Synthesis of a Unique Dialkyl Substituted $B_2H_7^-$-Analog

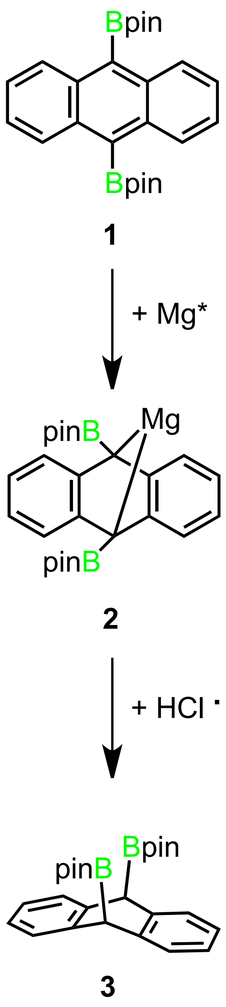
Steffen Pospiech, Michael Bolte, Hans-Wolfram Lerner, Matthias Wagner*
Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt am Main, Max-von-Laue Str. 7, 60438 Frankfurt am Main, Germany

Introduction

9,10-Bis(silyl)-substituted 9,10-dihydroanthracenes are common, whereas the 9,10-bis(boryl) analogs are essentially unknown. We report the synthesis and reactivity of *cis*-9,10-dihydro-9,10-bis(pinacolboryl)anthracene (**3**), which is accessible from the reduced anthracene **2** (cf. Bogdanović magnesium) and can be converted further into the hydridoborate **7**.

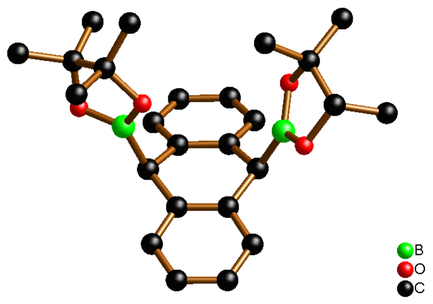
Subsequent elimination of one equivalent of LiH from **7** yields the singly hydrogen-bridged species **9**. Compound **9** represents a rare example of a stable diorganyl derivative of $B_2H_7^-$. The work has been extended further to include also relatives of **7** featuring a B–B two-electron two-center bond (cf. **12** and **13**) and a B–B propellane (**10**).[1]

Methods for Mono- and Dimetalation of Anthracenes and 9,10-Dihydroanthracenes

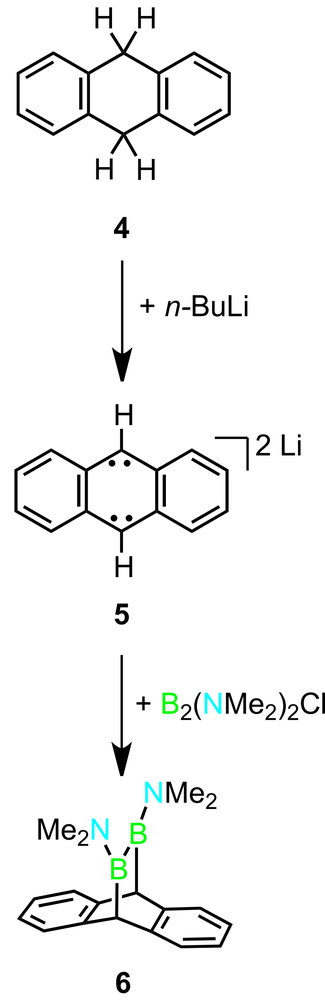


Bogdanović magnesium

+ Tolerates functional groups like silyl substituents or boronic esters
+ Pre-organized *cis*-configuration
+ Cheap reagents
– Long reaction times
– Laborious magnesium activation protocol
– Thermolabile
Pyrophoric

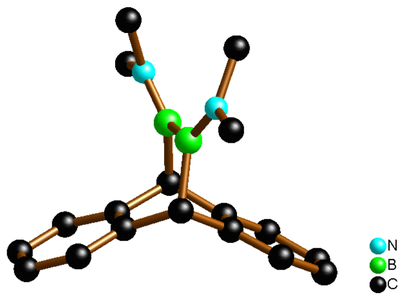


VS.

