Piers' Borane Induced Tandem Hydroboration-Carboboration of Cyclooctatetraene

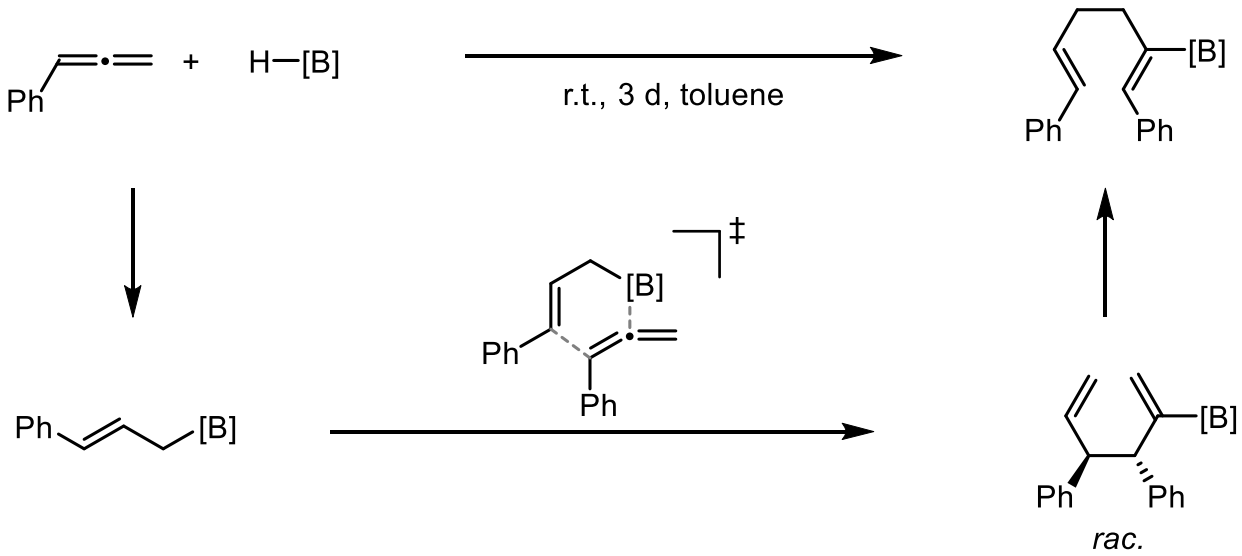
Tizian Müller

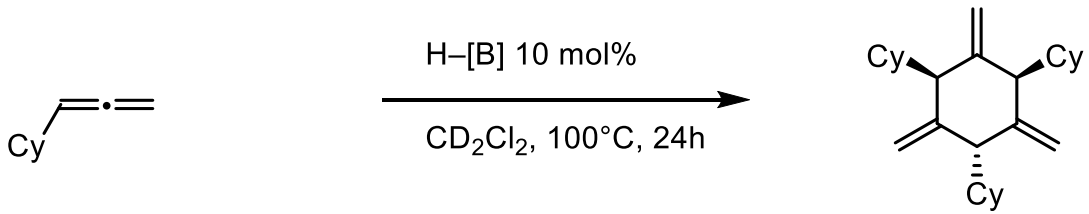
AG Gellrich

Institute for Organic Chemistry
Justus-Liebig University, Giessen

26.08.22

Carboborations of allenes

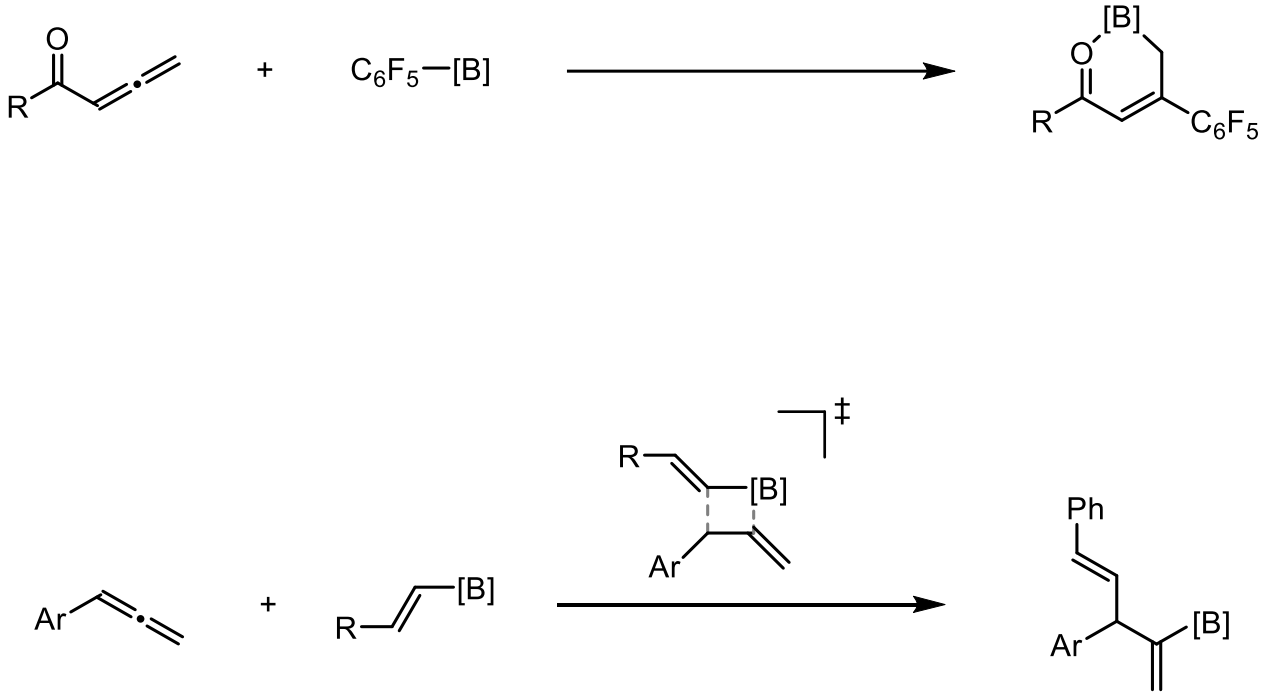




[B] = $B(C_6F_5)_2$

X. Tao, G. Kehr, C. G. Daniliuc, G. Erker, *Angew. Chem. Int. Ed.* **2017**, *56*, 1376 –1380;
X. Tao, C. G. Daniliuc, D. Dittrich, G. Kehr, G. Erker, *Angew. Chem. Int. Ed.* **2018**, *57*,13922 –13926

