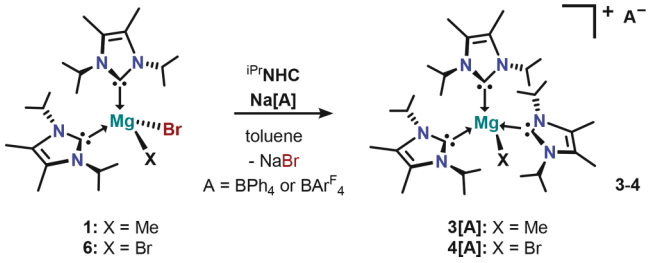
Scheme 3. Syntheses of Tris(N-heterocyclic carbene)-Stabilized Magnesium Cations



nature of the noncoordinating anion does not significantly influence the electronics in these tris(carbene)-stabilized magnesium cations. The methyl protons in **3**[$\mathbf{BAr^F_4}$] (δ −0.90) and **3**[$\mathbf{BPh_4}$] (δ −0.86) are significantly upfield of **1** (δ −0.45), suggesting increased nucleophilicity from the neutral Grignard.

Suitable single crystals of **3**[$\mathbf{BAr^F_4}$], **3**[$\mathbf{BPh_4}$], **4**[$\mathbf{BAr^F_4}$], and **4**[$\mathbf{BPh_4}$] were obtained and analyzed by X-ray diffraction, revealing the expected mononuclear complexes (Figure 3 and Figures S1 and S2). Each structure maintains a distorted tetrahedral geometry around the magnesium cation, which is stabilized by three ^{iPr}NHC ligands and one noncoordinating borate anion. The ^{NHC}C−Mg distances in **3** and **4** (see Table 1) are also comparable to those in **2** and the neutral bis-NHC complexes. The similarity in ^{NHC}C−Mg distances for **3**[$\mathbf{BAr^F_4}$] [(2.262(5), 2.276(6), 2.281(6) Å) is reflected in the geometry around the magnesium atom, where the bond angles (103.6−112.2°) only slightly deviate from the ideal 109.5° of a perfect tetrahedron. A detailed comparison of structural parameters for **2**−**5** is summarized in Table 1.

Compound **3** may also be prepared using THF, thus indicating that tris(NHC) stabilization affords the electronic benefit of persistent carbene coordination, which is competitive against donor solvents. In contrast, compound **4** is substantially more sensitive than **3** to adventitious moisture in THF, despite considerable effort to rigorously dry the reaction solvents. Therefore, crystallization of hydrolysis products of the type [(^{iPr}NHC)H][BR_4][18] (R = Ph, Ar^F) from THF solutions of **4** was consistently observed. Additionally, **3**[$\mathbf{BPh_4}$] displays significantly improved solubility in arene solvents in comparison to **2**, thus rendering it a more practical alternative for synthetic applications where donor solvents should be avoided. Notably, compounds **2**−**4** are stable as solids in an inert atmosphere for at least 3 months at room temperature and up to 2 weeks in anhydrous arene solvents at −37 °C.

N-heterocyclic Carbene Mediated Heterolysis of Magnesium Bromide. To further probe the electronic influence of multiple NHCs on magnesium complexes, we investigated the ionization of magnesium bromide ($MgBr_2$) in the absence of halide abstraction reagents. In order to maximize donor interactions with the metal center, the sterically unencumbered 1,3,4,5-tetramethylimidazol-2-ylidene (^{Me}NHC) ligand[19] was chosen for this investigation. Similar to the case for **6**,[12a] the neutral bis-NHC species (^{Me}NHC)$_2$$MgBr_2$ (**7**) was obtained as a colorless solid in 84% yield from the addition of 2 equiv of ^{Me}NHC to $MgBr_2$ in toluene (Scheme 4). The X-ray structure of **7** (Figure 4 and Table 1) reveals metrical parameters comparable to those of **6**.

Starting from a suspension of **7** in chlorobenzene, the addition of 1 or 2 equiv of ^{Me}NHC immediately yielded a colorless solution (Scheme 4). The ^{1}H NMR of the isolated product in C_6D_5Br revealed a single NHC coordination environment (two singlets at δ 3.55 and 1.60) with the α-CH_3 resonance (δ 3.55) being significantly broadened. This suggests a possible dynamic equilibrium in solution, although the existence of more than one unique species in solution could not be resolved using variable-temperature (VT) NMR experiments (C_6D_5Br, 373−248 K). Access to lower temperatures was limited by the freezing point of C_6D_5Br (−30.7 °C) and the overall poor solubility of this compound in common organic solvents. However, single-crystal X-ray diffraction studies revealed that two distinct molecules, **8a** and **8b**, cocrystallized in the solid state in a 1:1 ratio (Figure 5).

