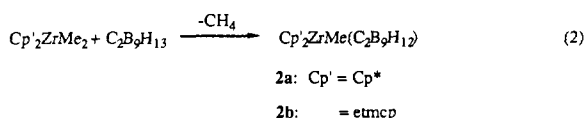


One of the aryl rings of the  $[\text{BPh}'_4]^-$  anion is metallated in the meta position with a Zr-C(13) distance of 2.154 (4) Å. The C-H bond ortho to boron acts as a ligand to the zirconium atom through an agostic interaction,<sup>15</sup> with a Zr-H(12) distance of 2.14 (3) Å. This unique proton appears in the <sup>1</sup>H NMR spectrum of **1c** at 4.77 δ. The metallated aryl ring is highly distorted with a Zr-C(13)-C(14) angle of 155.0 (3)° and a Zr-C(13)-C(12) angle of 87.2 (2)°. This distortion, which might be considered a static intermediate between aryl and benzyne hydride resonance structures, may be due to the coulombic interaction between the zirconium cation and boron anion; the related d<sup>0</sup> complex (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sc(C<sub>6</sub>H<sub>5</sub>) shows no similar agostic interactions.<sup>16</sup>

The large size and chemical inertness of high-nuclearity polyhedral carboranes also make them compatible anions. Cp\*<sub>2</sub>ZrMe<sub>2</sub> and (etmcp)<sub>2</sub>ZrMe<sub>2</sub> (etmcp = C<sub>5</sub>Me<sub>4</sub>Et) (10% excess) react with the diprotic carborane complex *nido*-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub><sup>17</sup> in pentane to form the monomethyl complexes Cp'<sub>2</sub>ZrMe(C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>) (**2a,b**) in high yield as bright yellow precipitates (eq 2).<sup>18</sup>



The solubility of **2a,b** in aromatic hydrocarbons suggested a tight ion pairing between the zirconocene monomethyl cation and the [C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> anion, but there was no spectroscopic evidence for an interaction. A single-crystal X-ray study of **2b** (Figure 2)<sup>19</sup> shows the [(etmcp)<sub>2</sub>ZrMe]<sup>+</sup> cation is bound to the [C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> anion solely through a Zr-H-B bond to a terminal hydride on the *nido* face of the anion. The Zr-H(9) distance of 2.12 (4) Å is much longer than that of terminal M-H (1.6-1.7 Å) or bridging M-H-M (ca. 1.8 Å) bonds.<sup>20</sup> Both the large size of the anion and the peralkylcyclopentadienyl ligands limit any closer approach of the anion to the metal. The B(9)-H(9) distance, 1.19 (4) Å, is about 0.1 Å longer than the average of the other terminal B-H distances in the cage (1.08 Å). A similar, but greater perturbation occurs in Fe(TPP)(CB<sub>11</sub>H<sub>12</sub>): the Fe-H-B distance is shorter (1.82 Å) while the B-H(br) distance is about 0.2 Å longer than the other B-H distances.<sup>21</sup> However, the problem of accurately determining hydrogen atom positions in an X-ray experiment is well known.<sup>22</sup>

Both **1a-c** and **2a,b** function as catalysts for the polymerization of ethylene to linear polyethylene under mild conditions.<sup>23</sup> Unlike the base-coordinated metallocene catalyst [Cp<sub>2</sub>ZrMe(THF)]-[BPh<sub>4</sub>], **1** and **2** show high activity even in low-dielectric solvents such as toluene or hexane. In the case of **1a-c**, there is no evidence that the tetraarylborate anion is the head group of the polymer chain. Our investigations into the chemistry of these compounds,

the mechanisms of chain initiation, polymerization behavior of the catalysts, and the characteristics of the polymer formed will be presented in future publications.

