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Syntheses and Structures of Magnesium and Zinc Boraamidinates: EPR and DFT Investigations of Li, Mg, Zn, B, and In Complexes of the [PhB(NtBu)2]− Anion Radical

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Abstract

The first magnesium and zinc boraamidinate (bam) complexes have been synthesized via metathetical reactions between dilithio bams and Grignard reagents or MCl₂ (M = Mg, Zn). The following new classes of bam complexes have been structurally characterized: the heterobimetallic spirocycles \{(L)μ-Li[PhB(μ-N¹Bu)₂]₂\}₂M (6a or 6b, M = Mg, L = Et₂O or THF; 6c, M = Zn, L = Et₂O), bis(organomagnesium) complexes \{[PhB(μ₃-N¹Bu)₂](MgR₂)(THF)₂\} (9a, R = iPr; 9b, R = Ph), and the mononuclear complex \{[PhB(μ-N¹Bu)₂]Mg(OEt₂)₂\} (10). Oxidation of 6a or 6c with iodine produces persistent pink (16a, M = Mg) or purple (16b, M = Zn) neutral radicals \{L₃μ-Li[PhB(μ-N¹Bu)₂]₂M]* (L = solvent molecule), which are shown by EPR spectra supported by DFT calculations to be C₅-symmetric species with spin density localized on one of the bam ligands. In contrast, characterization of the intensely colored neutral radicals \{[PhB(μ-N¹Bu)₂]₂M]* (5c, M = In, dark green; 5d, M = B, dark purple) reveals that the spin density is equally delocalized over all four nitrogen atoms in these D₂d-symmetric spirocyclic systems. Oxidation of the dimeric dilithio complex \{Li₂[PhB(μ-N¹Bu)₂]\}₂ with iodine produces the monomeric neutral radical \{[PhB(μ-N¹Bu)₂]Li(OEt₂)₃\}* (17), characterized by EPR spectra and DFT calculations. These findings establish that the bam anionic radical [PhB(N¹Bu)₂]⁻ can be stabilized by coordination to a variety of early main-group metal centers to give neutral radicals whose relative stabilities are compared and discussed.
**Introduction**

The coordination chemistry of the monoanionic amidinate (am) ligand \([RC(NR')_2]^\text{-}\) (Chart 1) has been extensively studied.\(^1\) For example, am complexes of all the s-block elements have been reported.\(^1\) In the context of the current work, a variety of magnesium am complexes have been identified. These include mono- and bis-am complexes of the general formulae \([RC(\mu-NR')_2]MgX\) and \([RC(\mu-NR')_2]_2Mg\) (R, R' = alkyl, aryl, SiMe\(_3\); X = alkyl, aryl, halide)\(^2\) in which the Mg centers are usually stabilized by a Lewis base. In addition, dinuclear Mg complexes with bridging am(s) \([RC(\mu-NR')_2][\mu-RC(NR')_2\kappa^2N,N']Mg\)\(_2\)\(^{2d,3}\) complexes involving pendant am(s)\(^4\), and mixed Mg/Al mono-am complexes \([\text{MeC}(\mu-NR')_2][\text{Me}_2\text{Al}(\mu-N\text{Pr})_2]Mg\) have been reported.\(^5\) Potential applications of Mg am complexes include their use as reagents for the synthesis of transition-metal complexes and in chemical vapour deposition (CVD). Group 13 am complexes are also of interest as potential single-source precursors to nitride materials and as selective reagents and catalysts. The most important classes include mono-am complexes \([RC(\mu-NR')_2]MX_2\) (M = Group 13 element; R, R' = alkyl, aryl, SiMe\(_3\); X = halide, hydride, alkyl, aryl)\(^6\), bis-am complexes \([RC(\mu-NR')_2]_2MX\)\(_{6b,6f,7}\) tris-am complexes \([RC(\mu-NR')_2]_3M\)\(_{6f,8}\) dinuclear Group 13 complexes with bridging am ligands, and complexes of the type \{[\mu-RC(NR')_2\kappa^2N,N']MX_2\}\(_2\) and \{[\mu-RC(NR')_2\kappa^2N,N']_2MX\}\(_2\)\(_{6f,9}\) incorporating pendant am(s)\(_{4a,10}\).

By comparison, the coordination chemistry of the dianionic boraamidinate (bam) ligand \([RB(NR')_2]^\text{-}\) (isoelectronic with am, Chart 1) is still in its infancy. For s-block metal complexes, only lithium derivatives have been reported.\(^11\) These reagents have provided the predominant method of transferring the bam ligand to other metal centers.\(^{11e}\)
The first X-ray structural determinations of dilithio bam complexes have shown that the extent of aggregation is influenced by the substituent (R) on boron, where the fundamental building block is the Li₂N₂B unit A (Chart 1). In the case of the dimers {Li₂[RB(μ₄-N₄Bu)₂]}₂ (1a, R = Ph; 1b, °Bu; 1c, ′Bu), two of these units participate in a face-to-face interaction through lithium–nitrogen contacts to give the bicapped cube B. In the unique example of a trimer {Li₂[RB(μ₄-N₄Bu)₂]}₃ (2, R = Me), three Li₂N₂B units associate edge-on through lithium–nitrogen contacts to give the tricapped hexagonal prism C. The solvated complex {(THF)₂(μ-THF)Li₂[PhB(μ₃-NDipp)₂]} (3) (Chart 1) is an unique example of a monomeric dilithio boraamidinate. An intriguing observation during investigations of the dilithio bam complexes 1a–c was the formation of red solutions upon exposure to air or during the course of metathetical reactions with main-group element halides. In related polyimido anions of p-block elements, such behavior is associated with the formation of free radicals.
Until 1993, reports on p-block bam derivatives were restricted to Groups 14–16, with the exception of \{{[\mu-\text{Mes}*\text{B(NMe)}_2\text{N},N']\text{AlMe}_2}\}_2 for which a crystal structure has not been reported. Early investigations of the coordination chemistry of the bam dianion with transition metals were limited to Group 4, but recently, Nocera and co-workers have described complexes of Groups 5 and 6, including octahedral tris-bam complexes and a paramagnetic vanadium(IV) complex. We have described the characterization of the spirocyclic anions \{{[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{M}^-}\}_2 (4a, M = Al, 4b, M = Ga; 4c, M = In) as their lithium derivatives and showed that the oxidation
of 4a and 4b with iodine produces stable\textsuperscript{18} neutral radicals \{[PhB(\mu-N^tBu)\textsubscript{2}]_2M\}\textsuperscript{*} (5a, M = Al; 5b, M = Ga), which were characterized in the solid state by X-ray crystallography. A combination of EPR spectroscopic analyses and DFT calculations showed that spin delocalization is uniform over both bam ligands in 5a and 5b and that the spirocyclic structure is retained in solution (Scheme 1).\textsuperscript{17}

Herein, we describe studies that extend the coordination chemistry of the bam ligand to magnesium and zinc. The synthesis and characterization of a series of magnesium bams, including the heterobimetallic spirocyclic complexes \{(Et\textsubscript{2}O)\mu-Li[PhB(\mu-N^tBu)\textsubscript{2}]]_2M\} (6a, M = Mg; 6c, M = Zn), are discussed. The oxidation of 6a and 6c with iodine produces persistent\textsuperscript{18} radicals, which have been characterized by a combination of EPR spectra and DFT calculations. In addition, we have extended our earlier studies of Group 13 spirocyclic bam radicals \{[PhB(\mu-N^tBu)\textsubscript{2}]_2M\}\textsuperscript{*} to the characterization of the indium- and boron-containing analogues (Scheme 1; 5c, M = In; 5d, M = B). Finally, we describe the identification of the paramagnetic red species formed upon oxidation of dilithio bams.\textsuperscript{11c}
Results and Discussion

Syntheses and Spectroscopic Characterization of Mg and Zn bams. The reaction of Li₂[PhB(μ-NTBu)₂] (1a) and a Grignard reagent in a 1:1 stoichiometry was attempted in an effort to generate the mixed-metal Mg/Li mono-bam 7 (Scheme 2, Method 1). However, the reaction with 'BuMgCl affords the spirocyclic dilithio magnesium bis-bam complex {(Et₂O)μ-Li[PhB(μ-NTBu)₂]}₂Mg (6a, Scheme 2).