Complex **8a** is an unusual trigonal bipyramidal magnesium complex stabilized by three ^{Me}NHC ligands in the equatorial plane and two Br ligands in the axial positions. The Mg−Br distances in **8a** (2.694(3) and 2.883(3) Å) are significantly elongated by 0.18−0.40 Å from the neutral bis(NHC) complex **7** (2.487(3) and 2.510(3) Å), as well as the expected additive covalent radii between Mg and Br (2.53 Å).[20] Thus, **8a** may be considered as either a neutral L_3MgBr_2 complex or a cationic magnesium complex stabilized by a weakly coordinating bromide anion. In contrast, **8b** can only be described as an

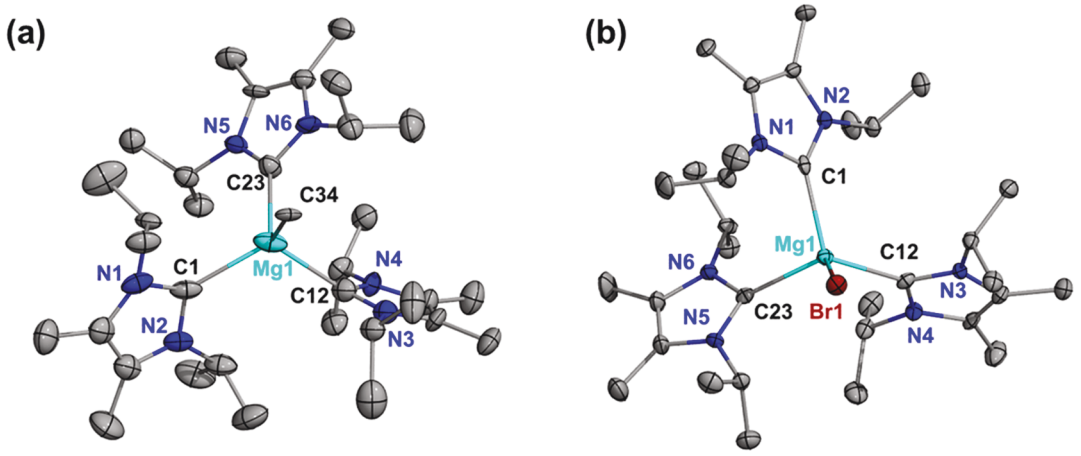


Figure 3. X-ray structures of BPh_4 salts for **3** (a) and **4** (b). Thermal ellipsoids are shown at 50% probability. H atoms and anions are hidden for clarity. Only the major occupied positions are shown for the disordered C12 and C23 imidazole frameworks and *N*-isopropyl substituents in (a). **3**[$\mathbf{BAr^F_4}$] (Figure S1) and **4**[$\mathbf{BAr^F_4}$] (Figure S2) are shown in the Supporting Information.

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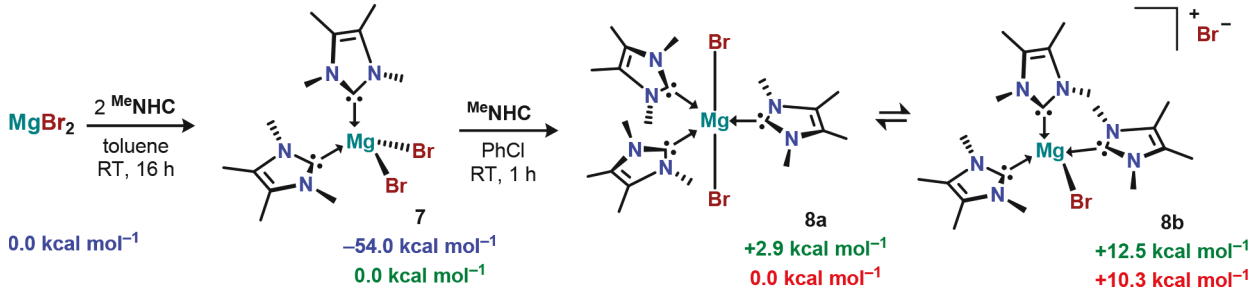
Table 1. Selected Bond Distances[a] and Angles[b] for Compounds 2−5, 7, and 8

	2	3[BAr^F_4]	3[BPh_4]	4[BAr^F_4]	4[BPh_4]	5[BPh_4]	7	8a	8b
^{NHC}C−Mg	2.233(12)	2.262(5)	2.277(2)	2.2360(18)	2.209(3)	2.260(2)	2.234(13)	2.214(5)	2.215(5)
	2.209(10)	2.276(6)	2.163(7)	2.2554(18)	2.210(3)	2.246(3)	2.217(13)		
	2.228(10)	2.281(6)	2.271(2)	2.2434(18)	2.251(3)				
	2.212(11)								
^{Me}C−Mg	2.223(11)	2.154(5)	2.2557(19)			2.178(14)			
	2.246(10)								
	2.215(10)								
	2.285(11)								
Mg1−Br1				2.4934(6)	2.5195(9)		2.510(3)	2.883(3)	2.513(3)[c]
Mg1−Br2							2.487(3)	2.694(3)	
C1−N1	1.363(13)	1.364(7)	1.369(3)	1.360(2)	1.394(3)	1.365(3)	1.333(13)	1.361(7)	1.348(7)[d]
C1−N2	1.356(13)	1.376(6)	1.391(3)	1.360(2)	1.364(3)	1.360(3)	1.339(13)	1.361(7)	1.359(7)[e]
C1−Mg1−C12	100.1(4)	108.85(19)	114.5(3)	113.16(6)	115.3(11)	99.32(9)	108.9(4)[h]	119.77(3)[h]	109.70(15)[f]
C1−Mg1−C23		111.4(2)	108.76(7)	107.38(6)	101.59(10)	98.60(8)[i]			
C1−Mg1−X[j]	115.7(4)	109.8(2)	112.87(7)	107.99(5)	107.33(8)	107.1(4)	106.3(3)	87.25(16)	109.24(15)[g]
	115.5(4)						108.0(3)	92.75(16)	
X^1−Mg−X^2	102.7(4)						119.41(11)	180.00(6)	
	101.7(4)								
N1−C1−N2	104.5(9)	103.2(4)	102.54(17)	103.94(14)	104.1(2)	103.51(19)	104.9(10)	102.6(4)	104.0(4)

[a]In angstroms. [b]In degrees. [c]Mg2−Br3. [d]C8−N3. [e]C8−N4. [f]C8−Mg2−C8′. [g]C8−Mg2−Br3. [h]C8 (7) and C1′ (8a) were used instead of C12. [i]O1 was used instead of C23 for 5[BPh_4]. [j]X represents Me or Br where applicable.