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**Supplementary Material Available:** Solid-state NMR experimental details and X-ray structure details and tables of crystal data, final atomic positional and isotropic thermal parameters, bond distances and angles, and anisotropic displacement parameters for **1c** and **2b** (48 pages); tables of observed and calculated structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

## Dopamine β-Monooxygenase Catalyzed Aromatization of 1-(2-Aminoethyl)-1,4-cyclohexadiene: Redirection of Specificity and Evidence for a Hydrogen Atom Transfer Mechanism

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Dopamine β-monooxygenase (DBM, E.C.1.14.17.1), a copper-dependent mammalian monooxygenase, catalyzes the conversion of dopamine to the neurotransmitter norepinephrine in the sympathetic nervous system.<sup>1-4</sup> Recent attention has been directed toward understanding the details of its catalytic mechanism for the purpose of rational development of specific inhibitors and alternate substrates as potential therapeutic agents for the modulation of adrenergic activity *in vivo*.<sup>5-7</sup> We now report that DBM catalyzes aromatization of 1-(2-aminoethyl)-1,4-cyclohexadiene [(I); (CHDEA)] in a facile process which exhibits the characteristics of the normal DBM reductive monooxygenation pathway but apparently does not entail oxygen transfer to the organic substrate.

CHDEA was synthesized, characterized,<sup>8</sup> and shown to be an excellent substrate for soluble bovine adrenal chromaffin granule DBM, with kinetic parameters comparable to those of the most

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(18) **2a**: <sup>1</sup>H NMR (room temperature, toluene-*d*<sub>6</sub>) δ 1.67 (30 H, C<sub>5</sub>-(CH<sub>3</sub>)<sub>5</sub>), 0.23 (3 H, Zr-CH<sub>3</sub>). **2b**: <sup>1</sup>H NMR (room temperature, toluene-*d*<sub>6</sub>) δ 2.24 (q, <sup>2</sup>J<sub>HH</sub> = 7 Hz, 4 H, -CH<sub>2</sub>CH<sub>3</sub>), 1.77 (d, <sup>1</sup>J<sub>HH</sub> = 8 Hz, 24 H, C<sub>4</sub>Et(CH<sub>3</sub>)<sub>4</sub>), 0.80 (t, <sup>2</sup>J<sub>HH</sub> = 7 Hz, 6 H, -CH<sub>2</sub>CH<sub>3</sub>), 0.30 (s, 3 H, Zr-CH<sub>3</sub>).

(19) Performed by Crystallitics, Co., Lincoln, NE. Crystallographic data for **2b**: monoclinic crystal system, *a* = 10.538 (3) Å, *b* = 10.876 (3) Å, *c* = 13.029 (3) Å, β = 92.73 (2)°, *V* = 1491.6 (7) Å<sup>3</sup>, *Z* = 2 in space group *Pn-an* alternate of *Pc-C*<sub>2</sub> (No. 7). *R* = 0.03 for 3495 observed reflections. Hydrogen atoms on C<sub>2</sub>B<sub>9</sub>H<sub>12</sub> were located by Fourier synthesis and refined as independent isotropic atoms.

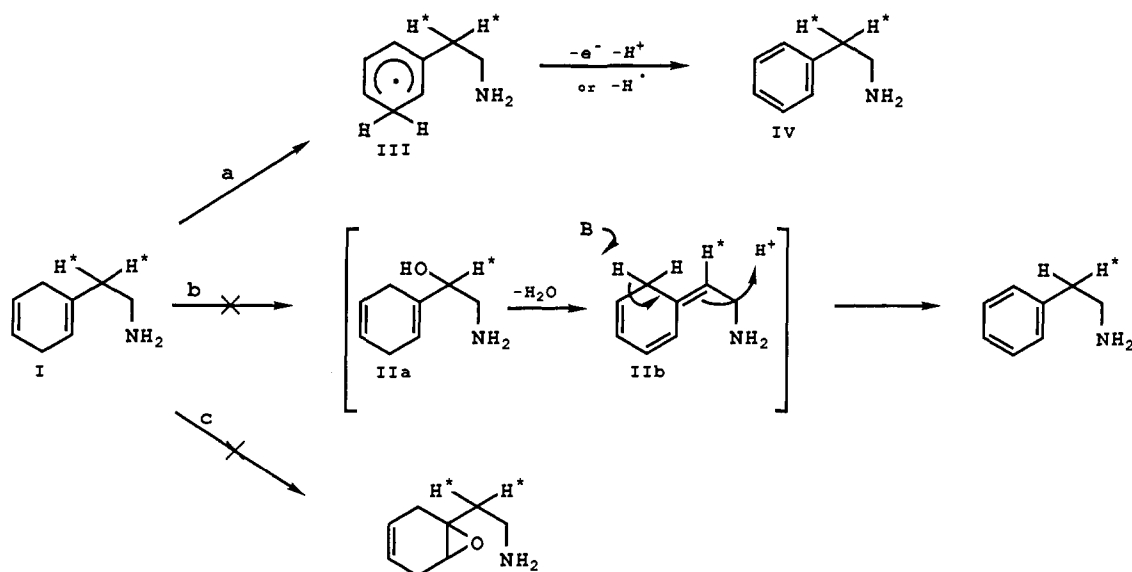
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Scheme I