Scheme 2

The proposed pathway involves the initial production of 7, which then undergoes redistribution to produce 6a (89 %) with the elimination of Mg'Bu₂ that was detected by ¹H NMR spectroscopy (~ δ 0.2). The generality of Method 1 (Scheme 2) was demonstrated in the reactions of 1a with a variety of Grignard reagents in diethyl ether, including MesMgBr, 'BuMgCl, and MeMgBr, all of which produce 6a. Similarly, the THF derivative {(THF)μ-Li[PhB(μ-NTBu)₂]}₂Mg (6b) is obtained from the reactions of the Grignard reagents PhMgCl or 'PrMgCl in THF and 1a in a 1:1 stoichiometry.
Complexes of type 6 may also be prepared by a direct approach (Method 2, Scheme 2). Treatment of two eq. of 1a with MCl₂ (M = Mg or Zn) in diethyl ether at −78 °C afforded 6a and the zinc analogue \{(Et₂O)₆-Li[PhB(μ-N³Bu)₂]₂\}Zn (6c) in 75 and 51 % yields, respectively. Colorless crystals of 6a and 6c, grown from concentrated solutions in Et₂O, were characterized by CHN analyses, ¹H, ¹¹B, ⁷Li, and ¹³C NMR spectra, and X-ray structural analyses (vide infra). For both 6a and 6c, the ¹H NMR spectra show resonances for the Ph and ¹Bu substituents and the coordinated Et₂O molecules in the appropriate relative intensities. However, the ¹H NMR spectrum for 6a displays two singlets for the four ¹Bu groups attached to the amide nitrogens of the bam; consistently, two signals assigned to the methyl groups of these ¹Bu substituents are observed in the ¹³C NMR spectrum. In contrast, only one ¹Bu resonance is observed in the ¹H NMR and ¹³C NMR spectra for 6c. The ¹¹B NMR spectra of 6a–c exhibit broad resonances at δ 37-38, consistent with three-coordinate boron centers.¹⁹ Singlets are observed in the ⁷Li NMR spectra of 6a–c at δ 1.44, 1.43 and 1.16, respectively.

When the reaction of 1a and ¹BuMgCl was carried out in a 1:2 stoichiometry, colorless crystals of the bis(organomagnesium) complex \{[PhB(μ-N³Bu)₂](Mg¹Bu)₂(μ-B-Cl)Li(OEt₂)₃\} (8, Scheme 3) were isolated. The ¹H NMR spectrum of 8 shows resonances for the Ph and ¹Bu substituents, along with the coordinated Et₂O molecules, in the appropriate relative intensities. The signals for the methyl groups of the two ¹Bu substituents attached to the amide nitrogen atoms appear at δ 1.44, while those on the two magnesium atoms are found at δ 1.12. The ¹¹B NMR resonance is observed at δ 39. A resonance is also observed at δ −0.37 in the ⁷Li NMR spectrum of 8 consistent with the presence of LiCl in this complex.
Treatment of 1a with 2 eq. of solutions of 1PrMgCl or PhMgCl in THF afforded \{[PhB(\mu_3-N^tBu)_2](Mg\textsuperscript{1Pr})_2(THF)_2\} (9a) and \{[PhB(\mu_3-N^tBu)_2](MgPh)_2(THF)_2\} (9b), respectively (Scheme 3). The \textsuperscript{1}H NMR spectrum of 9a shows resonances for the Ph, \textsuperscript{1}Bu, and \textsuperscript{1}Pr substituents and coordinated THF molecules, with relative intensities indicative of symmetrical-equivalent \textsuperscript{1}Bu and \textsuperscript{1}Pr substituents and the presence of two coordinated THF molecules in solution. Similarly, the intensities of the resonances observed in the \textsuperscript{1}H NMR spectrum of 9b indicate three Ph groups, two \textsuperscript{1}Bu substituents, and two coordinated THF molecules. The \textsuperscript{11}B NMR chemical shifts for 9a for 9b are \(\delta\) 39 and \(\delta\) 40, respectively. No signals are observed in the \textsuperscript{7}Li NMR spectra of 9a and 9b. Crystals of 9a or 9b suitable for X-ray structural determinations could not be obtained.

The reaction of PhB[N(H)Dipp]\textsubscript{2}\textsuperscript{11d} with \(n/s\)Bu\textsubscript{2}Mg (1:1) in boiling hexane produced the mono-bam complex \{[PhB(\mu-NDipp)_2]Mg(OEt\textsubscript{2})\} (10, Scheme 4), which was identified by multinuclear NMR spectroscopy and an X-ray structural analysis (\textit{vide infra}). The \textsuperscript{1}H NMR spectrum of 10 exhibits only one resonance for both the CH and CH\textsubscript{3} groups of the Dipp substituents; the corresponding signals are observed in the \textsuperscript{13}C
NMR spectrum. The $^{11}\text{B}$ NMR resonance of $\delta 31$ for 10 is shifted upfield compared to those observed for 6, 8, and 9 ($\delta ^{11}\text{B} 37–40$). Complete deprotonation was also indicated by the lack of an N–H stretch in the IR spectrum. For comparison, the reaction of $n$/sBu$_2$Mg with $p$-tolyIC[N(H)Dipp](NDipp) produces the $bis$-substituted square-planar complex $[p$-tolyIC($\mu$-NDipp)$_2$]$_2$Mg.$^{2a}$

**Scheme 4**

X-ray Structures of Mg and Zn $bam$ Complexes. The X-ray structures of 6a and 6c show that the spirocyclic dianion {[$\text{PhB(}\mu$-$\text{N}^3\text{Bu})_2$]$_2$M}$^{2-}$ ($M = \text{Mg, Zn}$) is $N$,$N'$-chelated to two monosolvated lithium cations. The molecular geometry and atomic numbering scheme for 6a and 6c are shown in Figure 1, and pertinent structural parameters are summarized in Table 1. The two 4-membered NBNM ($M = \text{Mg, Zn}$) rings are puckered with the M and B atoms on one side of the plane, while the two four-coordinate nitrogen atoms reside on the other side of the plane.
Figure 1. Thermal ellipsoid plot of \{(\text{Et}_2\text{O})\mu-\text{Li}[\text{PhB(\mu-N^\text{t}Bu)_2}]\}_2\text{M} \ (\text{M} = \text{Mg, 6a}; \text{M} = \text{Zn, 6c}). \text{For} \text{ clarity, H atoms are} \text{ omitted and only the} \ \alpha\text{-carbons of the} \ ^{\text{t}}\text{Bu substituents and oxygen atoms of the Et}_2\text{O molecules are shown.}

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for \{(\text{Et}_2\text{O})\mu-\text{Li}[\text{PhB(\mu-N^\text{t}Bu)_2}]\}_2\text{M} \ (\text{M} = \text{Mg, 6a}; \text{M} = \text{Zn, 6c}).

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<td>1.449(2)</td>
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<tr>
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<td>1.436(8)</td>
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<td>2.01(1)</td>
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<tr>
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<td>2.03(1)</td>
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<td>2.03(1)</td>
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<tr>
<td>N(1)--M(1)--N(3)</td>
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<td>131.0(2)</td>
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<td>68.4(2)</td>
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<td>106.0(5)</td>
<td>106.0(5)</td>
<td>107.1(1)</td>
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<td>N(1)--B(1)--C(5)</td>
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The boron atoms in 6a and 6c exhibit distorted trigonal-planar geometries with substantial deviations from the ideal bond angles, although the sum of the angles is 360° in each case. The geometry about the nitrogen atoms is distorted tetrahedral (bond angle ranges: ca. 77–135°) with the smallest values associated with the B–N–Li angle. The NBN angles in 6a and 6c are equal within experimental error, while the B–N distances are intermediate between those of single- and double-bond values. 20 The geometry about the central metal atom is distorted tetrahedral [bond angle range: M = Mg: 67.54(5)–138.54(5)°; M = Zn: 68.4(2)–136.6(2)°] as a result of geometric constraints imposed by the bam ligands. The metal–nitrogen bond distances observed in complexes 6a and 6c are typical for Mg–N and Zn–N single bonds. 21

The X-ray structural analysis of \{[\text{PhB}(\mu_3\text{N}^1\text{Bu})_2]_2(\text{MgBu})_2(\mu_3\text{Cl})\text{Li(OEt}_2)_3\} (8) reveals that each nitrogen atom of the bam ligand coordinates to two magnesium tert-butyl groups. The molecular geometry and atomic numbering scheme for 8 are shown in Figure 2, while pertinent structural parameters are summarized in Table 2. The Mg–N bond distances are equal within experimental error (ca. 2.13 Å), cf., ca. 2.09 Å in the spirocyclic complex 6a. The magnesium atoms in the dimagnesiated derivative \{[\text{PhB}($\mu$-}
N'Bu₂)₂(Mg' Bu)₂} are also bridged by the chloride ion of a ClLi(OTE₂)₃ molecule. The structure of 8 is reminiscent of the framework observed for the dilithiated complex 3, with the bridging THF ligand in 3 replaced by ClLi(OTE₂)₃ in 8.

Figure 2. Thermal ellipsoid plot of \{[[PhB(\mu-\mathbf{N'}Bu)₂](Mg'Bu)₂(\mu-Cl)Li(OTE₂)₃]} (8). For clarity, H atoms are omitted and only the \(\alpha\)-carbons of the \(\mathbf{1}'\)Bu substituents and oxygen atoms of the Et₂O molecules are shown.