Scheme 4. NHC-Mediated Heterolysis of $MgBr_2$: Syntheses and Calculated Reaction Energetics[a]



[a]SMD-ωB97X-D//ωB97X-D/BS1 reaction energetics (ΔG) using implicit solvation models for toluene (blue values), chlorobenzene (green values), and bromobenzene (red values) solvents.

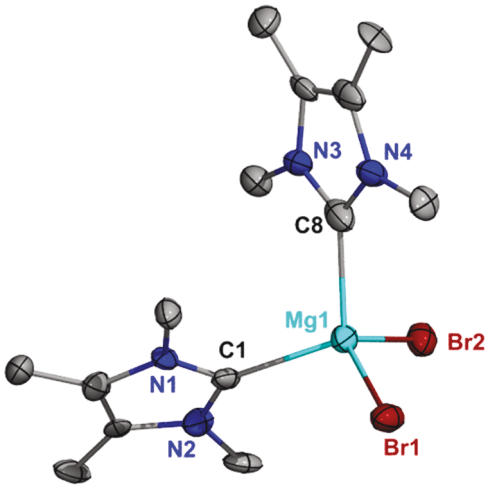


Figure 4. X-ray structure of 7. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

ionic [L_3MgBr][Br] complex. The crystal structure of **8b** reveals a tetracoordinate magnesium cation stabilized by three carbenes and a bromide ligand, with the second bromide acting as a noncoordinating anion. The closest contact between Mg2 and the noncoordinating bromide, Br4 (6.374(2) Å) is nearly double the expected van der Waals separation between Mg and Br (3.56 Å).[21] The Mg2−Br3 bond length in **8b** (2.513(3) Å) is significantly shorter than those of **8a** but is comparable to those of **4** and **7** (see Table 1). In both **8a** and **8b**, a crystallographic 3-fold rotation axis passes through the Mg−Br bond, and only one carbene is found in the asymmetric unit of each species. Thus, the ^{NHC}C−Mg bond distances for **8a** (2.214(5) Å) and **8b** (2.215(5) Å) are similarly identical. This results in a D_{3h} symmetry for **8a** where Br1−Mg−Br2 is exactly 180° and the ^{NHC}C−Mg−^{NHC}C angles are each 120°, as well as a C_{3v} symmetry for the cationic fragment in **8b**, which maintains a nearly perfect tetrahedral geometry (109.24−109.70(15)°) around the magnesium center.

Complexes **1** and **6** were found to be unreactive with ^{iPr}NHC under conditions similar to those for the reaction of **7** with ^{Me}NHC, likely due to steric hindrance from the isopropyl groups. This indicates that the formation of **3** and **4** proceeded via initial halide abstraction followed by carbene coordination. Theoretical calculations (SMD(chlorobenzene)-ωB97X-D//ωB97X-D/BS1) suggest a small energy penalty of +2.9 kcal mol^{-1} for the formation of **8a** by complexation of an additional

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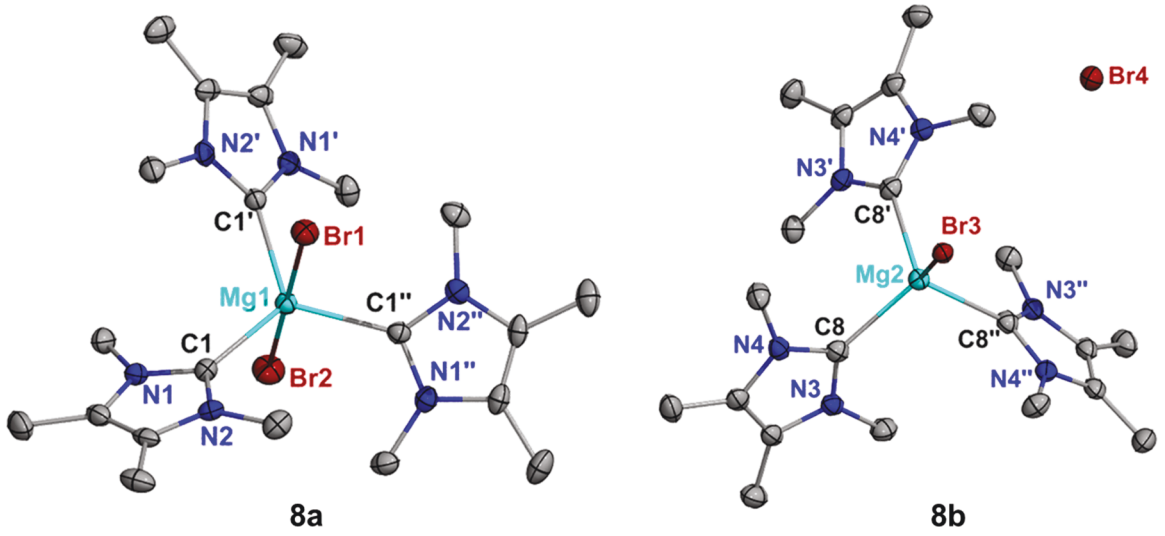

Figure 5. X-ray structures of **8a** and **8b**. Thermal ellipsoids are shown at 50% probability. H atoms are omitted for clarity.