Carboborations of allenes



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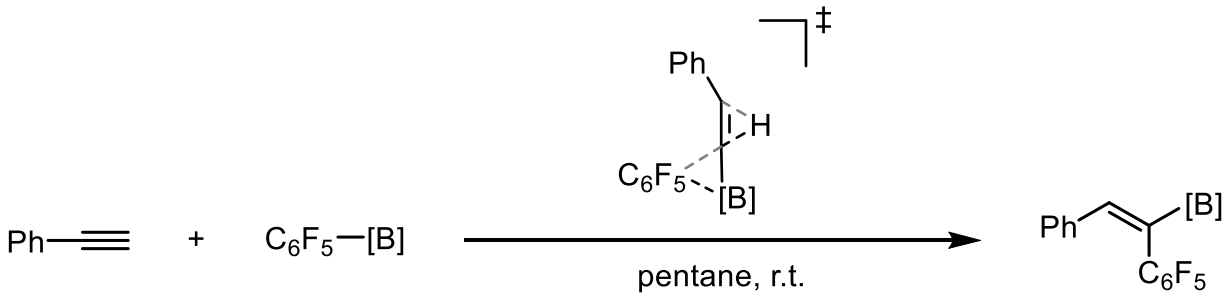
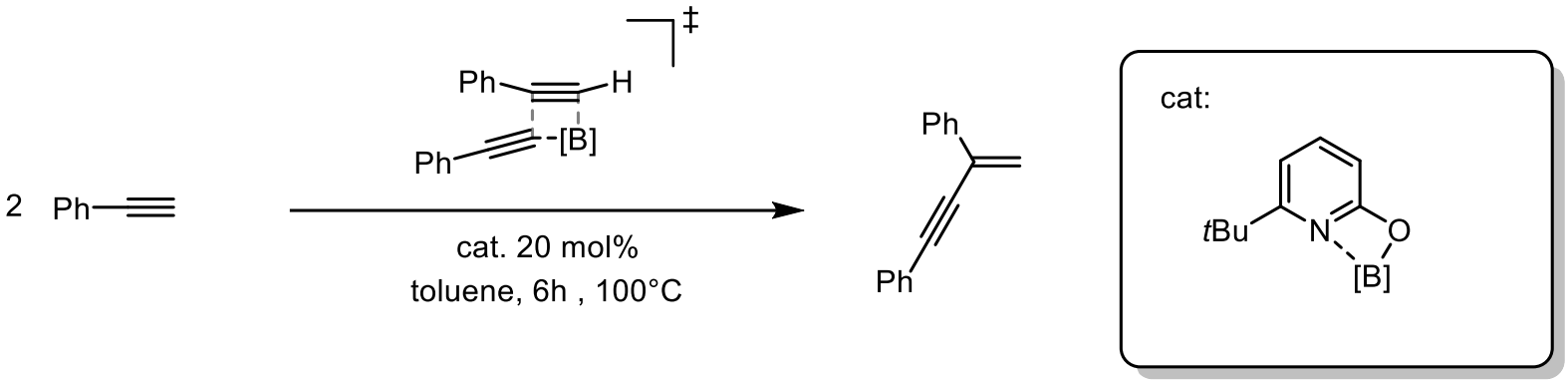
R. L. Melen, L. C. Wilkins, B. M. Kariuki, H. Wadepohl, L. H. Gade, A. S. K. Hashmi, D. W. Stephan, M. M. Hansmann, *Organometallics* **2015**, *34*, 4127; A. Averdunk, M. Hasenbeck, T. Müller, J. Becker, U. Gellrich, *Chemistry*, **2022**, 28, e202200470

Carboborations of alkynes





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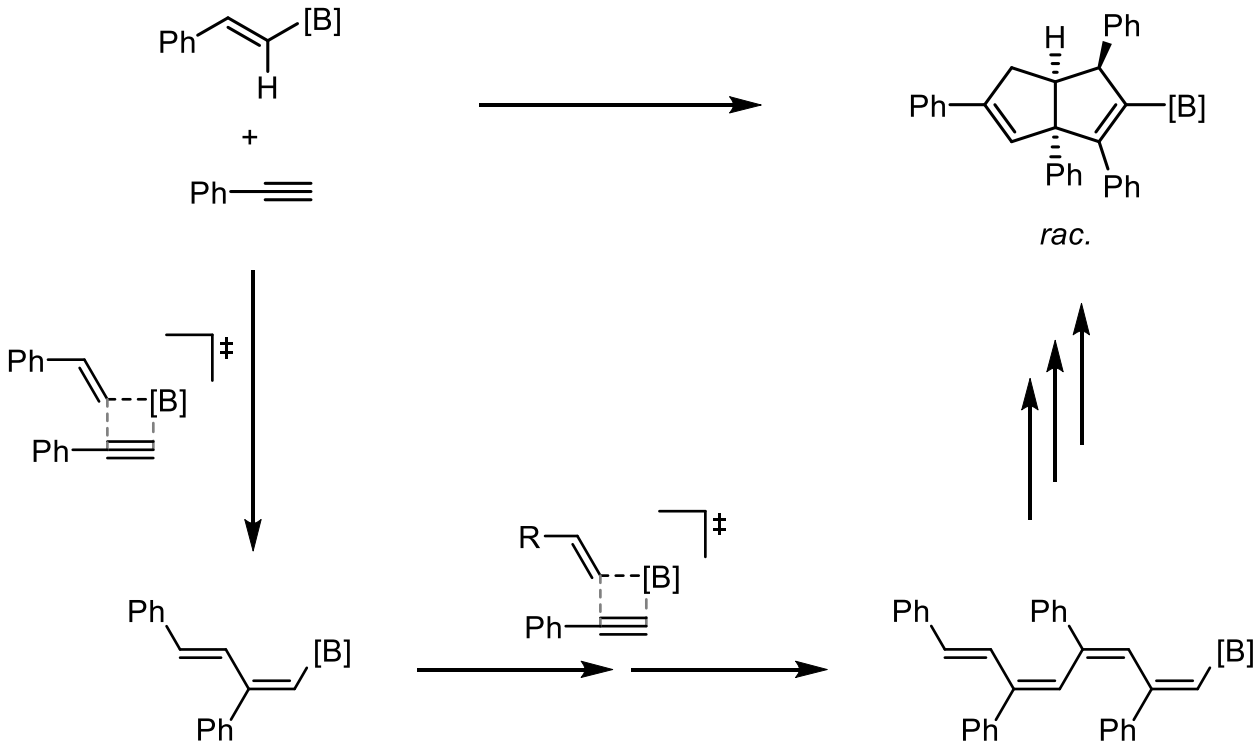
C. Chen, F. Eweiner, B. Wibbeling, R. Fröhlich, S. Senda, Y. Ohki, K. Tatsumi, S. Grimme, G. Kehr, G. Erker, *Chem.–Asian J.* **2010**, *5*, 2199-2208; M. Hasenbeck, T. Müller, U. Gellrich, *Catal. Sci. Technol.*, **2019**,9, 2438-2444

