COMMUNICATION

Cooperative Dinitrogen Capture by a Diboraanthracene/Samarocene Pair

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The combination of a boron Lewis acid and a decamethylsamarocene, specifically 9,10-Me_2-9,10-diboraanthracene with $(C_5Me_5)_2Sm^{II}(THF)_2$, in toluene leads to cooperative reductive capture of N_2. The product crystallizes as the salt, $[(C_5Me_5)_2Sm^{III}(THF)_2][(C_5Me_5)_2Sm^{III}(\eta^2\text{-}N_2B_2C_{14}H_{14})]$, 1, which formally is comprised of an $(N{=}N)^{2-}$ moiety sandwiched between a $[(C_5Me_5)_2Sm^{III}]^{1+}$ metallocene cation and the diboraanthracene ditopic Lewis acid.

The conversion of atmospheric N_2 into bioavailable forms is essential to all life. As such, the activation of N_2 has driven scientific exploration for decades, with considerable attention paid to the role of d- and f-block metals in this process in biological and synthetic contexts. A range of mono- and polynuclear metal complexes have been shown to mediate N_2 reduction, in some cases catalytically.[1-3] New approaches to N_2 activation continue to emerge, however. Recent pathbreaking studies by Braunschweig describe a low-valent boron compound capable of N_2 reduction.[4-6] Szymczak has explored the role of Lewis acids[7] and hydrogen bonding[8] in the activation of mononuclear transition metal N_2 complexes, and Simonneau has shown that borane adducts of Mo and W N_2 complexes enable hydroboration and hydrosilylation of the bound N_2 ligand via Frustrated Lewis Pair (FLP) reactivity.[9, 10] FLP activation of dinitrogen has also been observed with uranium.[11-16]

Along these lines, we became interested in the interplay of divalent lanthanide reducing agents[17, 18] and the redox-active diboron heterocycle 9,10-dimethyl-9,10-diboraanthracene (Me_2DBA).[19] Reduced diboraanthracene (DBA) and related diboron heterocycles have been shown to activate a range of E–H bonds[20-22] and unsaturated substrates (including CO_2 and O_2, but notably excluding N_2) via 1,4 cycloaddition chemistry at boron (Figure 1, top).[23-25] DBA can also function as a ditopic Lewis acid in the activation of phthalazines towards Diels-Alder reactions that ultimately liberate N_2 (Figure 1, bottom).[25, 26] The 9,10-dihydrocarbyl-substituted DBA species exhibit rich redox chemistry and can stabilize unusual species like anionic Au^{1-}.[27]

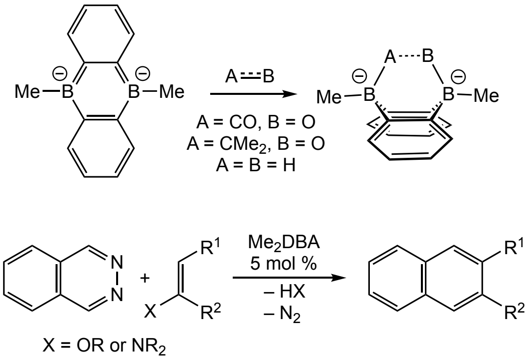
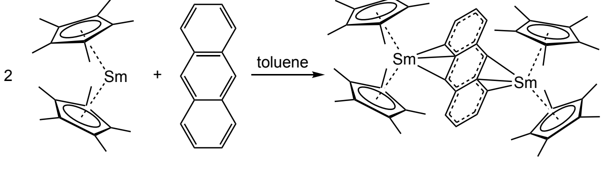


Figure 1. Examples of small molecule activation using Me_2DBA. Top: bond activation by Me_2DBA dianions; bottom: Me_2DBA-catalyzed Diels-Alder reactions of phthalazines with N_2 loss.[23-26]

The Sm(II) metallocenes, $(C_5Me_5)_2Sm(THF)_2$[28] and $(C_5Me_5)_2Sm$[29] were of interest as reducing agents since two equivalents of $(C_5Me_5)_2Sm$ reduce anthracene to a $(C_{14}H_{10})^{2-}$ dianion that should be bent, but was found to be planar, eq 1.[30]



(1)

In addition, unsolvated $(C_5Me_5)_2Sm$ is capable of N_2 reduction.[31] It was of interest to see how this chemistry translated to 9,10-dihydrocarbyl-substituted 9,10-diboraanthracenes. However, because $(C_5Me_5)_2Sm$ is so reactive,[31] initial studies were conducted with the solvated $(C_5Me_5)_2Sm(THF)_2$. This led to the unexpected cooperative capture and reduction of N_2 by the $Me_2DBA/(C_5Me_5)_2Sm(THF)_2$ pair. This reaction bears

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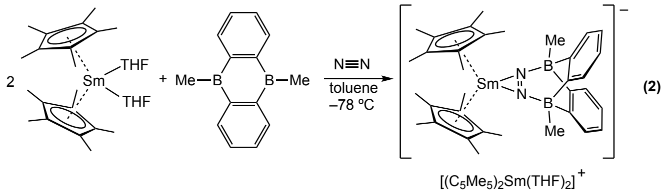
resemblance to FLP chemistry[32-34] in that neither of the two components reacts with N_2 on its own.