The mean B–N bond distances \([1.451(3) \text{ Å}]\) in 8 are equal within experimental error, cf., \([d(\text{B-N}) = 1.446(4) \text{ Å}]\) in 3. While the Li–O distances involving the bridging THF molecule in 3 are significantly different \([2.270(7) \text{ and } 2.013(6) \text{ Å}]\), the chloride ion in 8 bridges the magnesium atoms symmetrically \([2.536(1) \text{ Å}, \text{Mg}(1)–\text{Cl}(1); 2.530(1) \text{ Å}, \text{Mg}(2)–\text{Cl}(1)]\). The lithio am complex Li[\(\text{BuC}(\mathbf{N'}\text{Bu})₂] has been shown to entrap LiX salts to form complexes such as \{(Li[\(\text{BuC}(\mathbf{N'}\text{Bu})₂]₂·LiCl·THF\}_2.²²

The boron atom in 8 exhibits a distorted trigonal-planar geometry \([\Sigma \gtrless 360.0(2)°]\), while the magnesium atoms adopt distorted tetrahedral geometries \([\text{bond angle range } ca. 66–138.5°]\) with the smallest angles associated with the N–Mg–N angle. The NBN angle \([105.6(2)°]\) in 8 is similar to those in 6a \((ca. 107°)\), but significantly smaller than that in 3 \([111.4(3)°]\).¹¹d The larger angle in the latter presumably reflects the accommodation of
the bulkier NDipp groups in 3. As a result of the two four-coordinate nitrogen centers, the two four-membered N–B–N–Mg rings in 8 are puckered in a manner similar to that observed for 6a.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for \{[\text{PhB}(\mu_3-\text{NDipp})_2]\text{Mg}(\text{OEt}_2)_2\} \cdot 2\text{Mg} \cdot 2\text{Cl} \cdot \text{Li}(\text{OEt}_2)_3\} (8).

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The X-ray structure of \{[\text{PhB}(\mu_3-\text{NDipp})_2]\text{Mg}(\text{OEt}_2)_2\} (10) shows that the [PhB(NDipp)_2]^2– ligand is coordinated to a single Mg^{2+} cation in an $N,N'$-chelated fashion. The coordination sphere is completed by oxygen atoms from two THF molecules. The molecular geometry and atomic numbering scheme are shown in Figure 3, while pertinent structural parameters are summarized in Table 3.
Figure 3. Thermal ellipsoid plot of \{[\text{PhB}(\mu-\text{NDipp})_2]\text{Mg(OEt}_2\}_2\} (10). For clarity, H atoms are omitted and only the oxygen atoms of the Et_2O molecules are shown.

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for \{[\text{PhB}(\mu-\text{NDipp})_2]\text{Mg(OEt}_2\}_2\} (10).

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<td>124.3(3)</td>
<td></td>
<td></td>
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</tbody>
</table>
The Mg–N distances of ca. 1.98 Å in 10 are significantly shorter than those observed in the dimagnesiated complex 8 (ca. 2.13 Å). The formal 2+ charge on magnesium in 10 is a likely major contributor to the observed difference. The magnesium center in 10 adopts a distorted tetrahedral geometry [bond angle range: 74.7(1)–129.7(1)°] with the smallest angle associated with the N–Mg–N bond angle. The B–N distances [1.439(5) Å, B(1)–N(1); 1.449(5) Å, B(1)–N(2)] reflect substantial nitrogen–boron multiple-bond character.

The N–B–N bond angle of 112.5(3)° in 10 is larger than those observed in 6a and 8 (ca. 107°), but similar to that in the dilithiated bam complex 3 [111.4(3)°].\textsuperscript{11d} The larger NBN angles observed in 3 and 10 accommodate the bulkier NDipp groups in the bam ligand in these complexes. The geometries at the boron and nitrogen atoms of the [PhB(NDipp)\textsubscript{2}]\textsuperscript{2−} ligand in 10 are distorted trigonal planar [Σ∠(°): 360.0(3), B(1); 359.1(3), N(1); 357.3(3), N(2)]. The four-membered Mg(1)–N(2)–B(1)–N(1) ring is essentially planar [0.0040 Å mean dev.].

**Syntheses and Characterization of Group 13 bam complexes.** We have previously reported the syntheses and structural characterization of the monolithiated spirocyclic complexes \{(Et\textsubscript{2}O)\textmu-Li[PhB(\textmu-N\textsuperscript{t}Bu)\textsubscript{2}]\textsubscript{2}M\} (11b, M = Ga; 11c, M = In) by the reactions of 1a with MCl\textsubscript{3} in a 2:1 molar ratio.\textsuperscript{16} Attempts to prepare the analogous aluminum complex \{(Et\textsubscript{2}O)\textmu-Li[PhB(\textmu-N\textsuperscript{t}Bu)\textsubscript{2}]\textsubscript{2}Al\} (11a) by this method were unsuccessful. Complex 11a can be obtained, however, in a two-step process involving the initial preparation of the mono-bam complex \{[PhB(\textmu-N\textsuperscript{t}Bu)\textsubscript{2}]AlCl(OEt\textsubscript{2})\} (12), which can be isolated in 60% yield from the reaction of 1a and AlCl\textsubscript{3} in a 1:1 molar ratio, followed by treatment of 12 with 1a (Scheme 5).
The structure of 12 was established by a single-crystal X-ray analysis (Figure 4), and pertinent structural parameters are summarized in Table 4.\textsuperscript{23} Solvation of the aluminum centre by diethyl ether apparently prevents dimerization, cf., the dimeric structure of the unsolvated complex \{[PhB(\mu_3-N^tBu)(\mu-N^tBu)]Ga\}_2.\textsuperscript{16} The geometry around the aluminum center in 12 is distorted tetrahedral [bond angle range: 79.99(4)–124.62(4)°]. The bond angle N–Al–N is acute [79.99(4)°], but larger than the mean value of 70.91(5)° observed for aluminum \textit{am} complexes of the type RC(\mu-NR')_2AlCl_2 [R = Me, R' = \textit{i}Pr; R = \textit{t}Bu, R' = \textit{i}Pr, Cy].\textsuperscript{6b} The [PhB(\mu-N^tBu)_2]Al core in 12 forms a nearly planar metallacycle with an N(2)–Al(1)–N(1)–B(1) torsion angle of 3.05(7)°. The boron and three-coordinate nitrogen atoms exhibit distorted trigonal-planar coordination (\Sigma \angle ca. 360°), the latter atoms displaying a larger disparity [bond angle range at B(1): 106.36(9)–128.5(1)°; bond angle range at N(1) and N(2): \textit{ca} 87–140°].
Figure 4. Thermal ellipsoid plot of \{[\text{PhB}(\mu^-\text{N}^\text{tBu})_2]\text{AlCl(OEt}_2\text{)}\} (12). For clarity, H atoms are omitted.

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) for \{[\text{PhB}(\mu^-\text{N}^\text{tBu})_2]\text{AlCl(OEt}_2\text{)}\} (12).

<table>
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<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
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<tr>
<td>Al(1)–Cl(1)</td>
<td>2.1402(5)</td>
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<tr>
<td>Al(1)–N(1)</td>
<td>1.806(1)</td>
<td>Al(1)–N(2)</td>
</tr>
<tr>
<td>B(1)–N(1)</td>
<td>1.442(2)</td>
<td>B(1)–N(2)</td>
</tr>
<tr>
<td>N(1)–Al(1)–N(2)</td>
<td>79.99(4)</td>
<td>N(1)–Al(1)–Cl(1)</td>
</tr>
<tr>
<td>N(1)–Al(1)–O(1)</td>
<td>115.05(5)</td>
<td>N(2)–Al(1)–Cl(1)</td>
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<tr>
<td>B(1)–N(1)–C(10)</td>
<td>132.26(9)</td>
<td>B(1)–N(2)–C(20)</td>
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<td>B(1)–N(1)–Al(1)</td>
<td>86.83(7)</td>
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<td>C(10)–N(1)–Al(1)</td>
<td>140.19(8)</td>
<td>C(20)–N(2)–Al(1)</td>
</tr>
<tr>
<td>N(1)–B(1)–C(1)</td>
<td>128.5(1)</td>
<td>N(2)–B(1)–C(1)</td>
</tr>
<tr>
<td>N(1)–B(1)–N(2)</td>
<td>106.36(9)</td>
<td></td>
</tr>
</tbody>
</table>
The Al–Cl distance of 2.1402(5) Å in 12 falls between those reported for aluminum mono- and bis-am complexes, ca. 2.10 and 2.19 Å, respectively.\textsuperscript{6b} The B–N distances [1.442(2) and 1.455(2) Å] indicate significant multiple-bond character. The Al–N bond lengths [1.806(1) and 1.802(1) Å] are shorter by ca. 0.07 Å than the Al–N distances in related mono-am complexes,\textsuperscript{6b} presumably as a result of the dianionic charge of the bam ligand in 12. There are no intermolecular Al⋯Cl interactions present in the unit cell of 12.