Carboborations of alkynes



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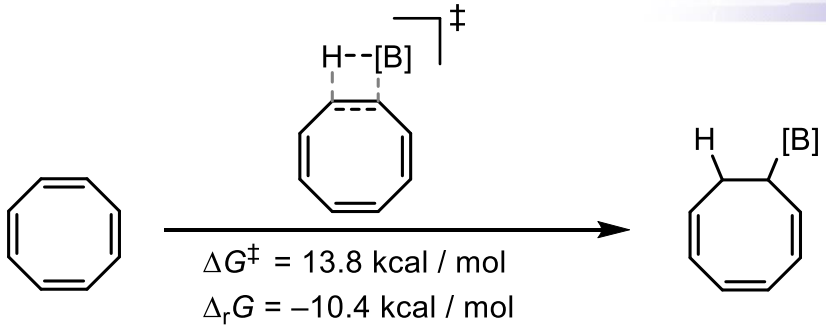
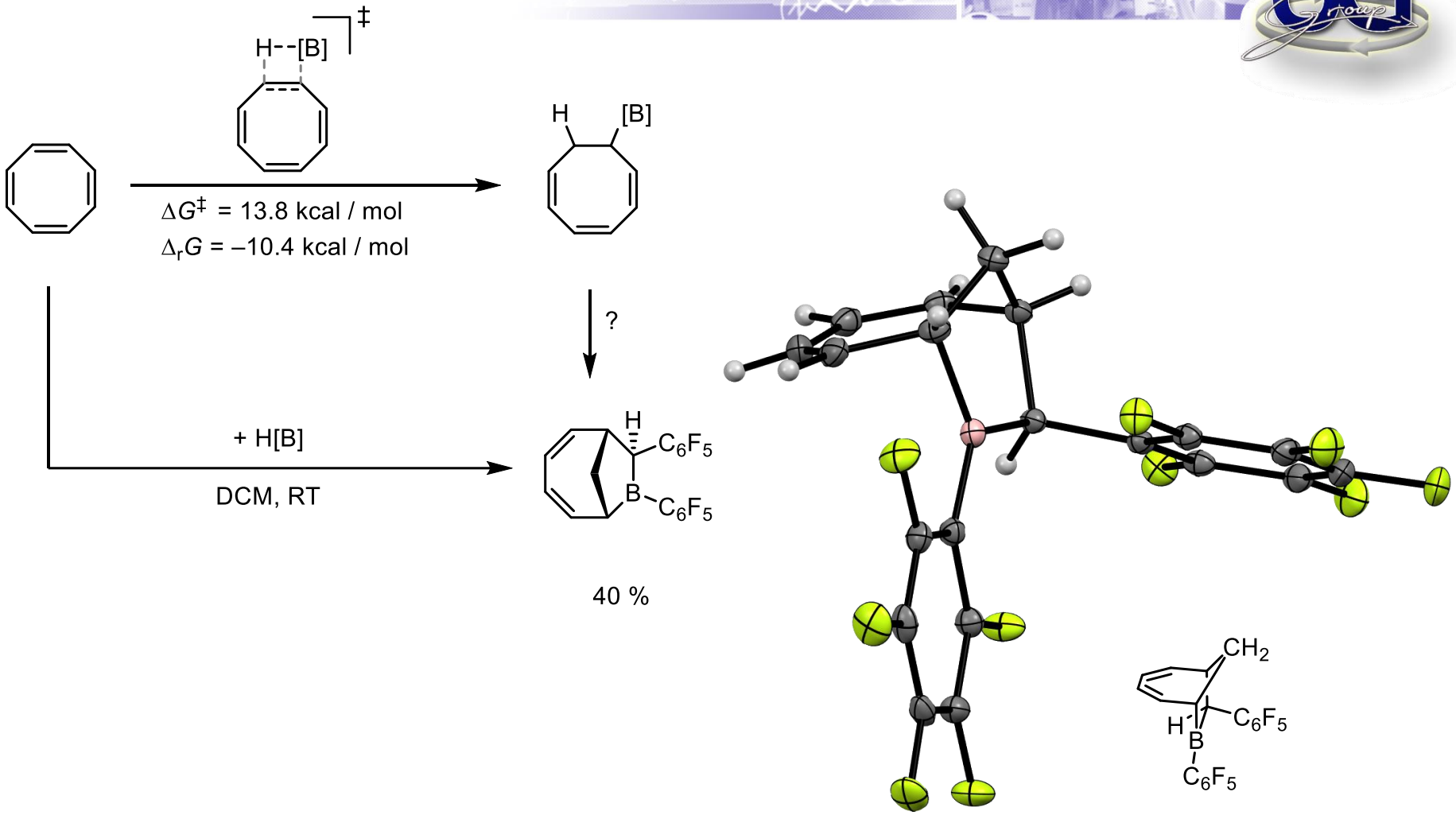
Motivation



[B] = $B(C_6F_5)_2$

PCM(DCM)-revDSD-PBEP86-D4/def2-QZVPP//PCM(DCM)-PBEh-3c
SC-XRD: 50% probability level shown, Hydrogen shown as spheres with arbitrary size

Observations



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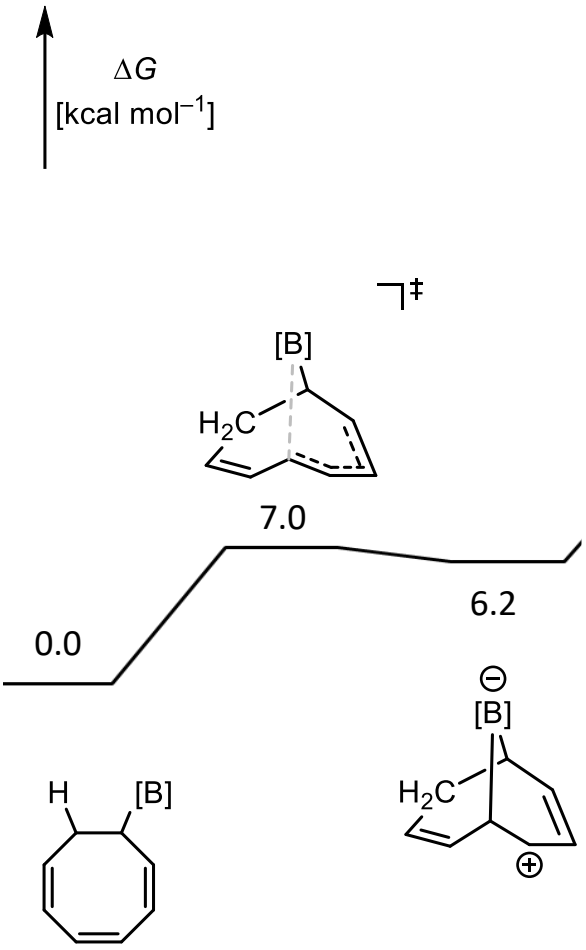
PES



