Dalton Transactions

Cooperative Dinitrogen Capture by a Diboraanthracene/Samarocene Pair

Journal:	*Dalton Transactions*
Manuscript ID	DT-COM-09-2021-003220.R1
Article Type:	Communication
Date Submitted by the Author:	15-Oct-2021
Complete List of Authors:	Xu, Song; University of California Irvine Essex, Laura; University of California Riverside, Chemistry Nguyen, Joseph; University of California Irvine Farias, Phillip; University of California Riverside, Chemistry Ziller, Joseph; University of California, Irvine, Department of Chemistry Harman, Hill; University of California Riverside, Chemistry; Evans, William; University of California- Irvine, Department of Chemistry

COMMUNICATION

Cooperative Dinitrogen Capture by a Diboraanthracene/Samarocene Pair

boReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Song Xu,[a] Laura Essex, [b] Joseph Q. Nguyen,[a] Phillip Farias,[b] Joseph W. Ziller,[a] W. Hill Harman,*[b] and William J. Evans*[a]

The combination of a boron Lewis acid and a decamethylsamarocene, specifically 9,10-Me$_2$-9,10-diboraanthracene with (C$_5$Me$_5$)$_2$Sm^{II}(THF)$_2$, in toluene leads to cooperative reductive capture of N$_2$. The product crystallizes as the salt, [(C$_5$Me$_5$)$_2$Sm^{III}(THF)$_2$][(C$_5$Me$_5$)$_2$Sm^{III}(η^2-N$_2$B$_2$C$_{14}$H$_{14}$)], 1, which formally is comprised of an (N=N)$^{2-}$ moiety sandwiched between a [(C$_5$Me$_5$)$_2$Sm^{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$_2$DBA).[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]

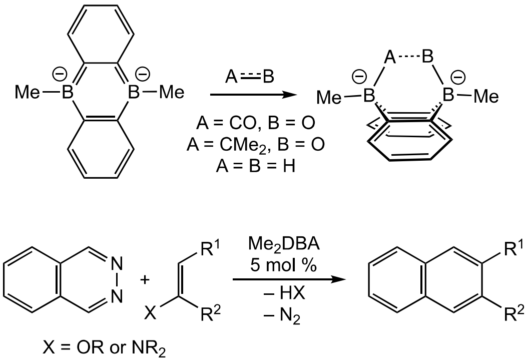
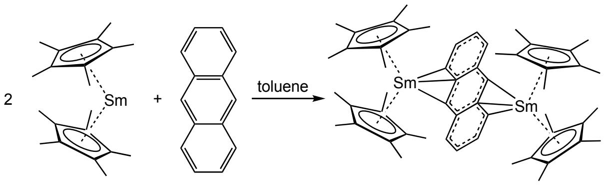


Figure 1. Examples of small molecule activation using Me$_2$DBA. Top: bond activation by Me$_2$DBA dianions; bottom: Me$_2$DBA-catalyzed Diels-Alder reactions of phthalazines with N$_2$ loss.[23-26]

The Sm(II) metallocenes, (C$_5$Me$_5$)$_2$Sm(THF)$_2$[28] and (C$_5$Me$_5$)$_2$Sm[29] were of interest as reducing agents since two equivalents of (C$_5$Me$_5$)$_2$Sm 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$_5$Me$_5$)$_2$Sm 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$_5$Me$_5$)$_2$Sm is so reactive,[31] initial studies were conducted with the solvated (C$_5$Me$_5$)$_2$Sm(THF)$_2$. This led to the unexpected cooperative capture and reduction of N$_2$ by the Me$_2$DBA/(C$_5$Me$_5$)$_2$Sm(THF)$_2$ pair. This reaction bears

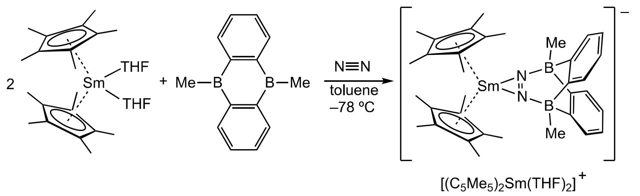
---

[a] Department of Chemistry, University of California, Irvine, California 92697-2025, United States. E-mail: wevans@uci.edu
[b] Department of Chemistry, University of California, Riverside, California 92521, United States. E-mail: hill.harman@ucr.edu

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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**.



(2)

1

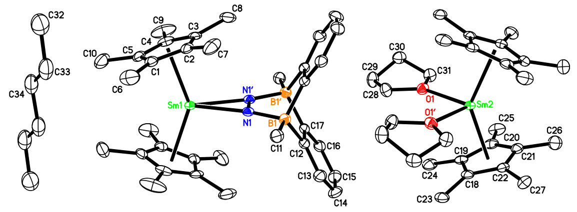


Figure 2. ORTEP diagram of $[(C_5Me_5)_2Sm^{III}(THF)_2][(C_5Me_5)_2Sm^{III}(\eta^2\text{-}N_2B_2C_{14}H_{14})]$ with hexane in the lattice with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

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 $(C_5Me_5)_2Sm(THF)_2$.