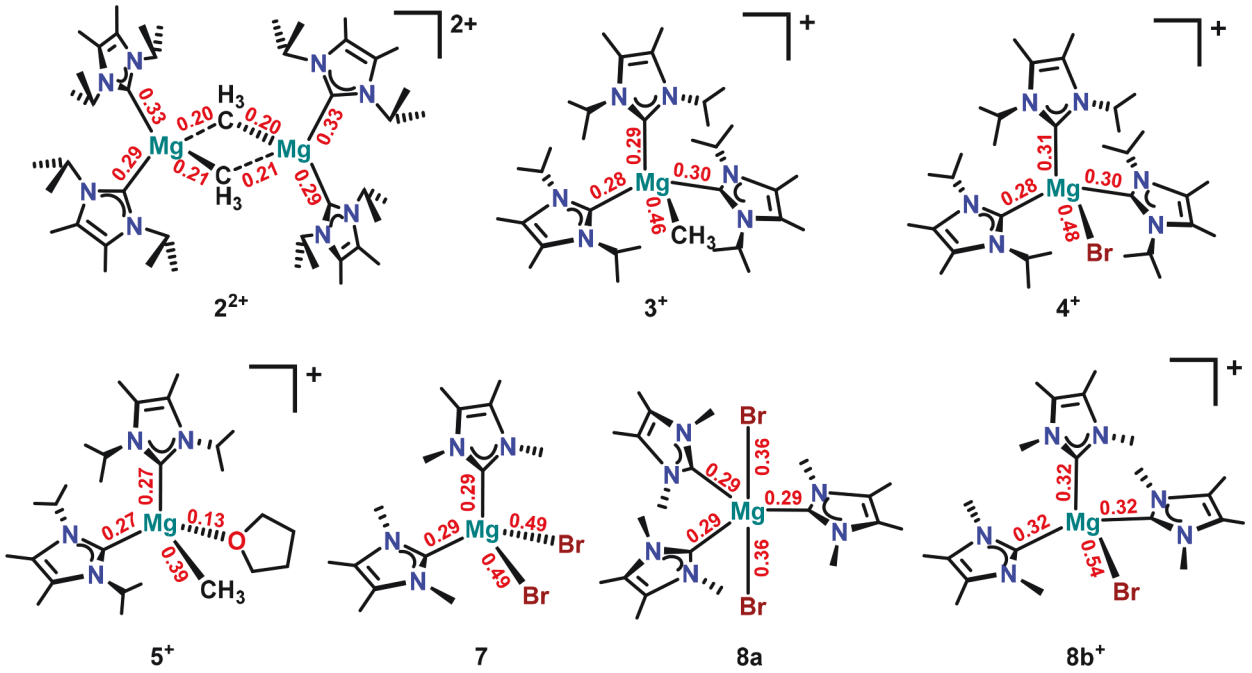

Figure 6. Comparison of NAO-Wiberg bond index (WBI) values for each reported compound.

NHC to **7**. Further displacement of a weakly coordinating bromide ligand to form **8b** is calculated to be endergonic by 9.6 kcal mol^{-1}, thus indicating a thermodynamic preference for **8a** in the suggested equilibrium. Nevertheless, the existence of **8a** and **8b** in the solid state indicates that multiple NHCs can easily ionize neutral magnesium complexes containing halides. The unique geometry of **8a**, owing to the use of sterically unencumbered carbenes, indicates that the magnesium center may be able to accommodate additional carbenes to access further ionized or polarized species. Ionization of the remaining covalent Mg−Br interaction using excess carbenes, extended reaction times, or halide abstraction reagents has resulted in species spectroscopically dissimilar from **7** and **8**, but their poor solubility hindered successful crystallization attempts. Likewise, we explored an alternate route to **8** by the direct addition of 3 equiv of ^{Me}NHC to a suspension of $MgBr_2$ in toluene. The resulting complex was spectroscopically comparable to **8** (δ 3.57 (broad) and 1.60), thereby indicating that the direct heterolysis of polymeric $MgBr_2$ could be achieved without initial isolation of the neutral bis(NHC)-stabilized species.

Theoretical Analysis. In order to gain more insight into the structure and bonding of the bis- and tris(NHC) magnesium systems, DFT geometry optimizations were performed at the ωB97X-D/BS1 level of theory. Overall, the Wiberg bond index (WBI) values computed for the ^{NHC}C−Mg bonds in the cationic complexes (Figure 6) are comparable to those of the neutral bis-NHC complexes,[12a] with only slight increase in values, which are most pronounced for $\mathbf{2}^{2+}$ (0.29 and 0.33) and $\mathbf{8b}^{+}$ (0.32).