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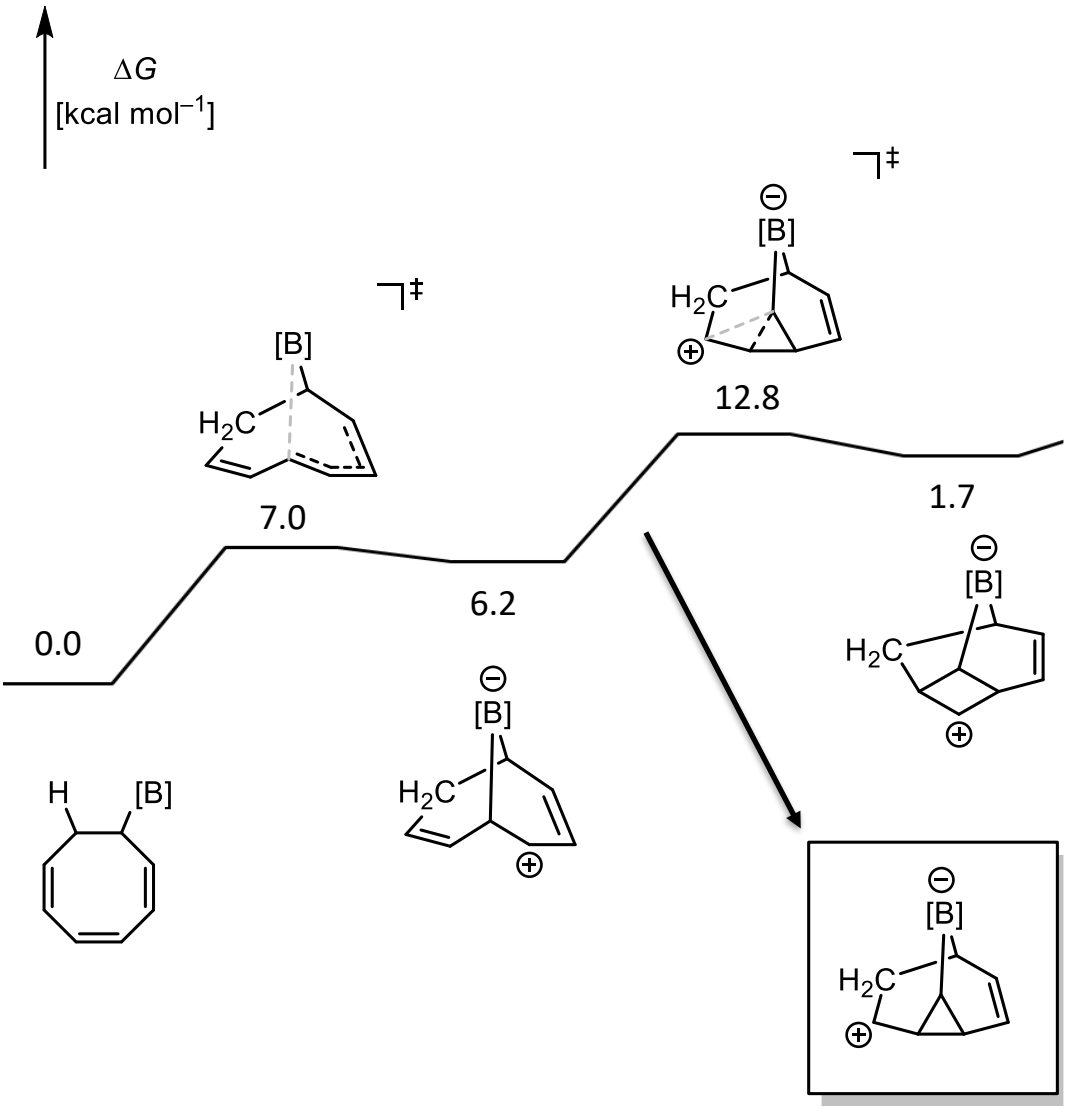

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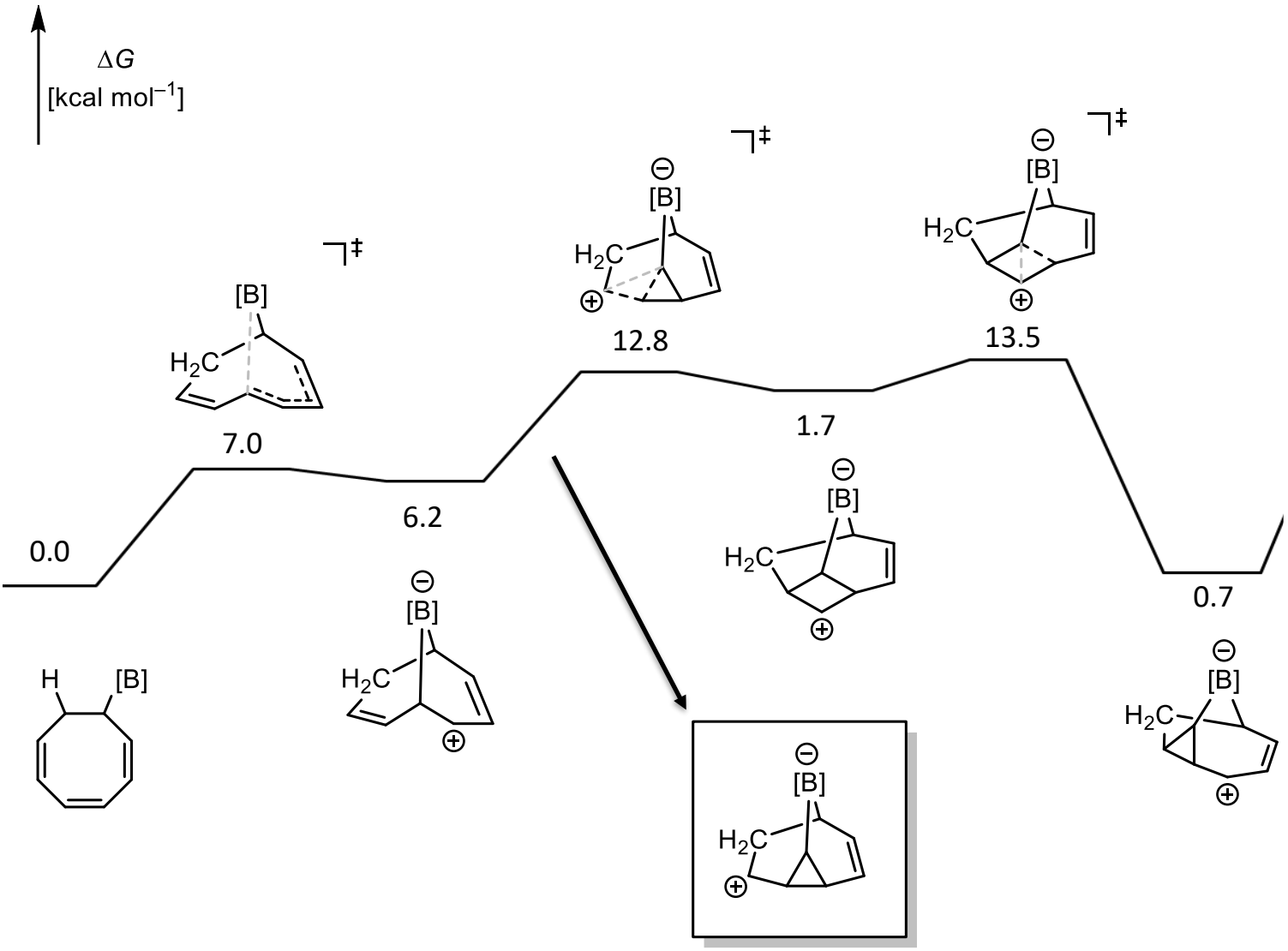