The reaction of 12 with 1a in a 1:1 molar ratio in boiling benzene in the presence of a small amount of diethyl ether produces \{((Et\textsubscript{2}O)\(\mu\)-Li[PhB(\(\mu\)-N\textsuperscript{t}Bu)\textsubscript{2}]\textsubscript{2}Al\} (11a) in 33 % yield (Scheme 6). The multinuclear NMR spectra of 11a are consistent with a spirocyclic structure similar to that previously established for 11b and 11c.\textsuperscript{16} The \textsuperscript{1}H NMR spectrum of 11a in C\textsubscript{6}D\textsubscript{6} shows resonances for the Ph and N\textsuperscript{t}Bu groups, in addition to the coordinated Et\textsubscript{2}O molecule, with the appropriate relative intensities. The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra of 11a in C\textsubscript{6}D\textsubscript{6} at room temperature reveal the equivalence of all four N\textsuperscript{t}Bu environments indicative of a fluxional process involving the lithium center, as observed for 11b and 11c.\textsuperscript{16} The \textsuperscript{27}Al, \textsuperscript{11}B, and \textsuperscript{7}Li NMR spectra of 11a exhibit singlets at \(\delta\) 488.2, 36, and 0.89, respectively.

In an attempt to synthesize the boron analogue of 11a, the reaction of 1a with BF\textsubscript{3}·OEt\textsubscript{2} in a 2:1 molar ratio was investigated. The \textsuperscript{1}H and \textsuperscript{11}B NMR spectra recorded as a function of time revealed the existence of more than one reaction pathway. The initial observation of two equally intense resonances at \(\delta\) 43 and 30 in the \textsuperscript{11}B NMR spectrum (indicative of inequivalent three-coordinate boron environments), associated with \textsuperscript{1}Bu and Ph resonances with relative intensities of 18:5 in the \textsuperscript{1}H NMR spectrum, is attributed to
the formation of the complex [PhB(μ-N\text{Bu})_2]BF (13) (Scheme 6). Subsequently, the generation of the spirocyclic complex 11d is indicated by the appearance of a broad resonance at δ 22 and a sharp singlet at δ 0 in the ^{11}B NMR spectrum (approximate intensity ratio 2:1), indicative of three- and four-coordinate boron environments, respectively.\textsuperscript{19} The borazine [PhF_2B_3N_3Bu_3] (14) has been isolated from this reaction and identified by X-ray crystallography and multinuclear NMR spectra.\textsuperscript{24} The NMR resonances for 14 grow at the expense of those attributed to 13 during the course of the reaction, and the formation of 14 is favored relative to 11d when the reaction is carried out on a 1:1 molar ratio. A possible route to 14 involving the cyclodimerization of 13 to an eight-membered ring 15 is shown in Scheme 6.\textsuperscript{25} However, in view of the known stability of related B_4N_4 rings, e.g., (CIBN\textsuperscript{3}Bu)_4, the direct formation of 14 from 13 cannot be ruled out.

Scheme 6
EPR and DFT Investigations of Early Main-Group Element and Zn bam Radicals. In a preliminary communication, we described the one-electron oxidation of the spirocyclic anions 4a and 4b to give the stable neutral radicals 5a (dark red) and 5b (dark green) (Scheme 1).\textsuperscript{17,18} In this work, we discuss the characterization of the indium and boron analogues, 5c and 5d, respectively.

The oxidation of 11c with one-half of an equivalent of iodine generates a dark green solution of complex 5c (Figure 5) that, in contrast to 5a and 5b, is unstable at ambient temperature. Thus the oxidation was carried out at \(-78^\circ\text{C}\), and the paramagnetic species formed were investigated by variable-temperature (VT) EPR spectroscopy. The bright purple solutions of complex 5d (Figure 5) formed by air oxidation of the products of the reaction of 1a with BF\(_3\)-OEt\(_2\) in a 2:1 molar ratio (\textit{vide supra}) were also investigated by EPR spectroscopy. Whereas the intense dark green color of 5c lasts only for minutes at room temperature,\textsuperscript{27} diethyl ether solutions of radical 5d remain dark purple and exhibit similar EPR spectra even after two years.

\textbf{Figure 5.} Photographs of diethyl ether solutions of the neutral spirocyclic radicals \{[PhB(\mu-N'Bu)\_2]M\}\(^*\) (left, M = In, 5c; right, M = B, 5d).
Theoretical calculations were first carried out on the $D_{2d}$-symmetric diamagnetic model systems $\{[\text{PhB(μ-NMe)}_2]_2M\}^{-}$ ($M = \text{In, B}$) to evaluate their frontier orbitals. The HOMOs (highest-occupied molecular orbitals) of these diamagnetic anions are non-degenerate and exhibit equal delocalization of spin density over all four nitrogen centers. Thus, like 5a and 5b, the corresponding spirocyclic radicals $\{[\text{PhB(μ-N}^t\text{Bu)}_2]_2\text{In}]^*$ (5c) and $\{[\text{PhB(μ-N}^t\text{Bu)}_2]_2\text{B}]^*$ (5d) are expected to retain the $D_{2d}$ symmetry of their parent diamagnetic anions in solution. The calculated structures for the model radicals $\{[\text{PhB(μ-NMe)}_2]_2M\}^*$ ($M = \text{In, B}$) can be compared to the structures determined for the analogous aluminum and gallium systems by X-ray crystallography. As expected, the M–N bond lengths in $M = \text{In}$ and B derivatives are considerably longer (2.073 Å) and shorter (1.532 Å), respectively, than the corresponding bond lengths in $M = \text{Al}$ or Ga derivatives. The geometries of the two MNBN rings are close to square planar in the all-boron system $\{[\text{PhB(μ-NMe)}_2]_2\text{B}]^*$ (bond angle range: ca. 85–97°), whereas the indium analogue displays distinctly asymmetric InNBN rings with very acute N–In–N bond angles (68°); the geometries of the MNBN rings in the $M = \text{Al}$ and Ga derivatives fall between the values calculated for the indium and boron systems. These differences in binding of the two $\text{bam}$ ligands to the central atom reflect the different sizes of the Group 13 elements $M = \text{B, Al, Ga, In}$.

Considering the composition of the SOMO (singly-occupied molecular orbital) of the model radicals $\{[\text{PhB(μ-NMe)}_2]_2M\}^*$, the experimental EPR spectra of both 5c and 5d will exhibit hyperfine structure due to interaction of the unpaired electron with four equivalent nitrogen ($^{14}\text{N}, I = 1, 99.6 \%$) centers. In addition, hyperfine structure due to the central metal (5c: $^{113}\text{In}, I = \frac{9}{2}, 4.3 \%$; $^{115}\text{In}, I = \frac{9}{2}, 95.7 \%$; 5d: $^{10}\text{B}, I = 3, 19.9 \%; ^{11}\text{B}, I = \frac{3}{2}, 19.8 \%$).
$^3/2$, 80.1 %) and two equivalent boron atoms of the $bam$ ligands may be observed due to spin polarization effects. The experimental EPR spectra of 5c obtained at $-40$ °C and 5d obtained at $25$ °C are shown in Figures 6a and 7a, respectively. The experimental EPR spectra are best simulated by assuming interactions of the unpaired electron with the central main group element, four equivalent nitrogen centers, and two equivalent boron atoms. The simulations shown in Figures 6b and 7b for 5c and 5d, respectively, were obtained by using the hyperfine coupling (hfc) constants given in Table 5, in which there is a fairly good agreement between the experimental and the calculated hfc values (Table 5). Hence, the experimental and simulated EPR spectra, together with DFT calculations, indicate that the neutral radicals $\{[\text{PhB}(\mu-\text{N}^t\text{Bu})_2]_2\text{In}\}^\bullet (5c)$ and $\{[\text{PhB}(\mu-\text{N}^t\text{Bu})_2]_2\text{B}\}^\bullet (5d)$ adopt spirocyclic structures in solution as depicted in Scheme 1.

**Figure 6.** Experimental (a) and simulated (b) X-band EPR spectra of a diethyl ether solution of $\{[\text{PhB}(\mu-\text{N}^t\text{Bu})_2]_2\text{In}\}^\bullet (5c)$ at $-40$ °C.
**Figure 7.** Experimental (a) and simulated (b) X-band EPR spectra of a diethyl ether solution of \([\text{[PhB(\mu-N^tBu)₂]B}}]^-\) at 25 °C.

**Table 5.** Experimental and Calculated Hyperfine Coupling Constants [G] for \([\text{[PhB(\mu-NR')₂]M}}]^-\) (M = In, B; R' = \(^tBu, Me)).^a

<table>
<thead>
<tr>
<th>([\text{[PhB(\mu-NR')₂]M}}]^-)</th>
<th>isotope</th>
<th>n</th>
<th>exptl. (R' = (^tBu))</th>
<th>calc. (R' = Me)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = In</td>
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<td>22.50 / 41.00</td>
<td>c</td>
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<tr>
<td></td>
<td>(^{14})N</td>
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<td>4.70</td>
<td>4.10</td>
</tr>
<tr>
<td></td>
<td>(^{10})B / (^{11})B</td>
<td>2</td>
<td>1.70 / 5.18</td>
<td>-2.03 / -6.10</td>
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<tr>
<td>M = B</td>
<td>(^{10})B / (^{11})B</td>
<td>1</td>
<td>2.31 / 6.92</td>
<td>-2.81 / -8.43</td>
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<tr>
<td></td>
<td>(^{14})N</td>
<td>4</td>
<td>5.46</td>
<td>4.59</td>
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<tr>
<td></td>
<td>(^{10})B / (^{11})B</td>
<td>2</td>
<td>1.85 / 5.56</td>
<td>-2.21 / -6.64</td>
</tr>
</tbody>
</table>

^a Projected parameters were determined from simulations optimized to match the experimental spectra. 100% Lorentzian line shapes. \(g = 2.00407\), M = In; \(g = 2.00405\), M = B.