Relative to their neutral precursors, higher Mg−X WBI values are generally observed for the cationic complexes. The Mg−Me bond in $\mathbf{3}^{+}$ (WBI 0.46) displays a greater degree of covalency in comparison to those in **1** (0.37) and $\mathbf{5}^{+}$ (0.39). The lower WBIs for the Mg−(μ-Me) bonds in $\mathbf{2}^{2+}$ (0.21, 0.20) relative to the terminal Mg−Me bonds in **1**, **3**, and **5** suggest a significantly

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greater degree of charge separation between the Mg cations and bridging methyl anions. This observation is further supported by an inspection of the natural charges (Table S2) and Pipek–Mezey localized molecular orbitals for the Mg–(μ-Me) interactions in $\mathbf{2}^{2+}$ (Figure S31). Expectedly, the WBI value for Mg–Br in (^{Me}NHC)$_2$MgBr$_2$ (**7**) is the same as that previously reported for (^{iPr}NHC)$_2$MgBr$_2$.[12a] However, the value for the Mg–Br bond in the ^{iPr}NHC-stabilized cation $\mathbf{4}^+$ (0.48) is lower than that of the ^{Me}NHC-stabilized cation $\mathbf{8b}^+$ (0.54), despite only slight differences in their ^{NHC}C–Mg WBI values ($\mathbf{4}^+$: 0.28, 0.30, 0.31; $\mathbf{8b}^+$: 0.32). The larger difference in WBI values for the Mg–Br bonds in **8a** (0.36) and $\mathbf{8b}^+$ (0.54), which are on either side of **7** (0.49), corroborates the weakly coordinating nature of the bromide anions in **8a**.

CONCLUSION

We have isolated the first examples of organomagnesium cations benefiting from untethered bis- and tris(carbene) stabilization. The bis(NHC)-stabilized complexes exhibited solvent-dependent Schlenk-type ligand rearrangements to hitherto unknown organomagnesium complexes benefiting from unsupported tris(carbene) stabilization. The facile and high yielding syntheses of **3** and **4** demonstrate that tris(carbene)-supported ionization using easily accessible halide abstraction reagents can be extended to other magnesium halide systems. We further explored the electronic influence of tris(carbene) stabilization in the NHC-mediated heterolysis of polymeric magnesium bromide. These types of solvent-free, base-saturated species are expected to have beneficial applications in molecular alkaline-earth reduction chemistry[22] and small molecule activation.[1a,7a,23] Thus, investigations into the reactivity of these cations with hydride sources, small molecule substrates and reducing agents are currently underway and will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques or in a MBRAUN LABmaster glovebox equipped with a –37 °C freezer and operating at <0.1 ppm of H_2O and O_2. Glassware were oven-dried at 190 °C overnight. Halogenated solvents (dichloromethane, bromobenzene, and chlorobenzene) were purified by distillation over calcium hydride for at least 48 h and degassed with 3× freeze–pump–thaw cycles. Toluene, hexanes, and THF were distilled over sodium. Deuterated solvents were purchased from Acros Organics and Cambridge Isotope Laboratories and dried the same way as their protic analogues. The NMR spectra were recorded on the following instruments: a Varian Inova 500 MHz (^{1}H, 500.13 MHz), a Varian NMRS 600 MHz (^{1}H, 600 MHz; ^{13}C, 150.90 MHz; ^{11}B NMR, 192.55 MHz), and a Bruker Avance III 800 MHz (^{1}H, 800.13 MHz; ^{13}C, 201.19 MHz). Proton and carbon chemical shifts are reported in ppm and are referenced to $SiMe_4$ using the residual proton and carbon signals of the deuterated solvent (^{1}H, C_6D_6, δ 7.16; ^{13}C, C_6D_6, δ 128.06; ^{1}H, CD_2Cl_2, δ 5.32; ^{13}C, CD_2Cl_2, δ 53.84, ^{1}H, C_6D_5Br, δ 6.95 (*m*-H); ^{13}C, C_6D_5Br, δ 122.21). Boron chemical shifts were referenced using an external standard (^{11}B, $BF_3{\cdot}Et_2O$, δ 0.0). Data are ordered as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constants (*J*/Hz), and integration. X-ray intensity data were measured on a Bruker Kappa APEXII Duo system. An Incoatec Microfocus IμS (Cu Kα, λ = 1.54178 Å) and a multilayer mirror monochromator were used for **2**, **3**[$\mathbf{BAr^F_4}$], **4**[$\mathbf{BAr^F_4}$], **5**[$\mathbf{BPh_4}$], and **8**, and a fine-focus sealed tube (Mo Kα, λ = 0.71073 Å) and a graphite monochromator were used for **3**[$\mathbf{BPh_4}$], **4**[$\mathbf{BPh_4}$], and **7**. Each structure was solved and refined using the Bruker SHELXTL Software Package[24] within APEX3[25] and OLEX2.[26] Crystallographic data are summarized in Table S1. Anhydrous $MgBr_2$ (98%, Strem Chemicals) and Na[BPh_4] (>99.5%, Sigma-Aldrich) were used as received. Na[BAr^F_4],[27] ^{iPr}NHC,[19] and ^{Me}NHC[19,28] were prepared according to literature and recrystallized before use. (^{iPr}NHC)$_2$MgMeBr (**1**) and (^{iPr}NHC)$_2$MgBr$_2$ (**6**) were prepared as previously reported.[12a] Elemental analyses yielded overall unsatisfactory results due to the extreme air and moisture sensitivity of these compounds. Similar challenges with determining the purity of group 2 complexes using combustion microanalysis have been well documented.[13,29] Therefore, NMR spectroscopy was used to determine bulk purity, and the spectra of all compounds are provided in the Supporting Information.