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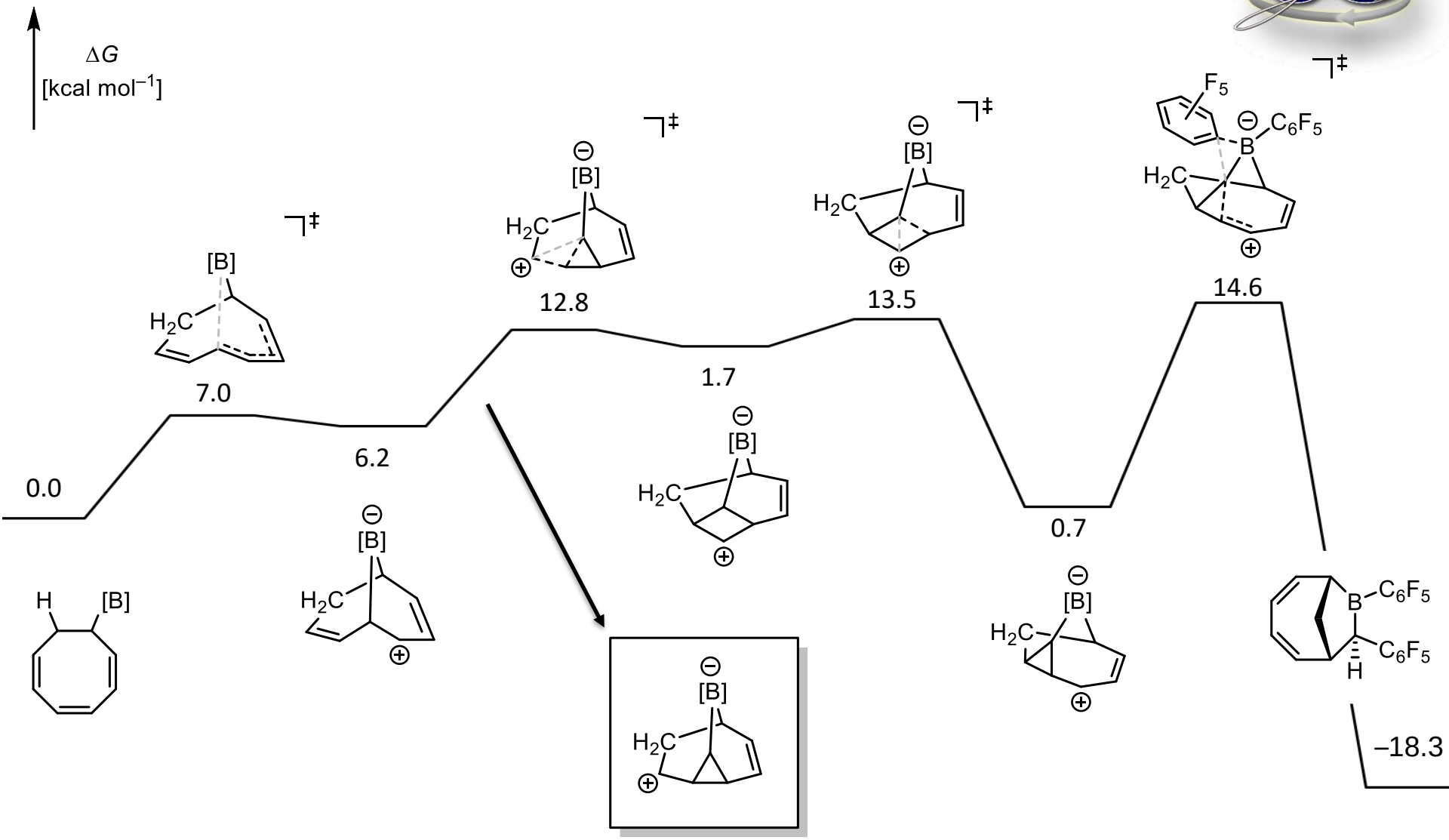

