Electronic Supplementary Material (ESI) for Chemical Science

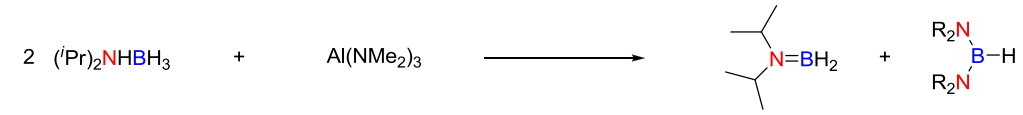
Group 13 BN dehydrocoupling reagents, similar to transition metal catalysts but with unique reactivity

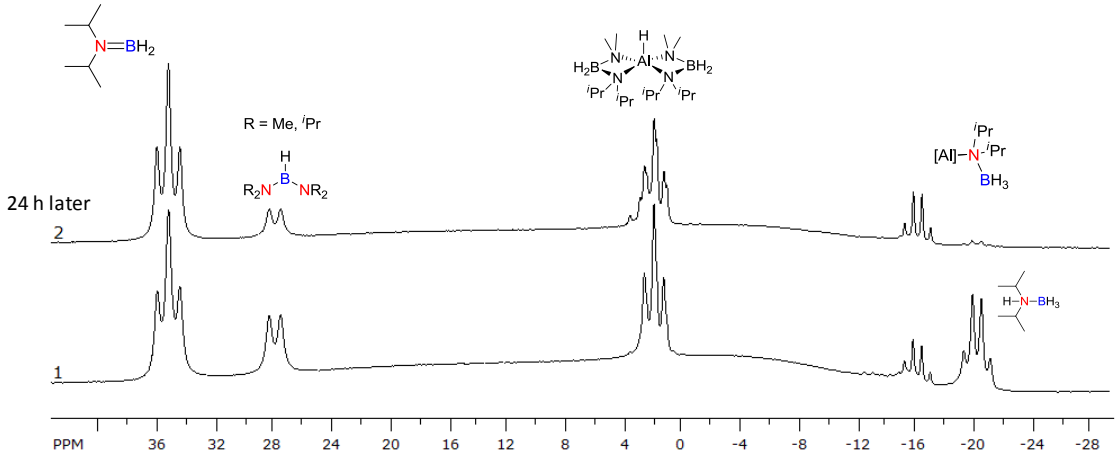
M. M. Hansmann, R. L. Melen and D. S. Wright

Part A: NMR Studies

ESI 1

^{11}B NMR spectrum of the 2:1 reaction of $^{i}Pr_2NHBH_3$ with $Al(NMe_2)_3$ in d_6-benzene