^b Number of nuclei.

^c Unavailable (see Experimental Section).
The oxidation of the dilithiated Mg or Zn spirocyclic bis-
\textit{bam} complexes 6a and 6c (Scheme 7) was also investigated by EPR spectroscopy. Addition of one-half of an equivalent of iodine to colorless solutions of 6a or 6c in diethyl ether at room temperature generates persistent pink or bright purple solutions, respectively (Figure 8). DFT calculations for the neutral radicals \{(Et\textsubscript{2}O)Li[PhB(\textmu-N\textprime Bu)\textsubscript{2}]\textsubscript{2}M\}\textsuperscript{*} (16a, M = Mg; 16b, M = Zn) predict \(C\textsubscript{5}\)-symmetric structures and localized spin density on the \textit{bam} ligand that is not coordinated to Li\textsuperscript{+} (see Scheme 7 and Figure 9). Consequently, the EPR spectra of both radicals are expected to show hyperfine structure resulting from interaction of the unpaired electron with two inequivalent nitrogen atoms. In addition, hyperfine structure arising from interactions with the central metal (16a: \(^{25}\text{Mg}, I = 5/2, 10 \%\); 16b: \(^{67}\text{Zn}, I = 5/2, 4.1 \%\), one boron atom, and minor contributions from the adjacent \textit{bam} ligand, \textit{i.e.}, two equivalent nitrogen atoms and/or one boron atom, is expected due to spin polarization effects.

\textbf{Scheme 7}

\begin{align*}
\text{M = Mg, 6a; Zn, 6c} & \quad + 0.5\text{I}_2 \quad \text{Et}_2\text{O, 25\textdegree C} \quad \text{- LiI} \\
\text{M = Mg, 16a; Zn, 16b} & \quad \text{Li(\textsubscript{Et}_2\textsubscript{O})}_2
\end{align*}
Figure 8. Photograph of diethyl ether solutions of the radicals \{(Et_2O)Li[PhB(\mu-N^\text{t}Bu)_2]_2M\}^\bullet (left, M = Mg, 16a; right, M = Zn, 16b).

The experimental EPR spectrum obtained at room temperature for 16b is shown in Figure 10a; the spectrum for 16a exhibits a similar pattern owing to the low natural abundance of the spin-active isotopes for magnesium and zinc. Excellent simulations (Figure 10b) were obtained by using the hfc constants given in Table 6. The experimental and calculated hfc values are in close agreement. Hence, for both radicals, the EPR spectra support the prediction from DFT calculations that the unpaired electron is localized on one \textit{bam} ligand. The EPR spectra for the zinc radical 16b reveal minor interactions with the adjacent \textit{bam} ligand, as well as some low-intensity satellites due to coupling of the unpaired electron to the \textsuperscript{67}Zn nucleus.
Figure 9. Optimized structure (left; bond lengths in Å, bond angles in deg.) and SOMO (right; isosurface values ± 0.06) of \{(\text{Me}_2\text{O})\text{Li}[\text{PhB}(\mu-\text{NMe})_2]\text{Mg}\}^*.

Figure 10. Experimental (a) and simulated (b) X-band EPR spectra of a diethyl ether solution of \{(\text{Et}_2\text{O})\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{Zn}\}^* (16b) at 25 °C.
Table 6. Experimental and Calculated Hyperfine Coupling Constants [G] for 
{(Et₂O)Li[PhB(μ-NR’₂)₂]₂M}⁺ (M = Mg, Zn; R’ = ’Bu, Me).a

<table>
<thead>
<tr>
<th></th>
<th>isotope</th>
<th>nᵇ</th>
<th>exptl. (R’ = ’Bu)</th>
<th>calc. (R’ = Me)</th>
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<tr>
<td><strong>M = Mg</strong></td>
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<tr>
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<td>−0.01</td>
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<tr>
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<td>3.61 / 10.70</td>
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<tr>
<td></td>
<td>⁷Li</td>
<td>1</td>
<td>a</td>
<td>−0.03</td>
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</table>

ᵃ Parameters were determined from simulations optimized to match the experimental spectra. 100% Lorentzian line shapes. g = 2.00446, M = Mg; g = 2.00526, M = Zn.

ᵇ Number of nuclei. ᶜ a indicates no observable hfc constant.

The first indications of the formation of paramagnetic early main-group metal bam complexes came from investigations of lithium derivatives of the type 1.¹¹c It was observed that the initially colorless solutions of 1a–c became red upon exposure to air. In preliminary EPR studies, only coupling to two equivalent ¹⁴N nuclei (a five-line pattern) was resolved. In the absence of resolved coupling to ⁷Li centers, it was not possible to speculate on the state of aggregation of the radical species.¹¹c

We have now carried out the oxidation of 1a with one-half of an equivalent of iodine in diethyl ether at room temperature (Scheme 8). The bright pink species so
formed is unstable at room temperature. Consequently, the solutions used for VT EPR studies were prepared at −78 °C. The EPR spectrum obtained at −40 °C is shown in Figure 11a. This spectrum is best simulated (see Table 7) with hyperfine interactions of the unpaired electron with one lithium atom (\(^{7}\text{Li}, I = \frac{3}{2}, 92.41 \%\); \(^{6}\text{Li}, I = 1, 7.59 \%\)), two equivalent nitrogen centers, and one boron atom, suggesting the formation of the monocyclic radical \([\text{PhB(\(\mu\)-N\text{Bu})\(_2\)}\text{Li(OEt}_2\text{)}\x]\*) (17), in which the radical monoanion [PhB(N\text{Bu})\(_2\)]\(\text{-}\) is chelated to a diethyl ether-solvated lithium center.

Scheme 8

\[
\begin{align*}
\text{1a} & \\
0.5 \text{I}_2 & \xrightarrow{\text{Et}_2\text{O}} \text{Li} & \text{17}
\end{align*}
\]

Figure 11. Experimental (a) and simulated (b) X-band EPR spectra of a diethyl ether solution of \([\text{PhB(\(\mu\)-N\text{Bu})\(_2\)}\text{Li(OEt}_2\text{)}\x]\*) (17) at −40 °C.
Table 7. Experimental and Calculated Hyperfine Coupling Constants [G] for \{[\text{PhB}(\mu-\text{NR'})_2]\text{Li}\}^* (R' = \text{tBu, Me}).^a

<table>
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<tr>
<th>Isotope</th>
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<th>exptl. (R' = \text{tBu})</th>
<th>calc. (R' = \text{Me})</th>
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<tr>
<td>$^{10}$B / $^{11}$B</td>
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<td>3.67 / 11.18</td>
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<td>$^{14}$N</td>
<td>2</td>
<td>8.51</td>
<td>7.59</td>
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<tr>
<td>$^7$Li</td>
<td>1</td>
<td>2.14</td>
<td>$-$2.39</td>
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</table>

$^a$ Parameters were determined from simulations optimized to match the experimental spectra. 100% Lorentzian line shapes. $g = 2.00443$. $^b$ Number of nuclei.

The plausibility of the assignment of the experimental EPR spectrum to the monocyclic radical was supported by DFT calculations. Figure 12 shows the optimized structure and SOMO calculated for the model system \{[\text{PhB}(\mu-\text{NMe})_2]\text{Li(OEt}_2)_x\}^*; the calculated hfc constants are listed in Table 7. The excellent match between the calculated and experimental values provides strong support for the identification of the transient radical as the monolithium species \{[\text{PhB}(\mu-N\text{'Bu})_2]\text{Li(OEt}_2)_x\}^*.

![Figure 12](image_url)
Conclusions

A variety of magnesium complexes of the dianionic bam ligand have been synthesized and structurally characterized. These magnesium reagents offer a potential alternative to the widely used lithium derivatives for the transfer of bam ligands to other metal centers. In common with other early main-group metal bam complexes, these novel magnesium and zinc complexes are readily oxidized to paramagnetic species. The one-electron oxidation of the metal-coordinated bam dianion \([\text{PhB}(\mu-\text{N}^\prime \text{Bu})_2]^{2-}\) to the corresponding radical anion \([\text{PhB}(\text{N}^\prime \text{Bu})_2]^*\) can be controlled by using the appropriate amount of iodine as the oxidizing agent. The combination of EPR spectroscopic analyses and DFT calculations provides information about both the molecular and electronic structures, *e.g.*, spin distribution, of these paramagnetic complexes in solution. Similar studies of complexes in which the radical anion \([\text{PhB}(\text{N}^\prime \text{Bu})_2]^*\) is coordinated to lithium or Group 13 metal centers indicate the qualitative trend in stabilities depicted in Chart 2.