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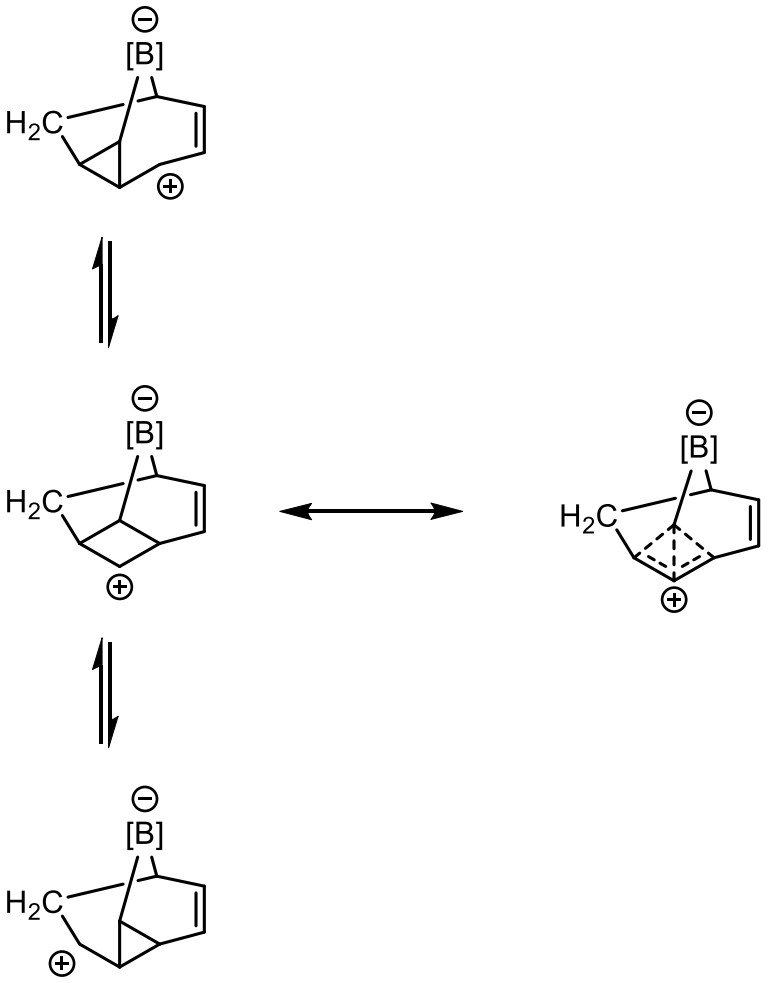
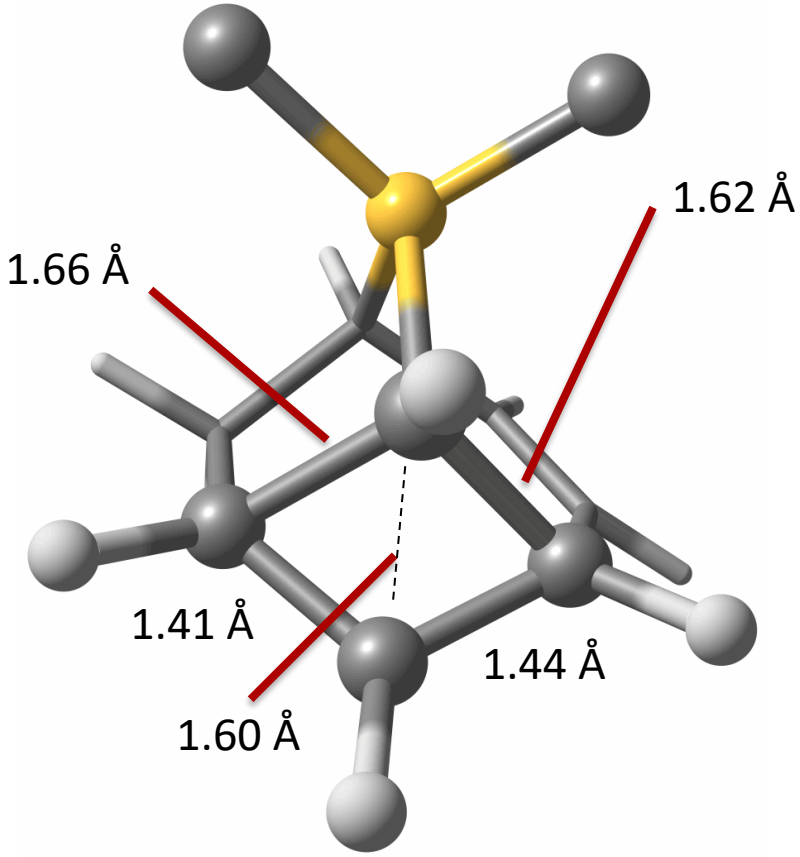
Nonclassical carbocation ?