Table I. Kinetic Parameters of DBM Reactions<sup>a</sup>

substrate	$k_{\text{cat}}$ (s <sup>-1</sup> )	$K_m$ (mM)	$k_{\text{cat}}/K_m$ (s <sup>-1</sup> M <sup>-1</sup> )
CHDEA	72.5 (±3.2)	1.3 (±0.2)	5.5 × 10 <sup>4</sup>
CHDEA- <i>d</i> <sub>2</sub>	65.4 (±4.5)	1.3 (±0.3)	5.0 × 10 <sup>4</sup>
tyramine <sup>b</sup>	120.0	2.0	6.0 × 10 <sup>4</sup>
CHEA <sup>b</sup>	90.1	6.1	1.5 × 10 <sup>4</sup>
2-phenylethylamine <sup>b</sup>	90.0	7.0	1.3 × 10 <sup>4</sup>

<sup>a</sup>Kinetic values were determined with DBM of 20–50 U/mg specific activity and normalized to 21 U/mg for comparison. <sup>b</sup>These kinetic values were previously reported.<sup>6a,d,14</sup>

active DBM substrate, tyramine (Table I). Only one product was detectable by HPLC analysis of the DBM/CHDEA reaction,<sup>9</sup> and this was unequivocally identified as 2-phenylethylamine by GC-MS and NMR. Product formation is strictly dependent on the presence of active enzyme, an electron donor, and molecular oxygen. A product/oxygen/ascorbate stoichiometry of 1.00:0.97:0.91 was determined for the DBM/CHDEA reaction by quantitative comparison of 2-phenylethylamine formation (by HPLC), oxygen consumption [measured polarographically<sup>5b</sup>], and ascorbate consumption [by HPLC-EC<sup>6c</sup>]. These quantitative experiments confirm that 2-phenylethylamine formation occurs via the normal reductive monooxygenation pathway of DBM and that 2-phenylethylamine is the *only* product formed during enzymatic turnover.<sup>9</sup> The DBM/CHDEA reaction is a facile, kinetically well-behaved reaction with no observable turnover-dependent enzyme inactivation under standard assay conditions.

The observed product, 2-phenylethylamine, could conceivably arise from initial hydroxylation at the exocyclic methylene (analogous to usual benzylic hydroxylation by DBM) followed by nonenzymatic or enzyme-assisted decomposition to the aromatic product (Scheme I, pathway b). As an initial test for this possibility, the DBM/CHDEA reaction was carried out in <sup>2</sup>H<sub>2</sub>O, since it would normally be expected that such a hydroxylation mechanism would result in deuterium incorporation into the benzylic position of the product during aromatization of species II (Scheme I). The products from paired enzymatic reactions, carried out in either <sup>2</sup>H<sub>2</sub>O (ca. 90 atom % <sup>2</sup>H) or H<sub>2</sub>O, were analyzed by <sup>1</sup>H NMR, <sup>2</sup>H NMR, and GC-MS. The products from both reaction mixtures showed identical GC-MS spectra with molecular ion peaks (M<sup>+</sup>) at 121 and with no detectable difference in the intensities of the (M + 1)<sup>+</sup> peaks at 122. As a complimentary, and more demanding, test of pathway b, dideuterated CHDEA