Synthesis of [{(^{iPr}NHC)$_2$Mg}$_2$(μ-Me)$_2$][($\mathbf{BAr^F_4}$)$_2$], (2). In a 20 mL scintillation vial, a chlorobenzene solution (5 mL) of Na[BAr^F_4] (93 mg, 0.105 mmol) was added dropwise to a stirred solution of **1** (50 mg, 0.104 mmol) in the same solvent. After 3 h, trace solids presumed to be NaBr were removed via filtration. The recovered light bronze solution was concentrated under reduced pressure before addition of hexanes (3 mL) to precipitate the product as a white solid, which was further washed with hexanes (1 × 5 mL) and dried under vacuum (83 mg, 63%). X-ray-quality single crystals were grown from a concentrated C_6H_5Cl/hexanes solution of **2** in a –37 °C freezer. Notably, **2** may also be prepared using the ether solvate Na[BAr^F_4]·3.5Et_2O. ^{1}H NMR (500 MHz, C_6D_5Br, 398 K): δ 8.07 (s, 8H, Ar(*o*-H)), 7.61 (s, 4H, Ar(*p*-H)), 4.30 (br s, 4H, CH-*i*Pr), 1.86 (s, 12H, C(CH_3)), 1.21 (d, *J* = 7.0 Hz, 24H), –1.02 (s, 3H, Mg(CH_3)). ^{11}B NMR (192.55 MHz, C_6D_5Br, 398 K): δ –6.02. Due to poor solubility, a sufficiently resolved ^{13}C NMR spectrum could not be obtained.

Synthesis of [(^{iPr}NHC)$_3$MgMe][$\mathbf{BAr^F_4}$] (3[$\mathbf{BAr^F_4}$]). In a 20 mL scintillation vial, free ^{iPr}NHC (19 mg, 0.104 mmol) and **1** (50 mg, 0.104 mmol) were dissolved in toluene (15 mL) and stirred. Then, Na[BAr^F_4] (93 mg, 0.105 mmol) was added slowly to the cloudy mixture and stirred for 6 h at room temperature. A clear solution was recovered via filtration, and the remaining solids were extracted with additional toluene (5 mL), leaving behind trace off-white solids presumed to be NaBr. The filtrate was concentrated under vacuum and stored at room temperature, yielding large colorless platelike crystals suitable for single-crystal X-ray diffraction. After drying under vacuum, **3**[$\mathbf{BAr^F_4}$] was recovered as a crystalline white solid (120 mg, 80%). Notably, **3**[$\mathbf{BAr^F_4}$] may also be prepared using THF without the formation of solvated products. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 8.33 (s, 8H, Ar(*o*-H)), 7.68 (s, 4H, Ar(*p*-H)), 4.72 (br s, 6H, CH-*i*Pr), 1.63 (s, 18H, C(CH_3)), 1.01 (br s, 36H, CH_3-*i*Pr), –0.90 (s, 3H, Mg(CH_3)). Due to poor solubility, a sufficiently resolved ^{13}C{^{1}H} NMR could not be obtained in C_6D_6. Although they were successfully characterized in CD_2Cl_2, complexes **3** and **4** slowly convert into unidentified products after 2 h in that solvent. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.71 (s, 8H, Ar(*o*-H)), 7.56 (s, 4H, Ar(*p*-H)), 4.84 (sept, *J* = 7.0 Hz, 6H, CH-*i*Pr), 2.20 (s, 18H, C(CH_3)), 1.32 (d, *J* = 7.7 Hz, 36H, CH_3-*i*Pr), –1.35 (s, 3H, Mg(CH_3)). ^{13}C NMR (150.90 MHz, CD_2Cl_2, 298 K): 186.2, 182.6, 135.2, 129.2, 126.3, 125.9, 124.1, 117.9, 22.6, 10.7, –8.9. ^{11}B NMR (192.55 MHz, CD_2Cl_2, 298 K): δ –6.67.

Synthesis of [(^{iPr}NHC)$_3$MgMe][$\mathbf{BPh_4}$] (3[$\mathbf{BPh_4}$]). In a 100 mL round-bottomed flask, ^{iPr}NHC (39 mg, 0.219 mmol) and **1** (102 mg, 0.213 mmol) were dissolved in toluene (50 mL) and stirred at room temperature before Na[BPh_4] (80 mg, 0.233 mmol) was added to the cloudy mixture. After 16 h, a colorless solution was recovered via filtration and reduced to incipient recrystallization, yielding large blocklike colorless crystals suitable for X-ray diffraction at room temperature. Solids recovered from filtration were further extracted with toluene (15 mL). After removal of volatiles, **3**[$\mathbf{BPh_4}$] was recovered as a crystalline white solid (135 mg, 71% yield). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 8.12 (m, 8H, Ar(*m*-H)), 7.36 (t, *J* = 7.3 Hz, 8H, Ar(*o*-H)), 7.21 (t, *J* = 7.3 Hz, 4H, Ar(*p*-H)), 4.73 (sept, *J* = 7.0 Hz, 6H, CH-*i*Pr), 1.66 (s, 18H, C(CH_3)), 1.04 (d, *J* = 7.1 Hz, 36H, CH_3-*i*Pr), –0.86 (s, 3H, Mg(CH_3)). ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, 298 K): δ 182.2, 137.5, 126.1, 122.1, 53.2, 22.4, 10.3. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.31 (m, 8H, Ar(*m*-H)), 7.02 (t, *J* = 7.5 Hz, 8H, Ar(*o*-H)), 6.87 (t, *J* = 7.2 Hz, 4H, Ar(*p*-H)), 4.84 (sept, *J* = 7.0 Hz, 6H, CH-*i*Pr), 2.21 (s, 18H, C(CH_3)), 1.34 (d, *J* = 8.1 Hz, 36H, CH_3-*i*Pr),

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−1.34 (s, 3H, Mg(CH_3)). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2, 298 K): δ 182.4, 164.7, 136.3, 126.3, 126.0, 122.1, 22.6, 10.8, −8.96. ^{11}B NMR (192.55 MHz, CD_2Cl_2, 298 K): δ −6.44.