^{11}B NMR

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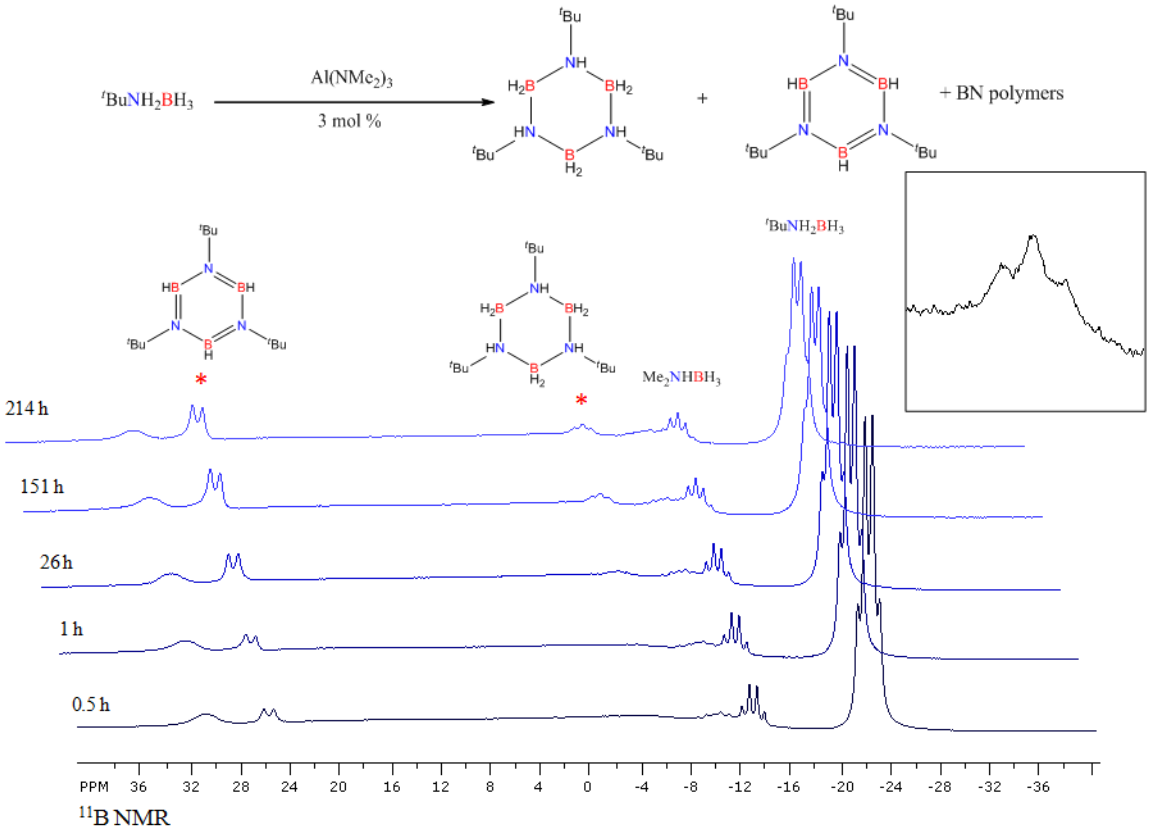
ESI 2

^{11}B NMR spectrum of the reaction of ^{t}BuNH$_2$BH$_3$ with Al(NMe$_2$)$_3$ (3 mol %) in d$_6$-benzene showing the build up of the borazine intermediate after 1 day (insert)



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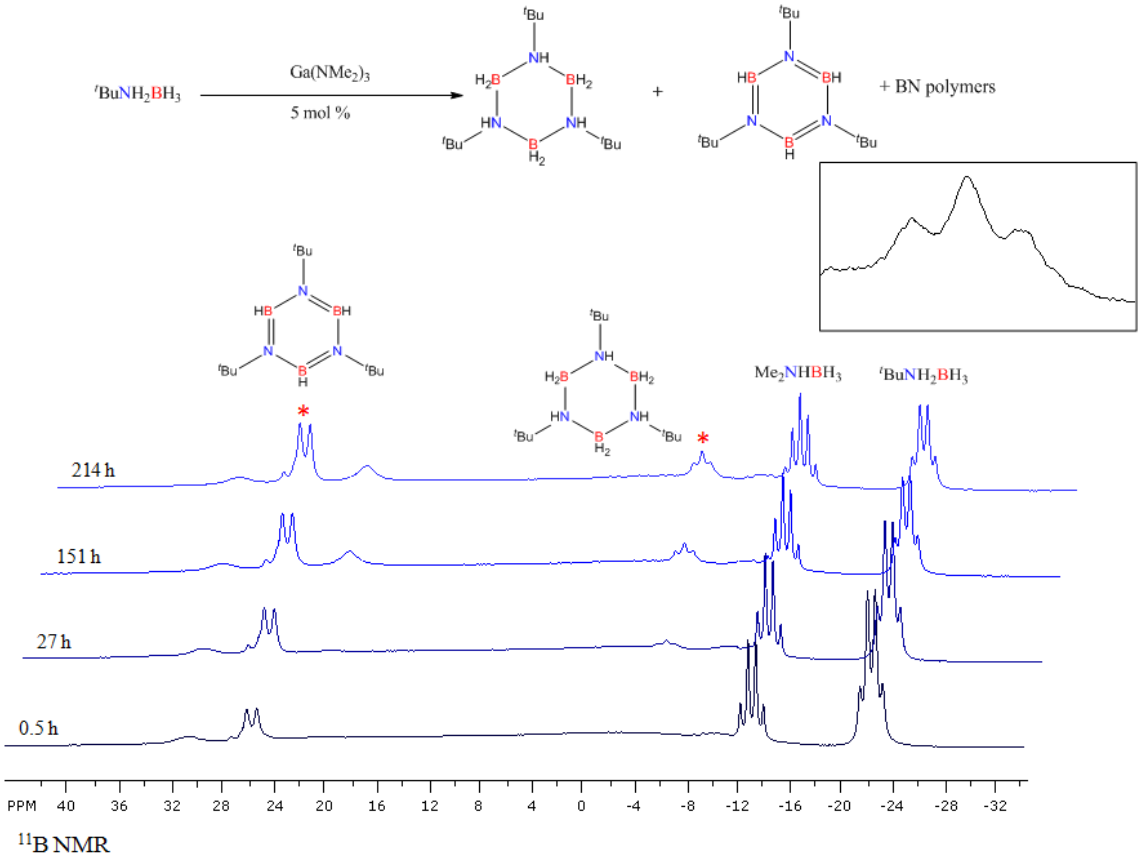
ESI 3