(CHDEA-*d*<sub>2</sub>) was synthesized, characterized,<sup>10</sup> and examined with DBM. CHDEA-*d*<sub>2</sub> was found to be an excellent substrate for DBM, and the steady state kinetic parameters were virtually identical with those of the nondeuterated compound. The product from the DBM/CHDEA-*d*<sub>2</sub> reaction was identified as 2-phenyl(2,2-<sup>2</sup>H)ethylamine (IV) by <sup>1</sup>H NMR with no incorporation of hydrogen into the benzylic position evident in the NMR spectrum. Furthermore, GC-MS analysis of the product from the DBM/CHDEA-*d*<sub>2</sub> reaction revealed no loss of deuterium at the benzylic position of the product, confirming the above results (Figure 1). In the initial hydroxylation event of pathway b, deuterium from the exocyclic methylene is transferred to oxygen to produce a molecule <sup>2</sup>HOH.<sup>5a</sup> Subsequently a second fully protonated water molecule (HOH) is formed upon dehydration of species IIa. Thus, our finding that fully deuterated 2-phenylethylamine is formed as the final product could be accommodated by pathway b if a specific rebound of *only* the deuterium from the first water molecule would occur during aromatization, a highly unlikely and to our knowledge unprecedented circumstance. Taken together, these two experiments effectively rule out a mechanism involving initial hydroxylation at exocyclic methylene followed by aromatization (pathway b). A mechanism consistent with our results is shown as pathway a in the scheme. We also note that no ring-oxygenated products are observed (pathway c), in contrast to the recent report of epoxidation of L-(2,5-<sup>2</sup>H<sub>2</sub>)phenylalanine by phenylalanine hydroxylase.<sup>11</sup>

1,4-Cyclohexadiene is structurally very similar to its aromatic cognates, and the ring carbon atoms are coplanar as evidenced by X-ray crystallographic studies on 2-(1,4-cyclohexadienyl)-glycine<sup>12</sup> and NMR studies on 1,4-cyclohexadiene.<sup>13</sup> On the basis of this structural similarity it is reasonable to assume that the binding of CHDEA to the active site of DBM is similar to binding of the regular DBM substrate, 2-phenylethylamine. Recently, we have also demonstrated that 1-(2-aminoethyl)-1-cyclohexene (CyHEA) is a facile DBM substrate, and the product has been identified as the corresponding (*S*)-allylic alcohol.<sup>14</sup>

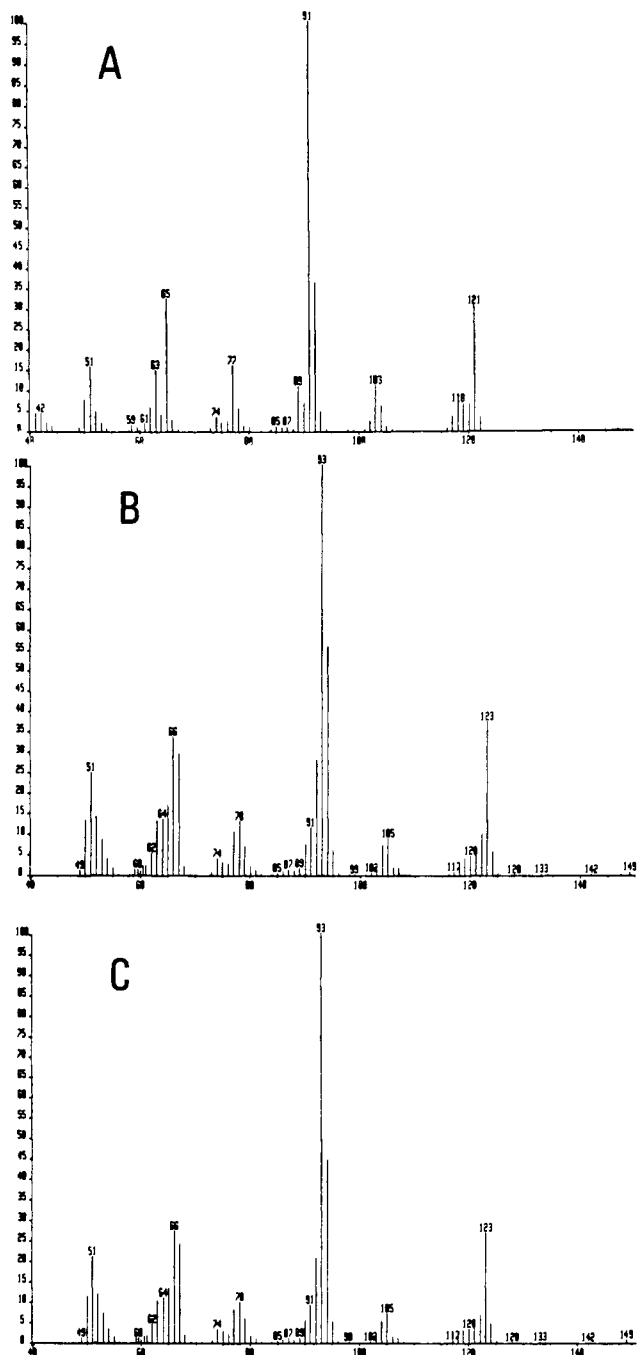
(10) 2-Phenyl(2,2-<sup>2</sup>H<sub>2</sub>)acetoneitrile was obtained by base-catalyzed exchange of benzylic protons with <sup>2</sup>H<sub>2</sub>O (100% benzylic deuterium by <sup>1</sup>H NMR and mass spectra). This nitrile was reduced with 1:1 mixture of LiAlH<sub>4</sub>/AlCl<sub>3</sub> essentially according to Nystrom, R. F. *J. Am. Chem. Soc.* **1955**, *77*, 2544–2545 (360 MHz <sup>1</sup>H NMR analysis indicated no loss of deuterium upon reduction). 2-Phenyl(2,2-<sup>2</sup>H<sub>2</sub>)ethylamine was converted to CHDEA-*d*<sub>2</sub> by Birch reduction under conditions identical with those of 1-(2-aminoethyl)-1,4-cyclohexadiene, and 360 MHz <sup>1</sup>H NMR and mass spectra indicated the presence of ca. 100% deuterium at the exocyclic methylene.