Synthesis of [(^{iPr}NHC)$_3$MgBr][BAr$^F_4$] (4[BAr$^F_4$]). The same procedure was followed as for the preparation of 3[BAr$^F_4$], using (^{iPr}NHC)$_2$MgBr$_2$ (57 mg, 0.104 mmol) and the corresponding molar equivalents of ^{iPr}NHC (19 mg, 0.104 mmol) and Na[BAr$^F_4$] (93 mg, 0.105 mmol) in toluene. After 6 h, a light bronze solution was recovered via filtration and the expected product further extracted from the precipitated solids using chlorobenzene (5 mL). The solutions recovered were concentrated under vacuum and, upon light agitation, precipitated colorless blocklike crystals, which were further dried under vacuum to obtain 4[BAr$^F_4$] a colorless solid (76 mg, 49% yield). ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.71 (s, 8H, Ar(*o*-H)), 7.56 (s, 4H, Ar(*p*-H)), 4.90 (sept, *J* = 7.0 Hz, 6H, CH-*i*Pr), 2.22 (s, 18H, C(CH_3)), 1.36 (d, *J* = 7.1 Hz, 36H, CH_3-*i*Pr). ^{13}C NMR (150.9 MHz, CD_2Cl_2, 298 K): δ 177.7, 162.7, 162.3, 162.0, 161.7, 135.2, 129.4, 129.2, 127.7, 127.1, 125.9, 124.1, 117.9, 54.1, 22.6, 10.7. ^{11}B NMR (192.55 MHz, CD_2Cl_2, 298 K): δ −6.67.

Synthesis of [(^{iPr}NHC)$_3$MgBr][BPh$_4$] (4[BPh$_4$]). The same procedure was followed as for the preparation of 3[BAr$^F_4$], using Na[BPh$_4$] (36 mg, 0.104 mmol) and the corresponding molar equivalents of (^{iPr}NHC)$_2$MgBr$_2$ and ^{iPr}NHC in toluene. After 3 days, colorless precipitates were collected over a fritted Buchner funnel and dried under vacuum. Due to the poor solubility of the product, NaBr was not removed prior to yield (111 mg, quantitative) and NMR analyses, the latter revealing a single pure product (Figure S14). An aliquot of the product was concentrated in C_6H_5Br and layered with hexanes, yielding X-ray-quality single crystals of 4[BPh$_4$] at −37 °C. Note: despite rigorous efforts at drying the reaction solvents, the hydrolysis product [(^{iPr}NHC)H][BPh$_4$][18] was regularly obtained alongside 4[BPh$_4$] during crystallization. ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.31 (m, 8H, Ar(*m*-H)), 7.02 (t, *J* = 7.4 Hz, 8H, Ar(*o*-H)), 6.87 (t, *J* = 7.3 Hz, 4H, Ar(*p*-H)), 4.90 (sept, *J* = 7.0 Hz, 6H, CH-*i*Pr), 2.23 (s, 18H, C(CH_3)), 1.37 (d, *J* = 7.1 Hz, 36H, CH_3-*i*Pr). ^{13}C NMR (150.9 MHz, CD_2Cl_2, 298 K): δ 186.2, 177.7, 165.0, 136.3, 127.11, 125.99, 125.98, 122.1, 54.1, 22.6, 10.8. ^{11}B NMR (192.55 MHz, CD_2Cl_2, 298 K): δ −6.60.

Synthesis of [(^{iPr}NHC)$_2$(THF)Mg(Me)][BAr$^F_4$] (5[BAr$^F_4$]). A THF (5 mL) solution of Na[BAr$^F_4$]·3.5Et$_2$O (60 mg, 0.0524 mmol) was added dropwise to a stirred colorless THF (5 mL) solution of **1** (25 mg, 0.0521 mmol) in a 20 mL scintillation vial. After 12 h, a colorless solution was recovered over a 0.45 μm pore syringe filter, and the volatiles were removed under vacuum with trituration/wash using hexanes (4 × 5 mL). After initial spectroscopic analysis, the off-white solid recovered was concentrated in toluene/THF and crystallized as the tris(carbene) adduct 3[BAr$^F_4$]. Notably, the THF coordination in the bulk sample 5[BAr$^F_4$] was found to be persistent against evacuation over several hours. ^1H NMR (600 MHz, C_6D_6, 298 K): δ 8.33 (s, 8H, Ar(*o*-H)), 7.68 (s, 4H, Ar(*p*-H)), 4.31 (br. s, 4H, CH-*i*Pr), 3.46 (s, O(CH_2)-THF), 1.57 (s, 12H, C(CH_3)), 1.36(s, CH_2(CH_2)-THF), 0.98 (m, 24H, CH_3-*i*Pr), −1.04 (s, 3H, Mg(CH_3)). Due to poor solubility, a sufficiently resolved ^{13}C NMR spectrum could not be obtained.