**Chart 2**

For the spirocyclic systems, the higher stability of the B, Al, and Ga-containing radicals compared to the Mg and Zn systems can be attributed to the delocalization of the unpaired electron over both bam ligands in the Group 13 complexes. The high stability of the boron-centered radical 5d in solution is noteworthy. In contrast to 5a and 5b,
however, it has not yet been possible to devise a synthetic route that will allow the isolation of 5d in the solid state. The lower stability of 5e may result from a combination of stronger intermolecular, \textit{i.e.}, radical-radical, interactions as a result of the larger In center and weaker In-N bonds compared to 5a, 5b, and 5d. Intermolecular association to form larger aggregates is likely the reason for the low stability of the mononuclear Li complex.

These results suggest that redox behavior is an important feature of the chemistry of the \textit{bam} ligand, as implied by the frequent observation of intensely colored solutions in the metathetical reactions of Li\textsubscript{2}bam reagents with main-group element halides. This fundamental difference between the behavior of main-group metal complexes of \textit{bam} ligands compared to that of \textit{am} ligands undoubtedly stems from the dianionic charge in the former.

\section*{Experimental}

\textbf{Reagents and General Procedures.} The compounds \textsuperscript{1}BuMgCl (2.0 M solution in Et\textsubscript{2}O), MesMgBr (1.0 M solution in Et\textsubscript{2}O), \textsuperscript{n}BuMgCl (2.0 M solution in Et\textsubscript{2}O), \textsuperscript{Me}MgBr (3.0 M solution in Et\textsubscript{2}O), MgCl\textsubscript{2} (anhydrous beads, 10 mesh, 99.99 \%), PhMgCl (2.0 M solution in THF), \textsuperscript{1}PrMgCl (2.0 M solution in THF), \textsuperscript{n/s}Bu\textsubscript{2}Mg (1.0 M solution in heptane), and BF\textsubscript{3}\cdot OEt\textsubscript{2} were commercial samples (Aldrich) and used as received. Anhydrous ZnCl\textsubscript{2} was prepared by heating ZnCl\textsubscript{2}\cdot H\textsubscript{2}O under vacuum (150 \textdegree C, 10\textsuperscript{-2} Torr, 18 h). The reagents AlCl\textsubscript{3} and I\textsubscript{2} were sublimed prior to use.
The compounds Li$_2$[PhB(μ-3-N$_t$Bu)$_2$] (1a), PhB[N(H)Dipp]$_2$, and {(Et$_2$O)$_2$Li[PhB(μ-3-N$_t$Bu)$_2$]}$_2$In (11c) were prepared by the literature methods.

Solvents were dried with appropriate drying agents and distilled onto molecular sieves before use. All reactions and the manipulation of moisture- and/or air-sensitive reagents or products were carried out under an atmosphere of argon or under vacuum using standard Schlenk techniques or a glovebox. All glassware was carefully dried prior to use.

**Instrumentation.** $^1$H NMR spectra were recorded on Bruker AC 200 and DRX 400 spectrometers, and chemical shifts are reported relative to Me$_4$Si in CDCl$_3$. $^7$Li, $^{11}$B, $^{13}$C, and $^{19}$F NMR spectra were measured on a Bruker DRX 400 or a Bruker AMX2-300 spectrometer. All NMR spectra were obtained on C$_6$D$_6$ solutions at 25 °C. Chemical shifts are reported relative to those of BF$_3$·OEt$_2$ in C$_6$D$_6$, Me$_4$Si in CDCl$_3$, 1.0 M LiCl in D$_2$O, and CFCl$_3$ in C$_6$D$_6$, respectively. Infrared spectra were obtained as Nujol mulls between KBr plates on a Nicolet Nexus 470 FT-IR spectrometer in the range 4000–350 cm$^{-1}$. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary. X-band EPR spectra were recorded on a Bruker EMX 113 spectrometer equipped with a variable-temperature accessory. EPR spectral simulations were carried out by using the XEMR v. 0.7$^{31a}$ and WINEPR SimFonia v. 1.25$^{31b}$ programs.

**Preparation of {(Et$_2$O)$_2$Li[PhB(μ-3-N$_t$Bu)$_2$]}$_2$Mg (6a). Method 1.** A solution of $^1$BuMgCl in Et$_2$O (2.0 M, 0.72 mL, 1.43 mmol) was added to a solution of 1a (0.35 g, 1.43 mmol) in toluene (50 mL) at room temperature producing a white slurry that was stirred for 18 h. The reaction mixture was filtered and the solvent removed in vacuo. The
resulting residue was dissolved in Et₂O, and concentration of the solution followed by storage at room temperature for 30 min. afforded X-ray quality colorless crystals of 6a (0.41 g, 0.63 mmol, 89 %). Complex 6a was also prepared in the manner described above by using the Grignard reagents MesMgBr (1.0 M solution in Et₂O), nBuMgCl (2.0 M solution in Et₂O), or MeMgBr (3.0 M solution in Et₂O). Method 2. A solution of 1a (0.75 g, 3.06 mmol) in Et₂O (100 mL) was added to solid MgCl₂ (0.15 g, 1.53 mmol) at −78 °C producing a dark burgundy reaction mixture, which was allowed to warm to room temperature over a period of 20 min then set to reflux for 18 h. The resulting colorless solution was filtered and the solvent removed in vacuo. The residue was washed several times with cold n-hexane gave white amorphous 6a (0.74 g, 1.14 mmol, 75 %). A concentrated solution of 6a in diethyl ether stored at −15 °C for 1 d provided colorless crystals suitable for X-ray diffraction studies. Anal. Calcd for C₃₆H₆₆B₂Li₂MgN₄O₂: C, 66.86; H, 10.29; N, 8.66. Found: C, 66.57; H, 10.86; N, 8.80. ¹H NMR: δ 7.96–7.20 (m, 10 H, −C₆H₅), 3.32 [q, 8 H, (CH₃CH₂)₂O], 1.47 [s, 18 H, −C(CH₃)₃], 1.32 [s, 18 H, −C(CH₃)₃], 0.98 [t, 12 H, (CH₃CH₂)₂O]. ¹¹B NMR: δ 38 (br s). ⁷Li NMR: δ 1.44 (s). ¹³C NMR: δ four resonances in the range 150.9–125.6 (−C₆H₅), 66.0 [(CH₃CH₂)₂O], 51.0 [−C(CH₃)₃], 38.3 [−C(CH₃)₃], 37.9 [−C(CH₃)₃], 15.1 [(CH₃CH₂)₂O].

Preparation of [(THF)µ-Li[PhB(µ-NᵗBu)₂]₂Mg (6b). A solution of PhMgCl in THF (2.0 M, 0.33 mL, 0.66 mmol) was added to a solution of 1a (0.16 g, 0.66 mmol) in toluene (25 mL) at room temperature producing a cloudy pale yellow mixture that was stirred for 18 h. The reaction mixture was filtered and the solvent was removed in vacuo. The residue was redissolved in THF and concentration of the solution followed by storage at −15 °C for 3 d afforded colorless crystals of 6b (0.15 g, 0.23 mmol, 71 %).
Anal. Calcd for C₃₆H₆₂B₂Li₂MgN₄O₂: C, 67.28; H, 9.72; N, 8.71. Found: C, 66.98; H, 10.18; N, 8.66. ¹H NMR: δ 8.18–7.21 (m, 10 H, −C₆H₅), 3.33 [br s, 8 H, O(CH₂)₂(CH₂)₂], 1.49 [s, 18 H, −C(CH₃)₃], 1.35 [s, 18 H, −C(CH₃)₃], 1.14 [br s, 18 H, O(CH₂)₂(CH₂)₂]. ¹¹B NMR: δ 38 (br s). ⁷Li NMR: δ 1.43 (s). ¹³C NMR: δ four resonances in the range 150.0–127.5 (−C₆H₅), 69.3 [O(CH₂)₂(CH₂)₂], 51.0 [−C(CH₃)₃], 50.9 [−C(CH₃)₃], 38.1 [−C(CH₃)₃], 38.0 [−C(CH₃)₃], 25.6 [O(CH₂)₂(CH₂)₂]. Complex 6b was also prepared in the manner described above by using the Grignard reagent iPrMgCl (2.0 M solution in THF).