^{11}B NMR spectrum of the reaction of ^{t}BuNH$_2$BH$_3$ with Ga(NMe$_2$)$_3$ (5 mol %) in d$_6$-benzene showing the build up of the borazine intermediate after 1 h (insert)



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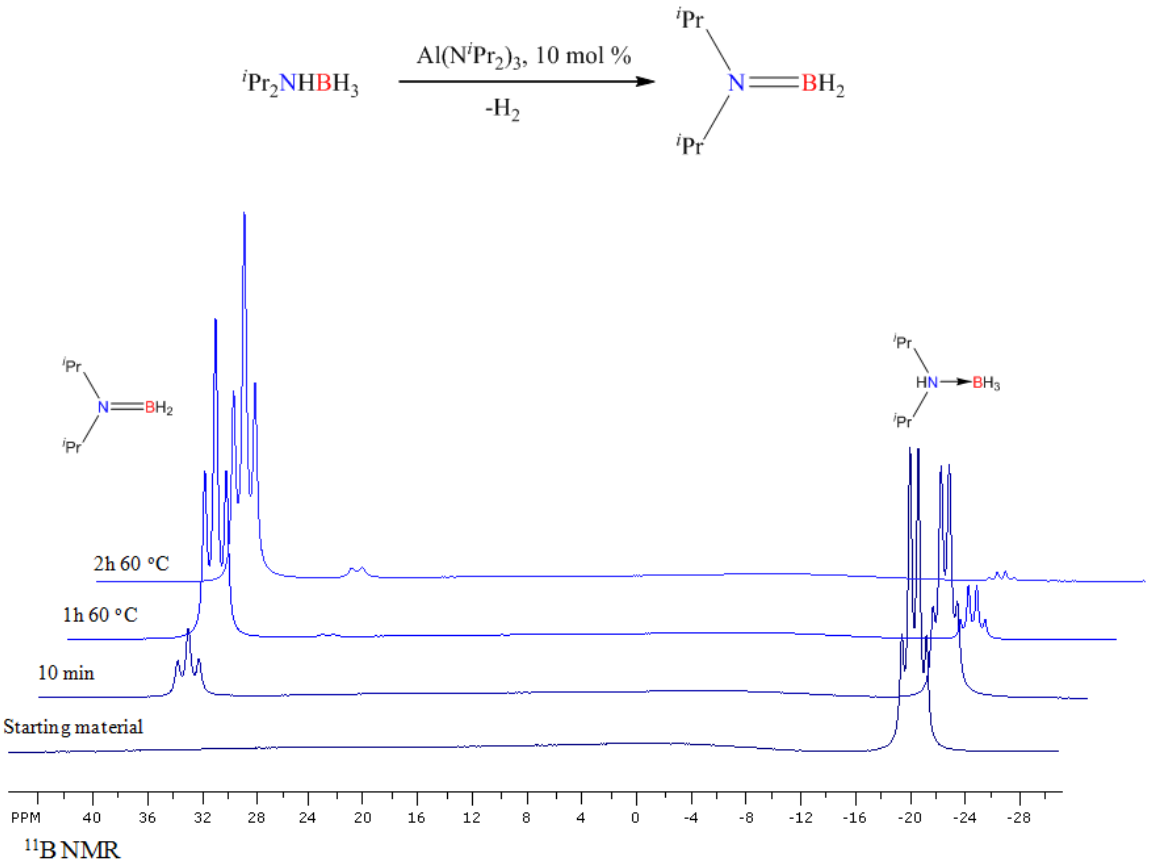
ESI 4