We thank the U.S. National Science Foundation for support under grants CHE-1752876 (to W.H.H.) and CHE-1855328 (to W.J.E.).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. G. Qing, R. Ghazfar, S. T. Jackowski, F. Habibzadeh, M. M. Ashtiani, C.-P. Chen, M. R. Smith and T. W. Hamann, *Chem. Rev.*, 2020, **120**, 5437.
2. N. Stucke, B. M. Flöser, T. Weyrich and F. Tuczek, *Eur. J. Inorg. Chem.*, 2018, **2018**, 1337.
3. Y. Nishibayashi, *Dalton Trans.*, 2018, **47**, 11290.
4. M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels and H. Braunschweig, *Science*, 2018, **359**, 896.
5. M.-A. Légaré, M. Rang, G. Bélanger-Chabot, J. Schweizer, I. Krummenacher, R. Bertermann, M. Arrowsmith, M. Holthausen and H. Braunschweig, *Science*, 2019, **363**, 1329.
6. M.-A. Légaré, G. Bélanger-Chabot, M. Rang, R. D. Dewhurst, I. Krummenacher, R. Bertermann and H. Braunschweig, *Nat. Chem.*, 2020, **12**, 1076.
7. J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 5952.

8. J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2019, **141**, 8550.
9. A. Coffinet, D. Specklin, L. Vendier, M. Etienne and A. Simonneau, *Chem. Eur. J.*, 2019, **25**, 14300.
10. A. Simonneau, R. Turrel, L. Vendier and M. Etienne, *Angew. Chem. Int. Ed.*, 2017, **56**, 12268.
11. L. Chatelain, E. Louyriac, I. Douair, E. Lu, F. Tuna, A. J. Wooles, B. M. Gardner, L. Maron, and S. T. Liddle, *Nat. Commun.*, 2020, **11**, 337.
12. S. Liddle, L. Doyle, and A. Wooles, *Angew. Chem. Int. Ed.*, 2019, **58**, 6674.
13. D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake, and S. T. Liddle, *Science*, **2012**, 337, 717.
14. D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster,W. Lewis, A. J. Blake, and S. T. Liddle, *Nat. Chem.*, 2013, **5**, 482.
15. D. M. King, P. A. Cleaves, A. J. Wooles, B. M. Gardner, N. F. Chilton, F. Tuna, W. Lewis, E. J. L. McInnes, and S. T. Liddle, *Nat. Commun.*, 2016, **7**, 13773.
16. S.F. McWilliams, D. L. J. Broere, C. J. V. Halliday, S. M. Bhutto, B. Q. Mercado, and P. L. Holland, *Nature*, 2020, **584**, 221.
17. F. Nief, *Dalton Trans.*, 2010, **39**, 6589.
18. M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857.
19. H. Schulz, H. Pritzkow and W. Siebert, *Chem. Ber.*, 1991, **124**, 2203.
20. E. von Grotthuss, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen and M. Wagner, *Angew. Chem. Int. Ed.*, 2016, **55**, 14067.
21. Y. Su, Y. Li, R. Ganguly and R. Kinjo, *Angew. Chem. Int. Ed.*, 2018, **57**, 7846.
22. J. W. Taylor and W. H. Harman, *Chem. Commun.*, 2020, **56**, 13804.
23. A. Lorbach, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2010, **29**, 5762.
24. B. Wang, Y. Li, R. Ganguly, H. Hirao and R. Kinjo, *Nat. Commun.*, 2016, **7**, 11871.
25. J. W. Taylor, A. McSkimming, C. F. Guzman and W. H. Harman, *J. Am. Chem. Soc.*, 2017, **139**, 11032.
26. S. N. Kessler and H. A. Wegner, *Org. Lett.*, 2010, **12**, 4062.
27. J. W. Taylor, A. McSkimming, M.-E. Moret and W. H. Harman, *Angew. Chem. Int. Ed.*, 2017, **56**, 10413.
28. W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1985, **107**, 941.
29. W. J. Evans, L. A. Hughes and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **106**, 4270.
30. W. J. Evans, S. L. Gonzales and J. W. Ziller, *J. Am. Chem. Soc.*, 1994, **116**, 2600.
31. W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6877.
32. C. Tang, Q. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. Song, S. Grimme and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2017, **56**, 16588.
33. D. W. Stephan, *Science*, 2016, **354**, aaf7229.
34. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46.
35. W. J. Evans, T. A. Ulibarri, L. R. Chamberlain, J. W. Ziller and D. Alvarez, *Organometallics*, 1990, **9**, 2124.
36. W. J. Evans and S. E. Foster, *J. Organomet. Chem.*, 1992, **433**, 79.
37. M. E. Fieser, D. H. Woen, J. F. Corbey, T. J. Mueller, J. W. Ziller and W. J. Evans, *Dalton Trans.*, 2016, **45**, 14634.
38. W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson and R. H. Crabtree, *J. Am. Chem. Soc.*, 1999, **121**, 6337.
39. A. Lorbach, M. Bolte, H. W. Lerne, and M. Wagner, *Chem. Commun.*, 2010, **46**, 3592.