Preparation of [(THF)μ-Li[PhB(μ-N₃Bu)₂]₂Zn (6c). A solution of 1a (0.27 g, 1.12 mmol) in Et₂O (100 mL) was added to solid ZnCl₂ (0.08 g, 0.56 mmol) at −78 °C producing a dark burgundy reaction mixture, which was allowed to warm to room temperature over a period of 20 min then set to reflux for 18 h. The mixture was filtered and the solvent removed in vacuo. The residue was washed several times with and cold n-hexane to give white amorphous 6c (0.20 g, 0.29 mmol, 51 %). Anal. Calcd for C₃₆H₆₆B₂Li₂N₄O₂Zn: C, 62.86; H, 9.67; N, 8.15. Found: C, 62.28; H, 9.98; N, 8.12. ¹H NMR: δ 7.74–7.20 (m, 10 H, −C₆H₅), 3.36 [q, 8 H, (CH₃CH₂)₂O], 1.39 [s, 36 H, −C(CH₃)₃], 0.98 [t, 12 H, (CH₃CH₂)₂O]. ¹¹B NMR: δ 37 (br s). ⁷Li NMR: δ 1.16 (s). ¹³C NMR: δ four resonances in the range 150.1–125.8 (−C₆H₅), 65.8 [(CH₃CH₂)₂O], 51.2 [−C(CH₃)₃], 37.6 [−C(CH₃)₃], 15.1 [(CH₃CH₂)₂O]. A concentrated solution of 6c in Et₂O stored at −15 °C for 6 h provided colorless crystals that were suitable for X-ray diffraction studies.

Preparation of [{[PhB(μ-N₃Bu)₂]₂}(MgBu)₂(μ-Cl)Li(OEt₂)₃} (8). A solution of iBuMgCl in Et₂O (2.0 M, 1.93 mL, 3.85 mmol) in toluene (10 mL) was added to a
solution of 1a (0.47 g, 1.93 mmol) in toluene (50 mL) at room temperature producing a white slurry that was stirred for 18 h. The reaction mixture was filtered and the solvent was removed in vacuo. The residue was washed twice with cold n-hexane affording a pale yellow powder (0.58 g, 0.88 mmol, 46 %). A concentrated solution of 8 in diethyl ether (1 week, −15 °C) provided colorless X-ray quality crystals. Anal. Calcd for C_{26}H_{51}BClLiMg_{2}N_{2}O (8 − 2 Et_{2}O): C, 61.29; H, 10.09; N, 5.50. Found: C, 61.13; H, 10.81; N, 6.09. \(^{1}\)H NMR: δ 7.75–6.99 (m, 5 H, −C_{6}H_{5}), 3.21 [q, 12 H, (CH_{3}CH_{2})_{2}O], 1.44 [s, 18 H, −C(CH_{3})_{3}], 1.12 [s, 18 H, −C(CH_{3})_{3}], 0.86 [t, 18 H, (CH_{2}CH_{2})_{2}O]. \(^{11}\)B NMR: δ 39 (br s). \(^{7}\)Li NMR: δ −0.37 (s). \(^{13}\)C NMR: δ four resonances in the range 138.2–126.0 (−C_{6}H_{5}), 65.7 [(CH_{2}CH_{2})_{2}O], 50.6 [−C(CH_{3})_{3}], 36.9 [−C(CH_{3})_{3}], 35.5 [−C(CH_{3})_{3}], 21.8 [−C(CH_{3})_{3}], 14.2 [(CH_{3}CH_{2})_{2}O].

Preparation of ([PhB(μ-NBu)]_{2})(MgPr)_{2}(THF)_{2} (9a). A solution of iPrMgCl in THF (2.0 M, 1.11 mL, 2.22 mmol) was added to a solution of 1a (0.27 g, 1.11 mmol) in toluene (50 mL) at room temperature producing a white slurry that was stirred for 5 h. The reaction mixture was filtered to give a pale yellow filtrate from which the solvent was removed in vacuo. The residue was redissolved in Et_{2}O and concentrated to afford 9a as colorless thin needle crystals (0.21 g, 0.41 mmol, 37 %). Anal. Calcd for C_{24}H_{45}BMg_{2}N_{2}O (9a − 1 THF): C, 65.96; H, 10.38; N, 6.41. Found: C, 65.41; H, 10.76; N, 6.22. \(^{1}\)H NMR: δ 7.87–7.25 (m, 5 H, −C_{6}H_{5}), 3.59 [br m, 8 H, O(CH_{2})_{2}(CH_{2})_{2}], 1.75 [d, 12 H, −CH(CH_{3})_{2}, \(^{3}\)J(1H−1H) = 8 Hz], 1.27 [br m, 8 H, O(CH_{2})_{2}(CH_{2})_{2}], 1.17 [s, 18 H, −C(CH_{3})_{3}], 0.32 [septet, 2 H, −CH(CH_{3})_{2}, \(^{3}\)J(1H−1H) = 8 Hz]. \(^{11}\)B NMR: δ 39 (br s). \(^{13}\)C NMR: δ four resonances in the range 133.9–126.6 (−C_{6}H_{5}), 70.5 [O(CH_{2})_{2}(CH_{2})_{2}], 50.4
Preparation of \{[\text{PhB}(\mu-N^\text{Bu})_2]\}(\text{MgPh})_2(\text{THF})_2\} (9b). A solution of PhMgCl in THF (2.0 M, 0.60 mL, 1.21 mmol) was added to a solution of 1a (0.15 g, 0.61 mmol) in toluene (50 mL) at room temperature producing a cloudy pale yellow reaction mixture that was stirred for 12 h. The reaction mixture was filtered isolating a pale yellow filtrate from which the solvent was removed \textit{in vacuo}. The residue was washed twice with \textit{n}-hexane affording 9b as a yellow powder (0.23 g, 0.40 mmol, 66 %). Thin needle crystals of 9b were isolated from a concentrated solution in \textit{Et}_2O (9 d, \(-15^\circ\text{C}\)). Anal. Calcd for C\textsubscript{30}H\textsubscript{41}BMg\textsubscript{2}N\textsubscript{2}O (9b – 1 THF): C, 71.34; H, 8.18; N, 5.55. Found: C, 70.88; H, 8.24; N, 5.82. \(^1\text{H}\) NMR: \(\delta\) 8.02–7.17 (m, 15 \(\text{H}\), –C\textsubscript{6}H\textsubscript{5}), 3.60 [br m, 8 \(\text{H}\), O(\text{CH}_2)_2(\text{CH}_2)_2], 1.33 [s, 18 \(\text{H}\), –C(CH\textsubscript{3})\textsubscript{3}], 1.09 [br m, 8 \(\text{H}\), O(\text{CH}_2)_2(\text{CH}_2)_2]. \(^{11}\text{B}\) NMR: \(\delta\) 40 (br s). \(^{13}\text{C}\) NMR: \(\delta\) eight resonances in the range 166.3–125.8 (–C\textsubscript{6}H\textsubscript{5}), 70.0 [O(\text{CH}_2)_2(\text{CH}_2)_2], 50.7 [–C(CH\textsubscript{3})\textsubscript{3}], 37.5 [–C(CH\textsubscript{3})\textsubscript{3}], 25.4 [O(\text{CH}_2)_2(\text{CH}_2)_2].

Preparation of \{[\text{PhB(\mu-NDipp)}_2]\}(\text{Mg(OEt})_2\}_2\} (10). A solution of \textit{n}^\text{Bu}_2\text{Mg} in heptane (1.0 M, 3.16 mL, 3.16 mmol) was added to a solution of PhB[N(H)Dipp]\textsubscript{2} (1.39 g, 3.16 mmol) in \textit{n}-hexane (150 mL) at \(-30^\circ\text{C}\) producing a red reaction mixture. The mixture was allowed to warm to room temperature over 20 min. and then set to reflux for 18 h. Concentration of the reaction mixture followed by layering with diethyl ether and cooling (\(-15^\circ\text{C}\), 2 d) gave X-ray quality colourless crystals of 10 (0.62 g, 1.01 mmol, 32 %). Anal. Calcd for C\textsubscript{38}H\textsubscript{59}BMgN\textsubscript{2}O\textsubscript{2}: C, 74.70; H, 9.73; N, 4.58. Found: C, 74.11; H, 9.50; N, 4.29. \(^1\text{H}\) NMR: \(\delta\) 7.55–7.02 (m, 11 \(\text{H}\), Ph and aryl of Dipp), 4.00 [septet, 4 \(\text{H}\), –CH(CH\textsubscript{3})\textsubscript{2}], \(^3J(1\text{H–}1\text{H}) = 8\) Hz], 3.16 [q, 8 \(\text{H}\), (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O], 0.97 [d, 24 \(\text{H}\), –CH(CH\textsubscript{3})\textsubscript{2},
Preparation of \{[\text{PhB}(&\mu\text{-N}^\text{t}Bu)_2]AlCl(OEt)}\} (12). A colorless solution of 1a (0.46 g, 1.86 mmol) in Et\textsubscript{2}O (50 mL) was added to solid AlCl\textsubscript{3} (0.25 g, 1.86 mmol) cooled to \(-78 \, ^\circ\text{C}\) producing a bright purple reaction mixture. After 15 min., the stirred reaction mixture was allowed to reach room temperature affording a clear colorless solution. After an additional 15 min. at room temperature, a cloudy pale yellow reaction mixture was produced that was stirred for 8 h. The resulting mixture was filtered to remove LiCl. Removal of solvent \textit{in vacuo} and addition of cold \textit{n}-hexane gave a pale yellow precipitate of 12 (0.41 g, 1.11 mmol, 60 \%) that was washed twice with cold \textit{n}-hexane. Anal. Calcd for C\textsubscript{14}H\textsubscript{23}AlClBN\textsubscript{2}: C, 58.95; H, 9.07; N, 7.64. Found: C, 58.42; H, 9.25; N, 7.72. \textsuperscript{1}H NMR: \(\delta\) 7.63 (d, 2 H, \(\text{-C}_6\text{H}_5\)), 7.24 (m, 3 H, \(\text{-C}_6\text{H}_5\)), 3.76 [q, 4 H, (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O], 1.22 [s, 18 H, \(\text{-C(C}_2\text{H}_5\))], 0.81 [t, 6 H, (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O]. \textsuperscript{11}B NMR: \(\delta\) 36 (br s). \textsuperscript{13}C NMR: \(\delta\) 155.0 (\(\text{-C}_6\text{H}_5\)), 132.7 (\(\text{-C}_6\text{H}_5\)), 127.4 (\(\text{-C}_6\text{H}_5\)), 126.3 (\(\text{-C}_6\text{H}_5\)), 66.4 [((CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O)], 49.7 [\(\text{-C(CH}_3\))], 35.6 [\(\text{-C(CH}_3\))], 15.8 [(CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}O]. X-ray quality crystals of 12 were isolated from a concentrated solution in Et\textsubscript{2}O (1 d, \(-15 \, ^\circ\text{C}\)).