^{11}B NMR spectrum of the reaction of $^{i}Pr_2NHBH_3$ with $Al(N^{i}Pr_2)_3$ (10 mol %) in d_6-benzene



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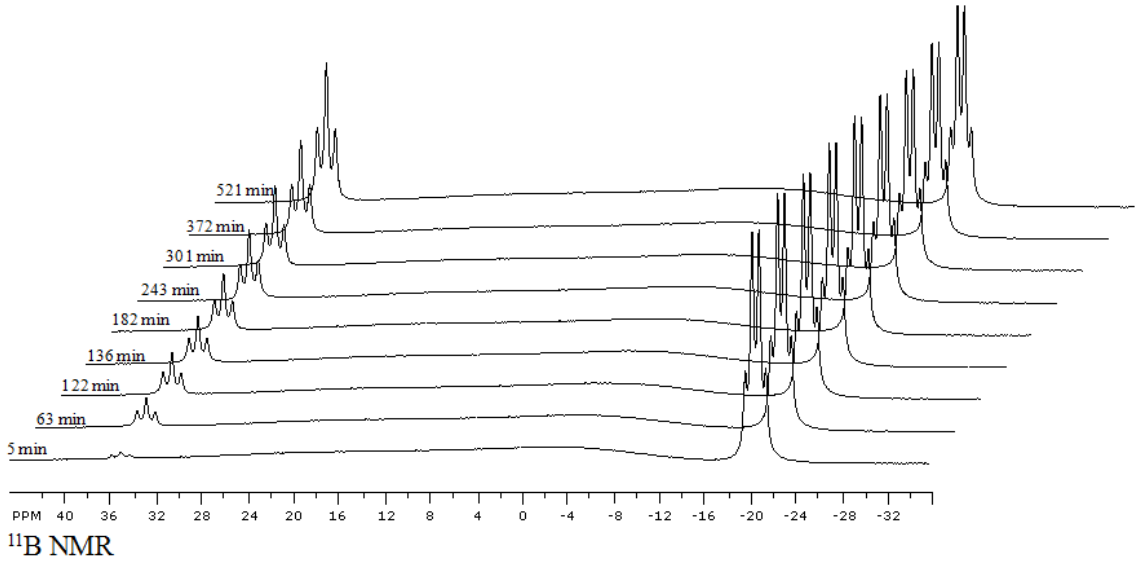
ESI 5

^{11}B NMR spectrum of the reaction of $^{i}Pr_2NHBH_3$ with $Al(N^{i}Pr_2)_3$ (2 mol %) in d_8-toluene



