

# An unpaired electron incarcerated within an icosahedral borane cage: synthesis and crystal structure of the blue, air-stable $\{[closo-B_{12}(CH_3)_{12}]^-\}^-$ radical

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Oxidation of the permethylated icosahedral borane  $[closo-B_{12}(CH_3)_{12}]^{2-}$  **1**, by ceric(IV) ammonium nitrate in acetonitrile affords the blue, air-stable paramagnetic anion  $\{[closo-B_{12}(CH_3)_{12}]^-\}^-$  **2**, which has been characterized, among other means, by X-ray crystallography.

Radicals differ significantly in reactivity as their persistence largely depends upon the unpaired electron's chemical and physical environment.<sup>1</sup> A major effect that stabilizes paramagnetic species is steric crowding. A radical center surrounded by bulky groups is more persistent than similar species without this protection. Recently, we reported the synthesis of the camouflaged permethylated *closo*-borane  $[closo-B_{12}(CH_3)_{12}]^{2-}$  **1**.<sup>2</sup> Here, we describe paramagnetic  $\{[closo-B_{12}(CH_3)_{12}]^-\}^-$  **2**, obtained from **1** by one-electron oxidation with ceric(IV) ammonium nitrate (CAN) in acetonitrile. In species **2** the unpaired electron is trapped within the hydrocarbon sheath of the permethylated borane cage. Hence, this deep blue radical-anion is surprisingly stable with respect to reaction with oxygen. The anion **2** was characterized by high-resolution fast atom bombardment mass spectrometry (HR-FAB-MS), electron paramagnetic resonance (EPR), UV-VIS spectroscopy, and cyclic voltammetry. Furthermore, the crystal structure of  $[Ph_3P=N=PPh_3]_2$  (PPN2), was determined by single crystal X-ray diffraction.

Following CAN oxidation of  $[NBu^n_4]_2$  (TBA)<sub>2</sub>**1**, in acetonitrile, the anion **2** was isolated as a PPN salt in 66% yield.† Reduction of **2** with  $NaBH_4$  in ethanol regenerated **1** in good yield (Scheme 1).

A solid sample of PPN2 exhibits an EPR signal with  $g = 2.0076$ . The UV-VIS spectrum (Fig. 1) of the blue salt  $[NET_4]_2$  (TEA2) in acetonitrile displays absorption in the visible region.

Cyclic voltammetry (100 mM  $NET_4PF_6$ , Ag/AgCl, MeCN) of **2** reveals a reversible wave with  $E_{1/2} = 0.44$  V for the one-electron process  $2 + e^- \rightarrow 1$ . The reduction potential of **2** matches the corresponding oxidation potential previously determined for **1**.<sup>2</sup> The X-ray crystal structure‡ (Fig. 2) confirms that **2** is a permethylated monoanionic *closo*-borane.

In the solid state, the anionic cluster of PPN2 is less distorted from icosahedral symmetry than the dianionic species **1** studied as a  $[(2-C_5H_4N)_2CH_2]^{2+}$  salt [B-B bond lengths: **2** 178.5(8)–180.5(7) pm, **1** 174(1)–181(1) pm, B-C bond lengths: **2** 159.8(9)–161.3(8) pm; **1** 159(1)–170(1) pm].<sup>2</sup> The maximum

across-cage methyl carbon separations average 668 pm for the dianionic species **1**,<sup>2</sup> compared to 663 pm for the monoanion **2**. The greater distortion of **1** may be explained by the charge-transfer interaction of the dipositive  $[(2-C_5H_4N)_2CH_2]^{2+}$  counter ion and the dianion **1**. This interaction is suggested by the unique color of the blood-red  $[(2-C_5H_4N)CH_2]_1$  salt.<sup>2</sup>

Paramagnetic persubstituted polyhedral *closo*-boranes such as  $\{[closo-B_6X_6]^-\}^-$  **3**,<sup>3</sup>  $\{[closo-B_9X_9]^-\}^-$  **4**<sup>4</sup> (X = Cl, Br, I) and  $[closo-CB_{11}Me_{12}]^+$  **5**,<sup>5</sup> have been reported previously. As in the synthesis of **2**, these species were obtained *via* metal-ion oxidation of the corresponding reduced borane clusters. In each case, solutions of these paramagnetic species are moderately stable, but decolorize after prolonged contact with air.

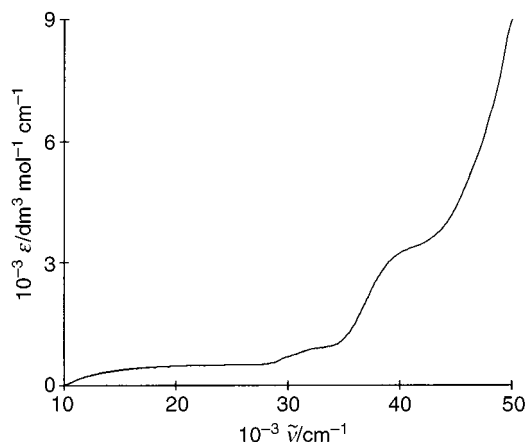


Fig. 1 UV-VIS absorption spectrum of TEA2 in acetonitrile.