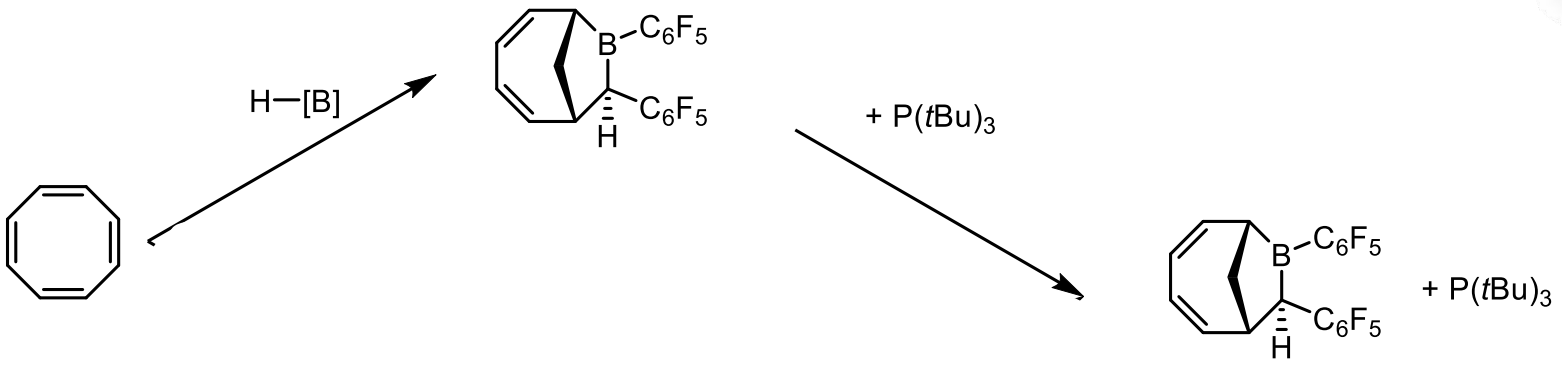




[B] = $B(C_6F_5)_2$

PCM(DCM)-PBEh-3c, C_6F_5 groups omitted for clarity

Capturing of intermediate



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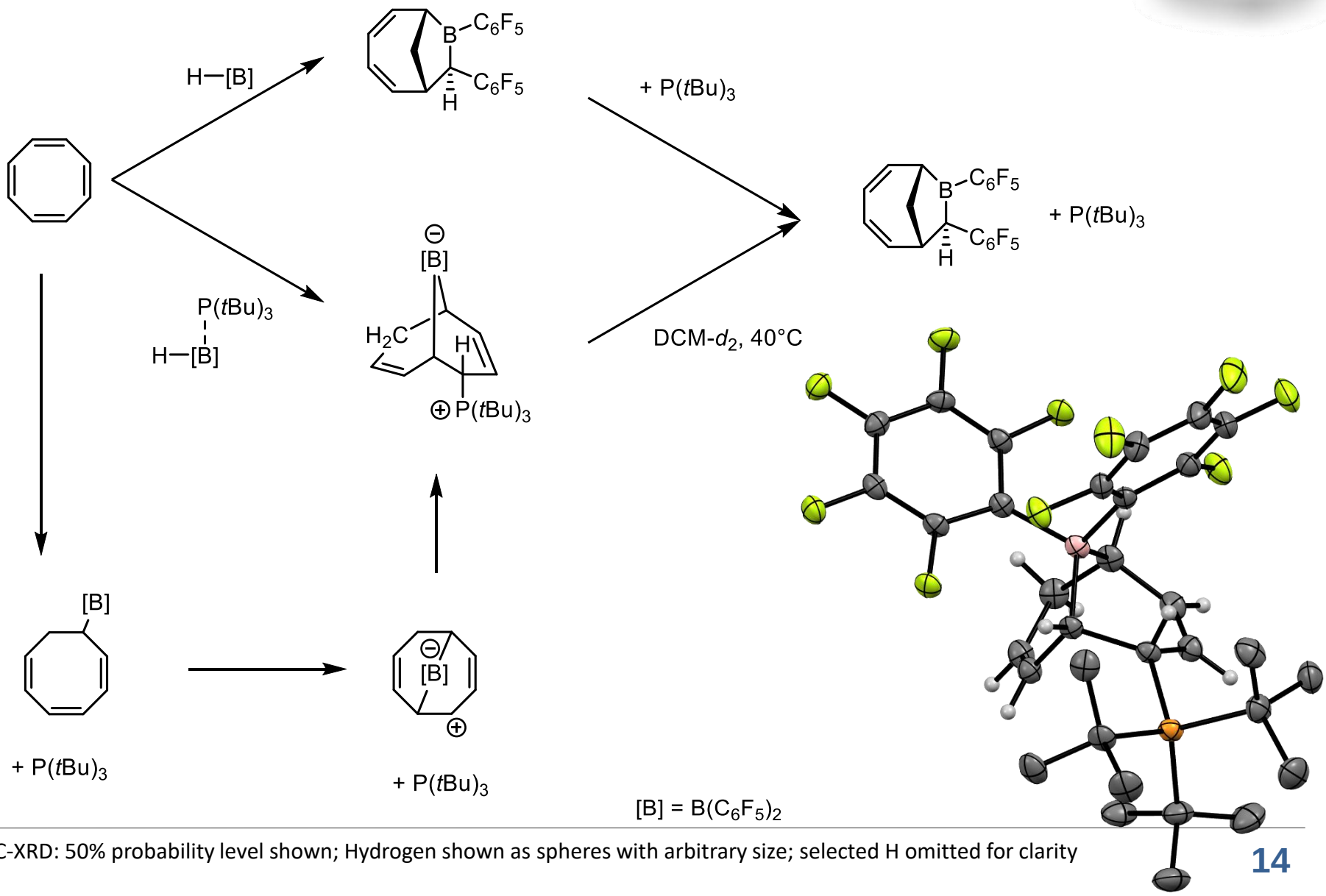
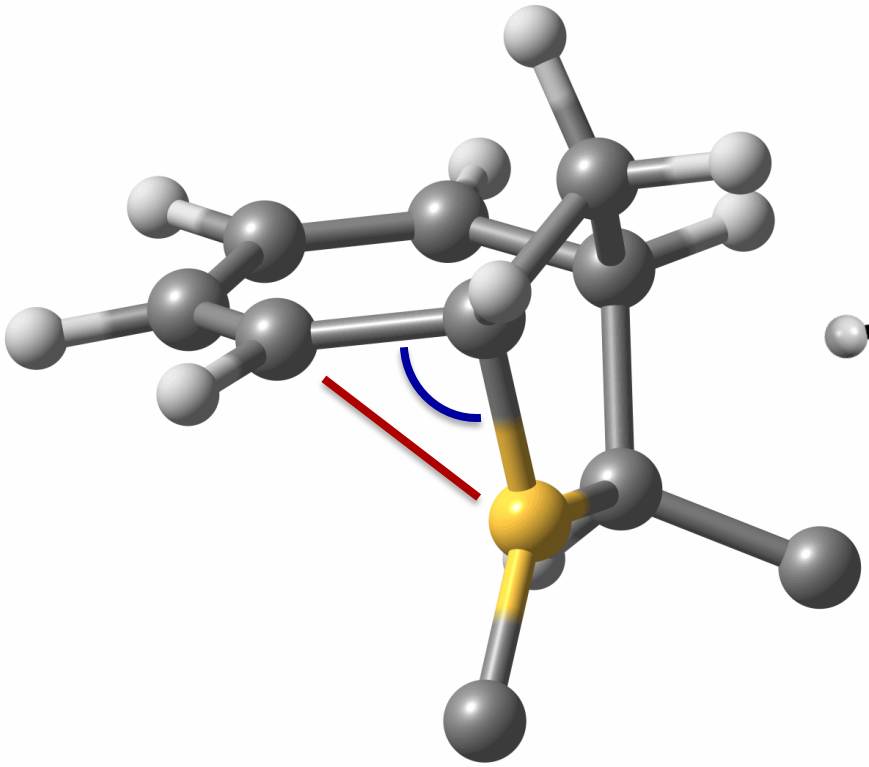
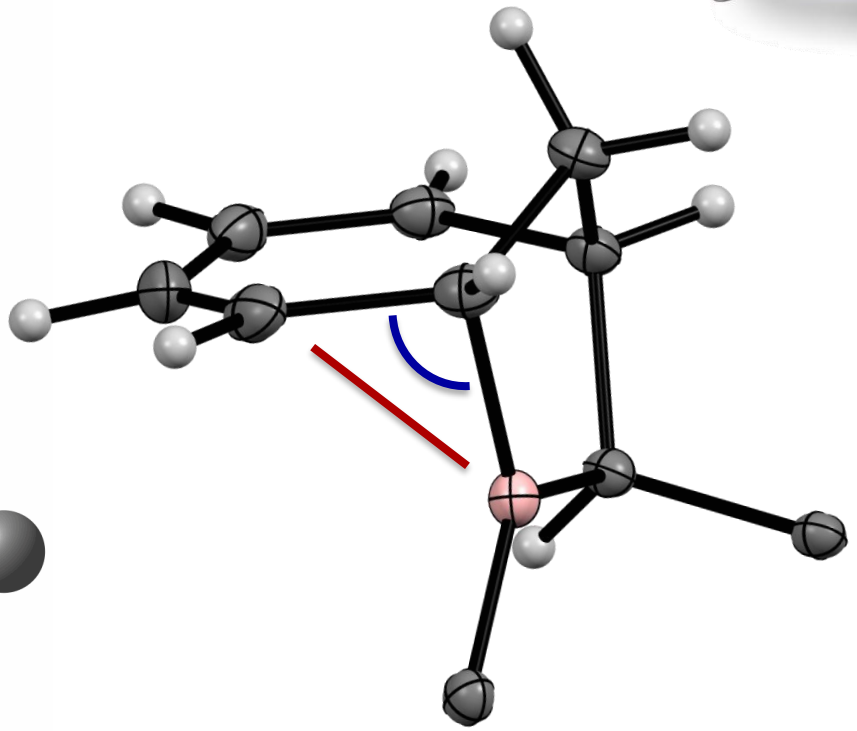