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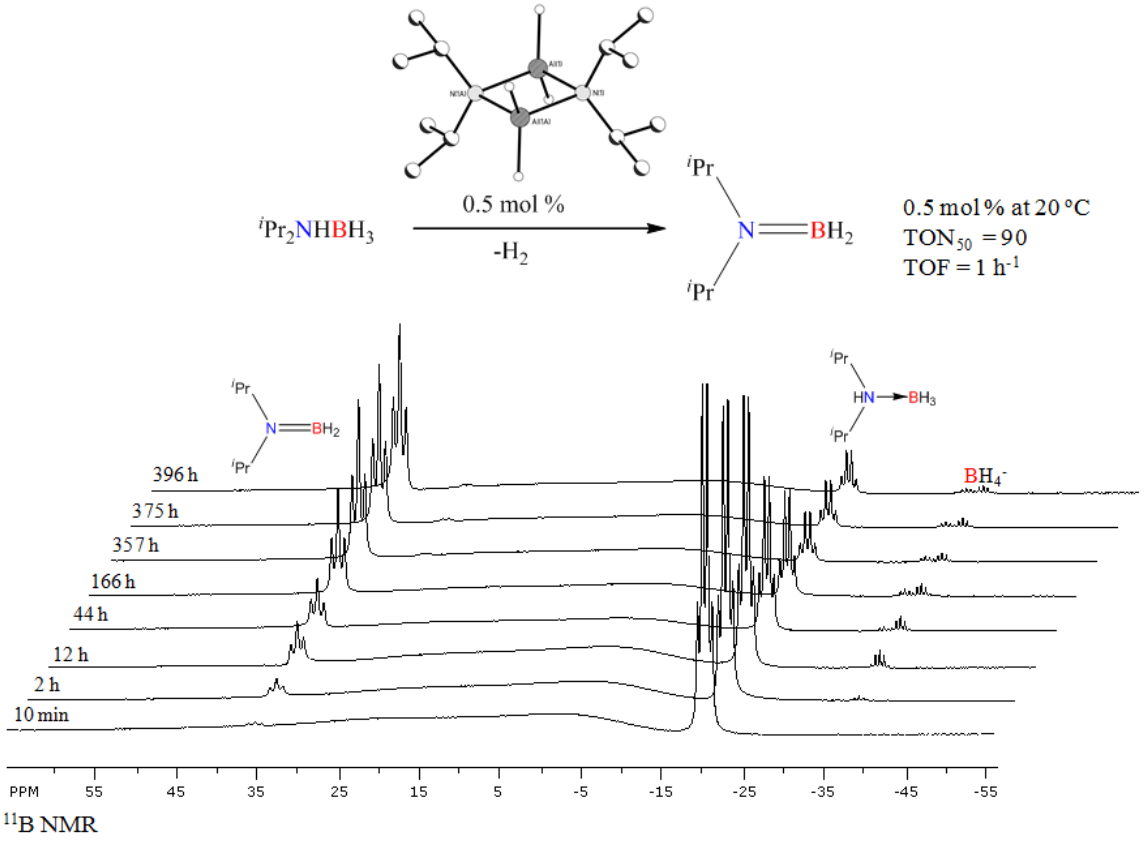
ESI 6

^{11}B NMR spectrum of the reaction of $^{i}Pr_2NHBH_3$ with $[^{i}Pr_2NAlH_2]_2$ (0.5 mol %) in d_6-benzene



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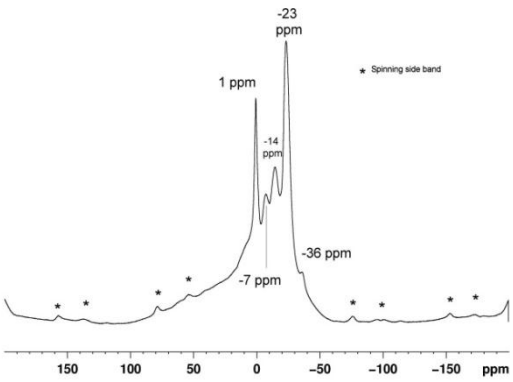
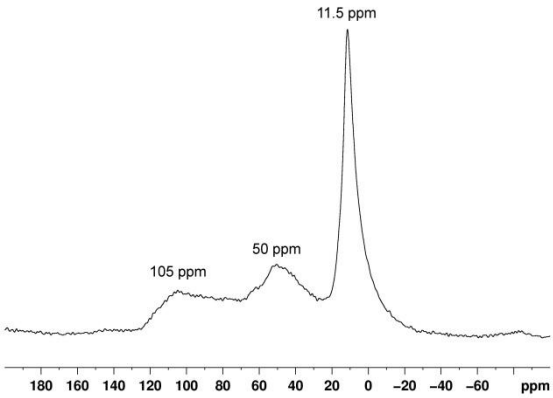
ESI 7