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**Figure 1.** GC-MS spectra of (A), authentic 2-phenyl(2,2- $H_2$ )ethylamine (B), and authentic 2-phenyl(2,2- $^2H_2$ )ethylamine (C). Enzymatic product from DBM/CHDEA- $d_2$  reaction.

Autooxidation of 1,4-cyclohexadienes<sup>15</sup> as well as their reactions with organic free radicals<sup>16</sup> have been shown to proceed exclusively through a free-radical pathway, involving initial generation of the cyclohexadienyl radical, leading to formation of the corresponding

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aromatic products. It has also been well-documented that peracids, known to carry out concerted oxygen-transfer reactions,<sup>17</sup> react with 1,4-cyclohexadienes to produce only the corresponding epoxides but not the aromatized products.<sup>18</sup> These facts suggest that DBM-mediated aromatization of CHDEA is indicative of initial abstraction of a hydrogen atom from a ring methylene, as opposed to a concerted two-electron process. Furthermore, the redirection of the specificity of DBM with CHDEA substrate—with the enzyme producing only aromatized product and not exocyclic allylic alcohol—is likely a consequence of the fact that initial abstraction of a hydrogen atom from a ring methylene of 1,4-cyclohexadiene is more favorable than abstraction of an allylic hydrogen atom from the exocyclic methylene.<sup>19</sup> Thus, our finding of DBM-mediated aromatization of CHDEA is best accommodated by a mechanism which involves initial abstraction of a hydrogen atom from a ring methylene by the activated copper oxygen species of DBM.

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## Scanning Tunneling Microscopy Investigations of a New Charge Density Wave Phase in Niobium-Doped Tantalum Disulfide

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Understanding the electronic and structural factors that determine metal/superconductor and metal/charge density wave (CDW) phase transitions is central to current research efforts in solid-state chemistry and physics.<sup>1</sup> Typical methods used to study such transitions (photoelectron spectroscopy, diffraction, etc.) generally provide information relevant to the average electronic and structural properties of materials. Many fundamental problems, however, such as understanding impurity effects are local in nature and difficult to address using these methods. The scanning tunneling microscope (STM),<sup>2</sup> which can provide atomic-resolution electronic and structural information, has been used to study superconducting<sup>3</sup> and CDW phases,<sup>4-7</sup> although few of these studies have probed local problems.<sup>6,7</sup> Herein we describe

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