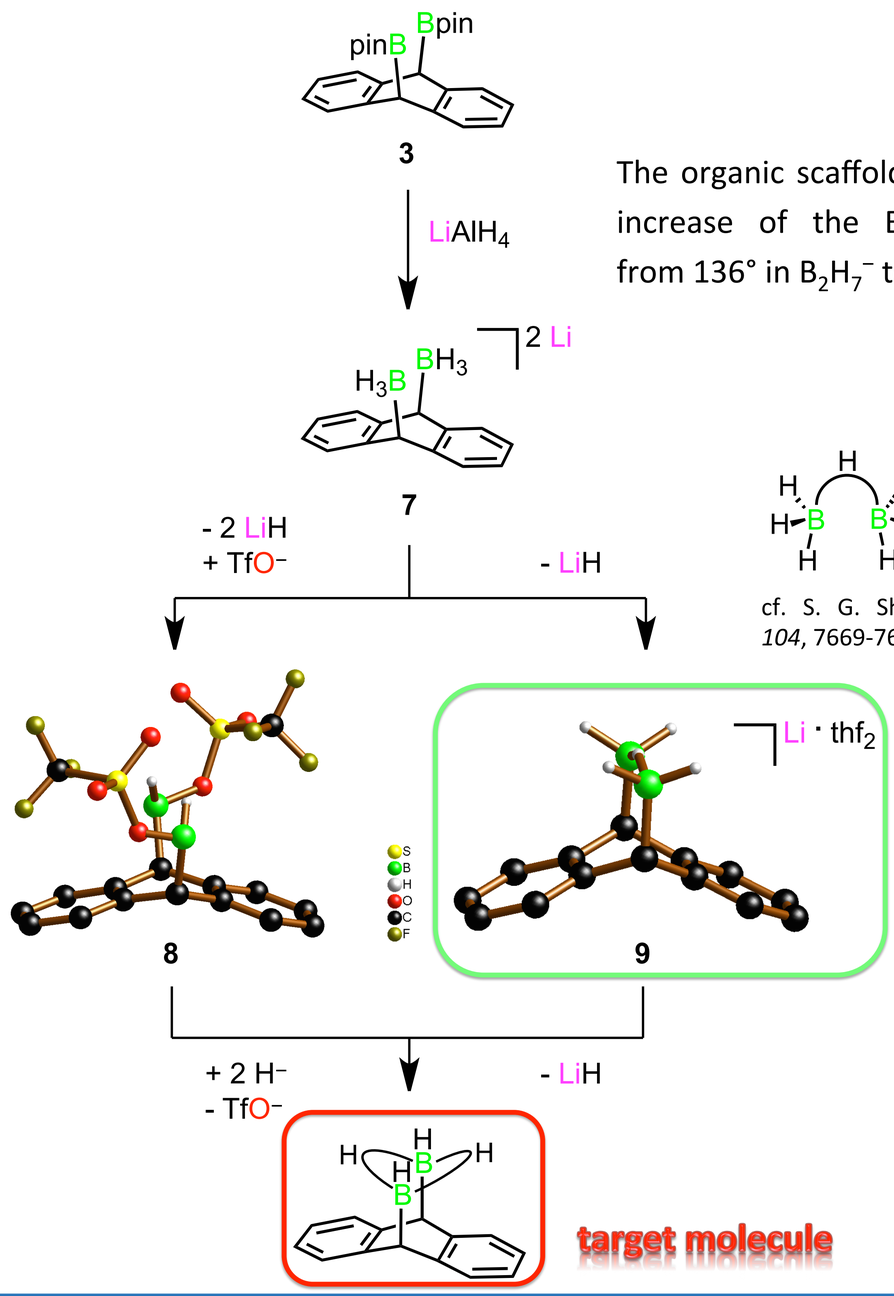


9,10-Dilithio-9,10-dihydroanthracenes

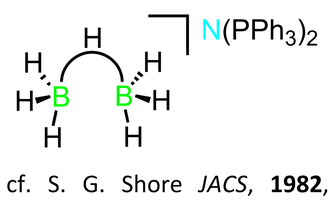
+ Excellent yields
+ Faster reaction
– Most 9,10-dihydroanthracenes accessible via a Birch reaction protocol
– Dilithiated species are limited to alkyl or aryl substituents
Pyrophoric