Addition of 1.0 equivalents of bright yellow 9,10-dimethyl-9,10-diboraanthracene to 2.0 equivalents of purple $(C_5Me_5)_2Sm(THF)_2$ in toluene in an N_2-containing glovebox at –78 °C generated a brown mixture that became orange after 8h at –78 °C. Layering hexanes over the orange solution at –35 °C generated yellow single crystals of $[(C_5Me_5)_2Sm^{III}(THF)_2][(C_5Me_5)_2Sm^{III}(\eta^2\text{-}N_2B_2C_{14}H_{14})]$, **1**, which were characterized by single crystal X-ray diffraction, IR, and NMR spectroscopy, Figure 2, eq 2. Reactions with a 1:1 stoichiometry gave smaller yields of the same product, **1**.



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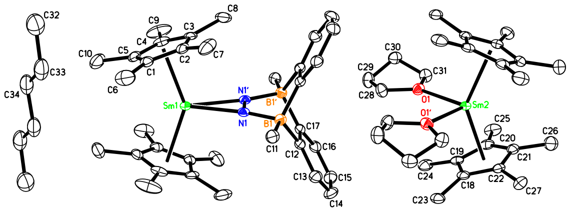

Figure 2. ORTEP diagram of $[(C_5Me_5)_2Sm^{III}(THF)_2][(C_5Me_5)_2Sm^{III}(\eta^2\text{-}N_2B_2C_{14}H_{14})]$ with hexane in the lattice with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The $[(C_5Me_5)_2Sm]^+$ unit in the anion and the $[(C_5Me_5)_2Sm(THF)_2]^+$ counter-cation each have 2.42 Å Sm-(C_5Me_5 ring centroid) distances, consistent with a Sm(III) assignment.[35, 36] For comparison, the analogous distances in bona fide Sm(II) metallocenes are much longer, as in the 2.60 Å distance observed in $(C_5Me_5)_2Sm(THF)_2$.[28, 36] Likewise, the N-N distance in **1** is 1.252(3) Å, in the range expected for a $(N{=}N)^{2-}$ unit.[37] The symmetry equivalent 2.3560(2) Å Sm–N bond distances are similar to the 2.347(6) and 2.368(6) Å distances in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ which has 2.45 Å Sm-(C_5Me_5 ring centroid) distances.[25] The 1.598(3) Å distances of the new B-N linkages are in the single bond range, cf. the single bond in $H_3B–NH_3$ is 1.58(2) Å.[38]

The ^1H NMR spectrum of freshly isolated material had resonances that could be attributed to the two types of C_5Me_5 ligands in **1** and the diboraanthracene protons, but the paramagnetism of Sm(III) did not allow a definitive assignment (Figure S1). The ^{11}B NMR displayed a single resonance at –0.9 ppm well shifted from the starting material resonance at 68 ppm, consistent with the presence of a four-coordinate boron species (Figure S2).[32, 39] The complex reacts with potassium graphite and MeI, but neither reaction cleanly separated the functionalized heterocycle (see SI).

Addition of 9,10-dimethyl-9,10-diboraanthracene to $(C_5Me_5)_2Sm(THF)_2$ in toluene under *argon* at –78 °C also generated a brown mixture, but the mixture never turned orange as in the formation of **1** and no crystallographically definable products could be isolated. The brown product, which displayed an EPR spectrum characteristic of an organic radical and a UV-visible spectrum distinct from **1** (Figures S4 and S5), did react with N_2 to generate **1**. Hence, the reaction appears to go stepwise. Complex 1 can also be generated from the reaction of $(C_5Me_5)_2Sm$ with Me_2DBA under Ar followed by exposure to N_2 and THF, but again, no complex was isolable from the reaction under Ar.

Reactions of a bulkier DBA derivative, 9,10-bis(2-(diisopropylphosphino)phenyl)-9,10-diboraanthracene, and simple triphenylborane, BPh_3, with $(C_5Me_5)_2Sm(THF)_2$ in toluene were attempted under dinitrogen but ^1H NMR spectroscopy indicated that no reaction occurred. $B(C_6F_5)_3$ reacts with $(C_5Me_5)_2Sm(THF)_2$ to form a red solution that contains multiple boron-containing species based on the ^{11}B NMR spectrum and an IR spectrum distinct from the starting materials, but crystalline products analogous to **1** were not isolated (see SI).

In conclusion, the ditopic Lewis acid 9,10-dimethyl-9,10-diboraanthracene in the presence of the Sm(II) reducing agent, $(C_5Me_5)_2Sm(THF)_2$, can capture and reduce dinitrogen. Neither the diboraanthracene nor $(C_5Me_5)_2Sm(THF)_2$ react with dinitrogen on its own. Although the new dinitrogen containing heterocycle was not readily cleaved from the product, this reaction shows the potential for the cooperative activation of small molecules with diboraanthracenes and organometallic reducing agents as unusual as $(C_5Me_5)_2Sm(THF)_2$.

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Conflicts of interest

There are no conflicts to declare.

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