Solid state NMR spectra of the product of the reaction of $Al(NMe_2)_3$ with NH_3BH_3. (See Reference 13)



MAS $^{11}B\{^1H\}$ NMR



MAS $^{27}Al\{^1H\}$ NMR

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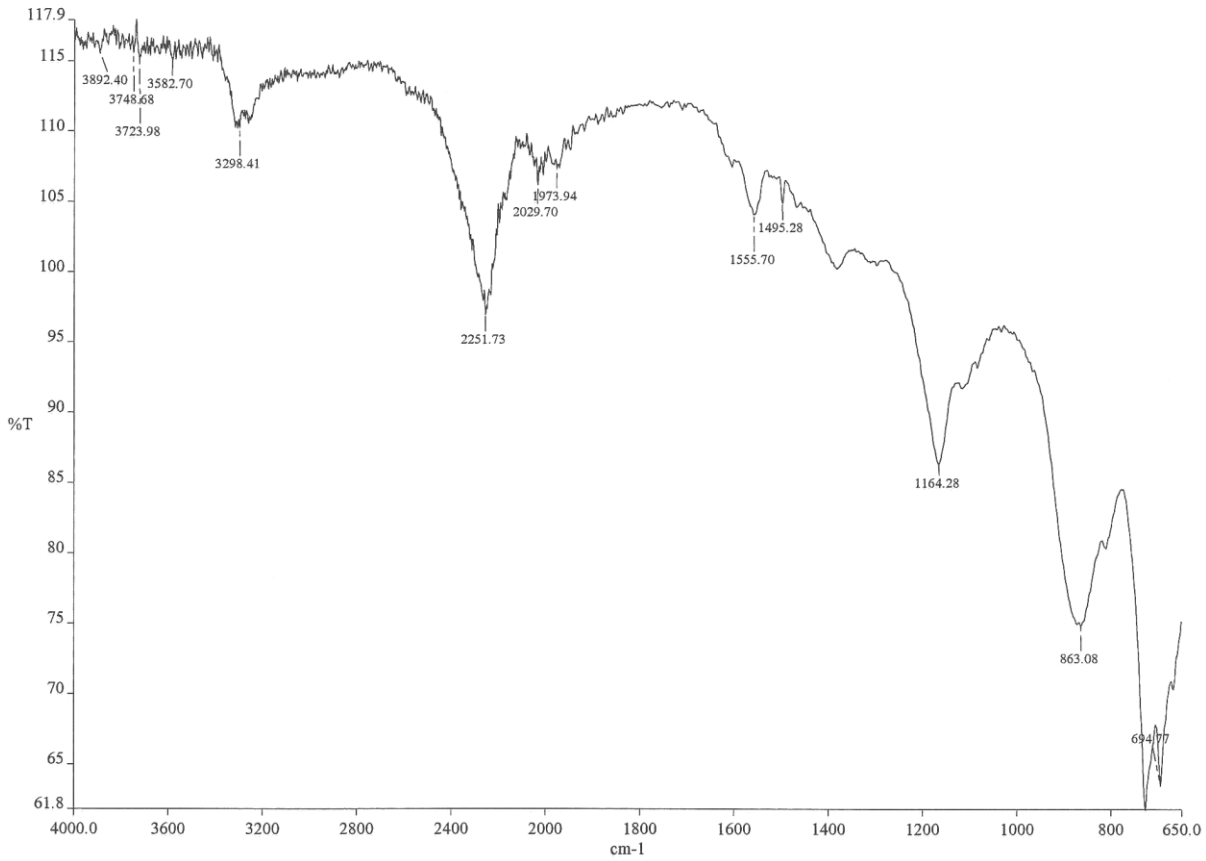
ESI 8