Preparation of \{[\text{PhB}(&\mu\text{-N}^\text{t}Bu)_2]_{2}\text{In}}\* (5c). A solution of I\textsubscript{2} in Et\textsubscript{2}O (0.60 mL, 0.0643 M, 0.038 mmol) was added to a colorless solution of \{(Et\textsubscript{2}O)\&\text{Li}[\text{PhB}(&\mu\text{-N}^\text{t}Bu)_2]_{2}\text{In}\} (11c) (0.050 g, 0.076 mmol) in Et\textsubscript{2}O (15 mL) at \(-80 \, ^\circ\text{C}\) instantly producing a dark green solution. The reaction mixture was kept at \(-80 \, ^\circ\text{C}\) prior to recording EPR spectra. UV-vis (Et\textsubscript{2}O): \(\lambda\text{max} = 481\) (br), 646 nm (br).
Preparation of \( \{(\text{Et}_2\text{O})\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{Mg}\}^* (16a) \). A solution of \( \text{I}_2 \) in \( \text{Et}_2\text{O} \) (0.70 mL, 0.024 M, 0.017 mmol) was added to a colorless solution of \( \{(\text{Et}_2\text{O})\mu-\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\}\text{Mg} (6a) \) (0.022 g, 0.034 mmol) in \( \text{Et}_2\text{O} \) (10 mL) at room temperature instantly producing a bright pink solution. The resulting reaction mixture was used for EPR studies. UV-vis (Et\(_2\)O): \( \lambda_{\text{max}} = 521 \) (br).

Preparation of \( \{(\text{Et}_2\text{O})\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{Zn}\}^* (16b) \). A solution of \( \text{I}_2 \) in \( \text{Et}_2\text{O} \) (0.84 mL, 0.044 M, 0.037 mmol) was added to a colourless solution of \( \{(\text{Et}_2\text{O})\mu-\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\}\text{Zn} (6c) \) (0.051 g, 0.074 mmol) in \( \text{Et}_2\text{O} \) (10 mL) at room temperature instantly producing a bright purple solution. The resulting reaction mixture was studied by EPR spectroscopy. UV-vis (Et\(_2\)O): \( \lambda_{\text{max}} = 562 \) (br).

Preparation of \( \{[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{Li}(\text{OEt}_2)_3\}^* (17) \). A solution of \( \text{I}_2 \) in \( \text{Et}_2\text{O} \) (0.84 mL, 0.044 M, 0.037 mmol) was added to a colorless solution of \( \text{Li}_2[\text{PhB}(\mu_3-\text{N}^\text{Bu})_2] \) (1a) (0.051 g, 0.074 mmol) in \( \text{Et}_2\text{O} \) (10 mL) at \( -80 \) °C instantly producing a pink solution. This solution was kept at \( -80 \) °C prior to recording EPR spectra.

X-ray Analyses

Relevant parameters for the data collections and crystallographic data are summarized in Table 8. Thermal ellipsoid plots are shown at the 30 % probability level and only selected carbon atoms are labeled.
Table 8. Selected Crystal Data and Data Collection Parameters for \{(\text{Et}_2\text{O})\mu-\text{Li}[\text{PhB}(\mu-\text{N}^\text{Bu}).\text{Bu})_2]\}_2\text{M} (\text{M} = \text{Mg, 6a;} \text{M} = \text{Zn, 6c}) \text{.} \{[\text{PhB}(\mu_3\text{N}^\text{Bu})_2]_2[\text{Mg}^\text{Bu})_2(\mu_3-\text{Cl})\text{Li(OEt})_2]\} (8), \{[\text{PhB}(\mu-\text{NDipp})_2]_2\text{Mg(OEt})_2]\} (10), \text{ and } \{[\text{PhB}(\mu-\text{N}^\text{Bu})_2]\text{AlCl(OEt})_2]\} (12).^a

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<td>\textbf{F(000)}</td>
<td>1416</td>
<td>1488</td>
<td>724</td>
<td>1336</td>
<td>792</td>
</tr>
<tr>
<td>\textbf{(R^e)}</td>
<td>0.0484</td>
<td>0.0749</td>
<td>0.0609</td>
<td>0.0754</td>
<td>0.0400</td>
</tr>
<tr>
<td>\textbf{(R_w^d)}</td>
<td>0.1166</td>
<td>0.1726</td>
<td>0.1548</td>
<td>0.1855</td>
<td>0.1137</td>
</tr>
</tbody>
</table>

\(^a\text{Temperature} = 173(2) \text{ K;} \text{ wavelength} = 0.71073 \text{ Å.} \text{ The complex crystallizes with two independent but chemically-equivalent molecules in the asymmetric unit.} \text{ }^bR = \Sigma||F_o|| - |F_c||/\Sigma|F_o| (I > 2.00\sigma(I)). \text{ }^cR = \Sigma\{\text{2}[F_o - F_c] \}^{1/2} (\text{all data}).\)
Computational Details

All calculations were done with the Gaussian 03 program. The structures of all compounds were optimized in their ground states using density functional theory. Hybrid PBE0 exchange-correlation functional and Ahlrichs' TZVP basis sets were used in all optimizations (the corresponding ECP basis set was used for indium). Hyperfine coupling constants of paramagnetic species were calculated by single point calculations employing the optimized geometries, PBE0 functional, TZVP basis sets, and unrestricted Kohn-Sham formalism. For {[PhB(µ-NMe)_2]In}^+, the use of a quasi-relativistic ECP for the heavier nucleus indium prevents the direct determination of its hfc constants using the applied method.

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Supporting Information Available: Full experimental details of the X-ray analyses. Crystallographic data in CIF format for complexes 6a, 6c, 8, 10 and 12. This material is available free of charge via the Internet at http://pubs.acs.org.
References


(18) The term “stable”, as applied to radicals, is taken to indicate “a species that can be isolated and shows no sign of decomposition under an inert atmosphere at room temperature”, whereas a “persistent” radical has “a relatively long lifetime under the conditions it is generated”. Power, P.P. *Chem. Rev.* **2003**, *103*, 789.


(23) Although complex 12 was mentioned in the preliminary communication,\(^{17}\) no structural details were given.


(27) After a few minutes, the EPR spectrum of 5c is replaced by an asymmetric spectrum indicating the presence of at least two radical species. The outer ends of this spectrum exhibit a pentet with 34 G width indicating hfc to two equivalent \(^{14}\)N nuclei (\(A = 8.5\) G). This pattern is repeated ten times suggesting coupling to a
single $^{115}\text{In}$ center. No coupling to boron was resolved. Although a possible candidate for this radical is the monocyclic $bam$ complex $[\text{PhB}(\mu-N^3\text{Bu})_2\text{In}]^*$, the calculated value of $A^{\text{eff}}_{\text{In}}$ for this radical is much higher than the observed value of $\sim 21 \text{ G}$.

(28) (a) Eloranta, J. *XEMR*, version 0.7; University of Jyväskylä: Jyväskylä, Finland, 2004. (b) *WINEPR SimFonia*, version 1.25; Bruker Analytische: Messtechnik, Germany, 1996.


(31) The basis sets were used as they are referenced in the Turbomole 5.7.1 internal basis set library. These basis sets can be downloaded from: ftp://ftp.chemie.uni-karlsruhe.de/pub/basen/ for free of charge. Site accessed, February 2005.