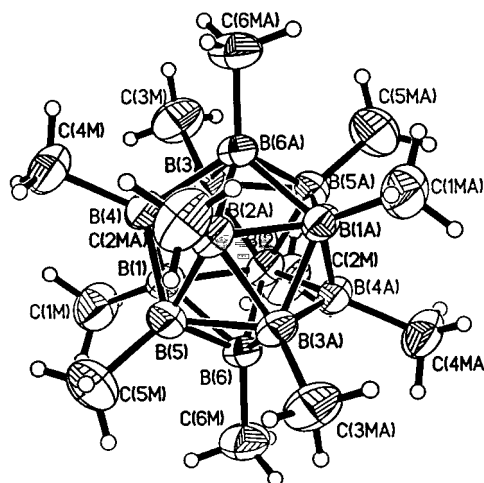
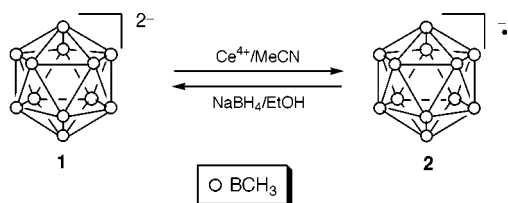
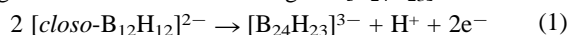


Fig. 2 ORTEP diagram of  $\{[closo-B_{12}(CH_3)_{12}]^-\}^-$  **2**. The ellipsoids represent a 30% probability level. Selected bond lengths (pm): B-B 178.5(8)–180.5(7), B-C 159.8(9)–161.3(8). Atoms X(n) and X(nA) are symmetry-related by an inversion center.



Scheme 1 Chemical interconversion of  $\{[closo-B_{12}(CH_3)_{12}]^-\}^-$  **2** and  $[closo-B_{12}(CH_3)_{12}]^{2-}$  **1**.

The species **2** presents unique possibilities inherent in the concept of camouflaged polyhedral boranes.<sup>7</sup> Here, the persubstitution stabilizes an unusual oxidation state that has not been obtained from the 'naked' parent species [*closo*-B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> **7**. Upon electrochemical oxidation ( $E_{1/2} = 1.43$  V vs SCE), the dianion **7** instead dimerizes [eqn. (1)] by an undetermined mechanism with loss of one *exo* H-atom and dimerization of B<sub>12</sub>-cages to form the B–H–B bridge of [B<sub>24</sub>H<sub>23</sub>]<sup>3-</sup>.<sup>8</sup>



The latter species is structurally related to [*a*<sup>2</sup>-B<sub>20</sub>H<sub>19</sub>]<sup>3-</sup>.<sup>9</sup> This reaction pathway is not available for the permethylated radical **1**.

In conclusion, we have presented the synthesis and characterization of {[*closo*-B<sub>12</sub>(CH<sub>3</sub>)<sub>12</sub>]<sup>•-</sup> **2**, a surprisingly air-stable paramagnetic *closo*-borane. The unique persistence of **2** provided by the steric encumbrance of the twelve methyl substituents suggests that **2** might find use in applications requiring a paramagnetic weakly coordinating anion.<sup>10</sup>

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## Notes and references

‡ *Synthetic procedure for PPN2*: A sample of (TBA)<sub>2</sub>**1** (0.23 g, 0.29 mmol) was dissolved in acetonitrile (5 ml) and an acetonitrile solution (5 ml) of ceric(IV) ammonium nitrate (0.16 g, 0.29 mmol) was added. The reaction mixture, which immediately turned deep blue, was stirred for 5 min and then added to 50 ml of water. The precipitate was separated by filtration, dissolved in ethanol (10 ml), and again filtered. To the filtrate, PPNCl (1.70

g, 2.90 mmol) dissolved in ethanol (10 ml) was added. Upon cooling overnight near 0 °C, the dark blue PPN**2** (0.16 g, 0.19 mmol, 66% yield) separated by crystallization.

Negative HR-FAB-MS: found: *m/z* 310.4022; calc. 310.4014.  
‡ *Crystal data for PPN2* C<sub>48</sub>H<sub>66</sub>B<sub>12</sub>NP<sub>2</sub>, *M* = 878.04, monoclinic, *a* = 3466(3), *b* = 934.2(8), *c* = 1869(2) pm, *U* = 5.120(7) nm<sup>3</sup>, *T* = 298 K, space group *C2/c*, *Z* = 4,  $\mu(\text{Mo-K}\alpha) = 1.2$  cm<sup>-1</sup>, 4900 unique reflections measured, 2489 reflections were considered observed [*I* > 2 $\sigma$ (*I*)] and all data were used in all calculations. The final *R* factor ( $R = \sum |F_o| - |F_c| / \sum |F_o|$ ) was 0.066 (for 2489 independent reflections). The structure was solved using statistical methods and refined by full-matrix least squares on *F*<sup>2</sup>. CCDC 182/1405. See <http://www.rsc.org/suppdata/cc/1999/2039/> for crystallographic files in .cif format.

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