Synthesis of [(^{iPr}NHC)$_2$(THF)MgMe][BPh$_4$] (5[BPh$_4$]). The same procedure was followed as for the preparation of 5[BAr$^F_4$] using Na[BPh$_4$] (35 mg, 0.104 mmol) instead of Na[BAr$^F_4$]. Colorless single crystals suitable for X-ray diffraction were obtained from a C_6H_5Br/hexanes solution. ^1H NMR revealed a complex mixture of 5[BPh$_4$] and the ligand rearrangement products 3[BPh$_4$] and 4[BPh$_4$], and the corresponding resonances were all identified (Figure S24). Notably, this reaction yielded similar results when it was performed with THF/toluene mixtures instead of pure THF. ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ 7.30 (m, 8H, Ar(*m*-H)), 7.02 (t, *J* = 7.4 Hz, 8H, Ar(*o*-H)), 6.87 (t, *J* = 7.2 Hz, 4H, Ar(*p*-H)), 4.64 (sept, *J* = 7.1 Hz, 4H, CH-*i*Pr), 3.87 (m, 4H, O(CH_2)-THF), 2.19 (s, 12H, C(CH_3)), 1.96 (m, CH_2(CH_2)-THF), 1.40 (d, *J* = 7.1 Hz, 24H, CH_3-*i*Pr), −1.42 (s, 3H, Mg(CH_3)). Due to unsuccessful attempts to isolate pure samples of 5[BPh$_4$] from the ligand rearrangement minor products, $^{13}C\{^1H\}$ NMR and yield analyses were not performed.

Synthesis of (^{Me}NHC)$_2$MgBr$_2$ (7). Free ^{Me}NHC (70 mg, 0.564 mmol) was added to a stirred toluene (15 mL) suspension of MgBr$_2$ (52 mg, 0.282 mmol). After 16 h, white precipitates were recovered via filtration and dried under vacuum to give compound **7** as a white solid (102 mg, 84% yield). This reaction was similarly successful when it was performed with THF instead of toluene. Single crystals suitable for X-ray diffraction were obtained from a C_6H_5Br/hexanes solution of **7**. ^1H NMR (600 MHz, C_6D_5Br, 298 K): δ 3.57 (br. s, 6H, N(CH_3)), 1.55 (s, 6H, C(CH_3)). $^{13}C\{^1H\}$ NMR (200 MHz, C_6D_5Br, 298 K): δ 178.1, 124.6, 34.6, 8.2.

Synthesis of (^{Me}NHC)$_3$MgBr$_2$ (8a) and [(^{Me}NHC)$_3$MgBr][Br] (8b). Free ^{Me}NHC (29 mg, 0.232 mmol) was added to a stirred suspension of **7** (50 mg, 0.116 mmol) in C_6H_5Cl (5 mL). A clear solution was observed after 5 min and was stirred for 1 h at room temperature. After filtration of trace solids, a layer of hexanes was added to the filtrate, precipitating colorless prismlike cocrystallized (1:1) adducts of **8a** and **8b** at room temperature after 1 day. After removal of the supernatant and drying under vacuum, the product was isolated as an off-white solid (33 mg, 41% yield). An alternative procedure involves the addition of ^{Me}NHC (70 mg, 0.564 mmol) to a stirred toluene solution of MgBr$_2$ (30 mg, 0.161 mmol). After 24 h, white solids were recovered via filtration and dried under vacuum (73 mg, 82% yield). Notably, VT-NMR (C_6D_5Br, 248−373 K) experiments could not resolve more than one unique product in solution. ^1H NMR (600 MHz, C_6D_5Br, 298 K): δ 3.55 (br. s, 6H, N(CH_3)), 1.60 (s, 6H, C(CH_3)). $^{13}C\{^1H\}$ NMR (200 MHz, C_6D_5Br, 298 K): δ 124.2, 34.6, 8.3. Due to poor solubility, the carbene carbon resonance was not observed.

Computational Details. The starting geometries of compounds **2**, **3**, **4**, **5**, **7**, **8a**, and **8b** were each extracted from the X-ray crystal structures. All density functional theory geometry optimizations and corresponding harmonic vibrational frequency computations were carried out using Gaussian 16 Revision B.01[30] at the ωB97X-D/BS1 level of theory.[31] The default pruned UltraFine integration grids were used for all energy computations (99 radial shells with 590 points per shell (99590) and pruned SG1 grids using 50 radial shells with 194 points per shell (50194) for Hessians. The default SCF convergence criteria (10^{-8}) was used. The basis set (designated as BS1) utilized cc-pVDZ for Mg, C, O, N, and H and cc-pVDZ-PP for Br.[32] For each compound, the Wiberg bond indices (WBI) formulated within the natural atomic orbital (NAO) basis and natural charges were calculated using NBO 3.1, as implemented in Gaussian 09 Revision D.01.[33]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00462.

Crystal structures of 3[BAr$^F_4$] and 4[BAr$^F_4$], NMR spectra, crystallographic refinement details, and computational data (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1998358−1998364 and 2018107 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Charles Edwin Webster − *Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States;* orcid.org/0000-0002-6917-2957; Email: ewebster@chemistry.msstate.edu

Robert J. Gilliard, Jr. − *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States;*

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orcid.org/0000-0002-8830-1064; Email: rjg8s@virginia.edu

Authors

Akachukwu D. Obi − *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States;* orcid.org/0000-0001-7118-7931

Jacob E. Walley − *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States;* orcid.org/0000-0003-1495-6823

Nathan C. Frey − *Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States;* orcid.org/0000-0001-7406-1736

Yuen Onn Wong − *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States*

Diane A. Dickie − *Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States;* orcid.org/0000-0003-0939-3309

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00462

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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