Synthesis of the $B_2H_7^-$ Analog

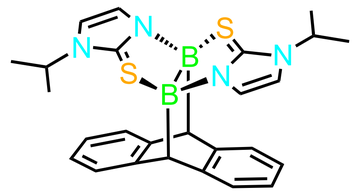


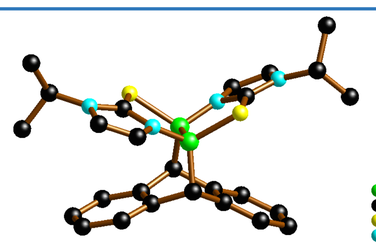
The organic scaffold leads to an increase of the B–H–B angle from 136° in $B_2H_7^-$ to 149° in **9**

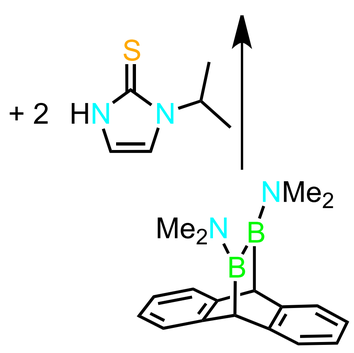


cf. S. G. Shore *JACS*, **1982**, *104*, 7669-7670

Selective Mono- and Difunctionalization of 6

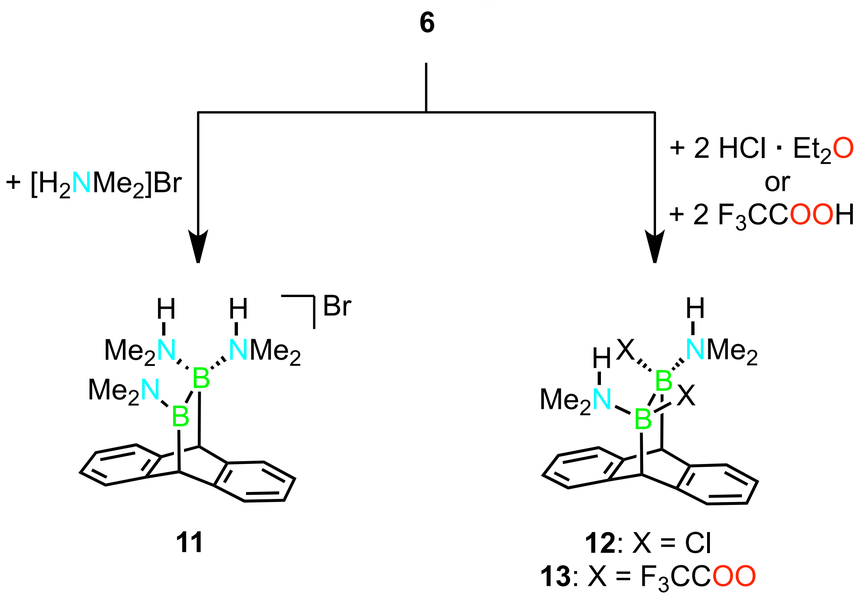






Use of a suitable ditopic ligand leads to the inorganic propellane **10**

Steric bulk of the base determines mono- or difunctionalization of **6**



Reference: [1] S. Pospiech, S. Brough, M. Bolte, H.-W. Lerner, H. F. Bettinger, M. Wagner, *Chem. Comm.* **2012**, *48*, 5886-5888

Steffen Pospiech wishes to thank the *Beilstein Institute*, Frankfurt/Main, Germany, for financial support within the research collaboration *NanoBiC*.