SC-XRD: 50% probability level shown; Hydrogen shown as spheres with arbitrary size; selected H omitted for clarity

p–π Interactions



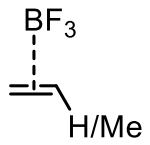


PBEh-3c		SC-XRD
2.19	d(BC²) / Å	2.22
91.2	α(BC¹C²) / °	92.3

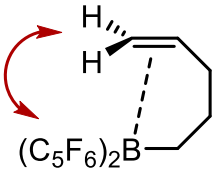
VdW Radii: B: 1.92 Å ;C: 1.70 Å

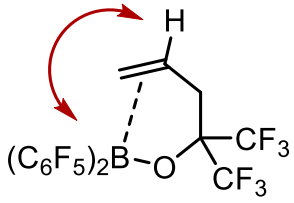
M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *The journal of physical chemistry. A* **2009**, *113*, 5806.
PCM(DCM)-PBEh-3c, 50% probability level, C_6F_5 groups omitted for clarity

p–π Interactions

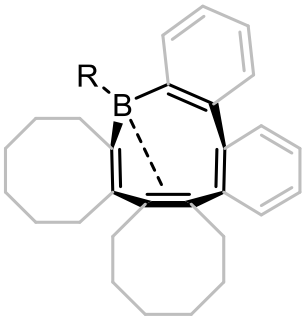


IR in L-Ar/L-N_2

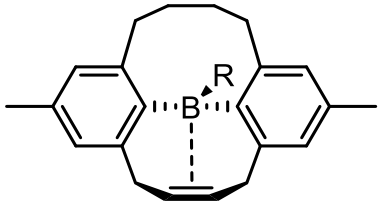




$^{1}H\{^{19}F\}$ HOESY NMR



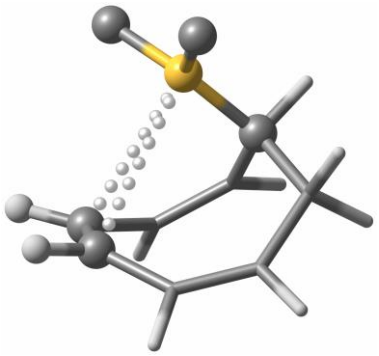
SC-XRD



UV/VIS

W. A. Herrebout, B. J. van der Veken, *J. Am. Chem. Soc.* **1997**, *119*, 10446; X. Zhao, D. W. Stephan, *Chem. Sci.* **2012**, *3*, 2123; X. Zhao, D. W. Stephan, *J. Am. Chem. Soc.* **2011**, *133*, 12448; Y. Murata, K. Matsunagi, J. Kashida, Y. Shoji, C. Özen, S. Maeda, T. Fukushima, *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 14630; R. Oshimizu, N. Ando, S. Yamaguchi, *Angew. Chem. Int. Ed. Engl.* **2022,** e202209394

p–π Interactions



2.91 / 2.97 Å

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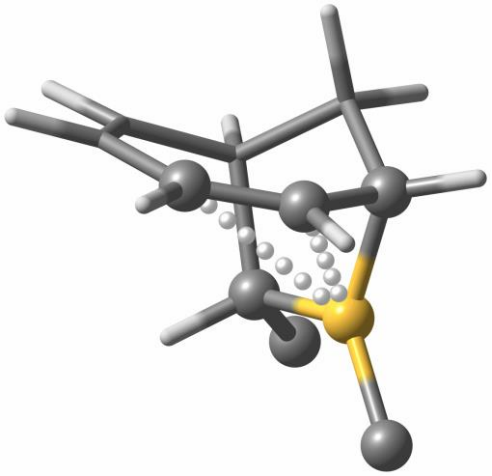
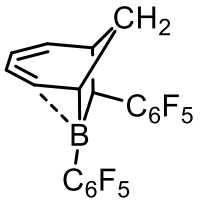
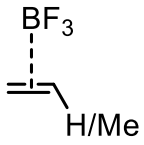
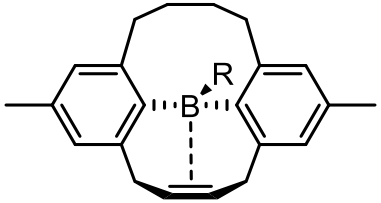




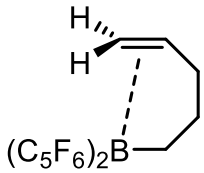
2.19 / 2.97 Å



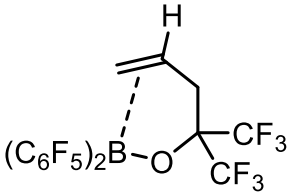
2.92 Å



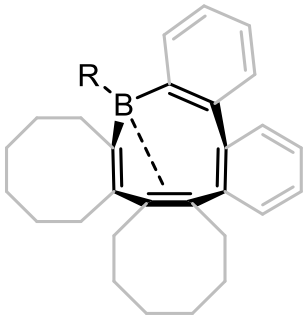
2.79 / 2.72 Å



3.05 / 3.27 Å



3.61 / 4.08 Å

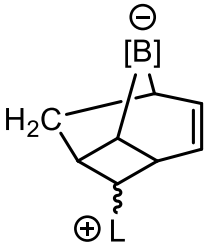


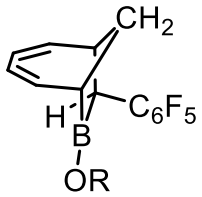
R = Cl: 2.51 / 2.61 Å

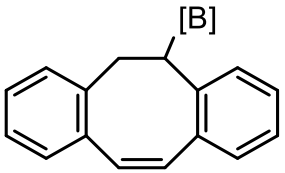
R = OMe: 2.74 / 2.99 Å

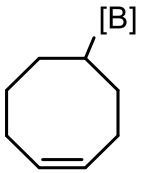
W. A. Herrebout, B. J. van der Veken, *J. Am. Chem. Soc.* **1997**, *119*, 10446; X. Zhao, D. W. Stephan, *Chem. Sci.* **2012**, *3*, 2123; X. Zhao, D. W. Stephan, *J. Am. Chem. Soc.* **2011**, *133*, 12448; Y. Murata, K. Matsunagi, J. Kashida, Y. Shoji, C. Özen, S. Maeda, T. Fukushima, *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 14630; R. Oshimizu, N. Ando, S. Yamaguchi, *Angew. Chem. Int. Ed. Engl.* **2022,** e202209394

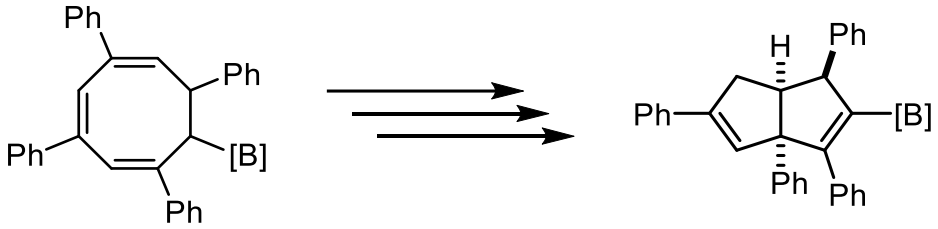
Outlook











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Acknowledgement

- Dr. Urs Gellrich
- Gellrich Group
- Dr. Gerbig , Dr. Hausmann and the analytics team
- Dr. Jonathan Becker
- Organic Chemistry Department