Solid state IR spectrum of the product of the reaction of $Al(NMe_2)_3$ with NH_3BH_3. (See Reference 13)



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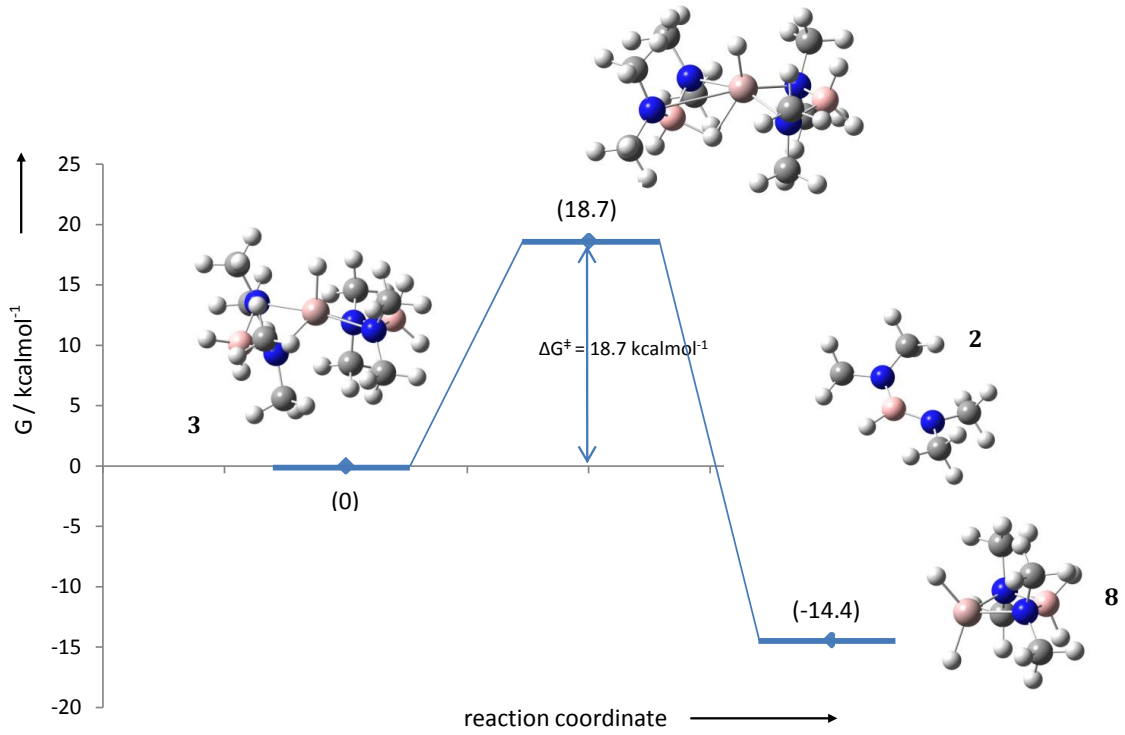
Part B: DFT calculations (B3LYP/cc-pVDZ)

Full DFT geometry optimizations and frequency calculations were undertaken using Gaussian 09[1] without symmetry restrictions. Calculations employed the B3LYP functional[2] and double ξ-quality, correlation consistent, cc-pVDZ basis set. Geometries were fully optimized without symmetry restrictions and transition states were determined using the QST3-approach. Gibbs free energies are corrected in respect to zero point energies which are calculated based on gas phase frequency calculations. All calculations were done using standard temperature and pressure (298.15 K, 1 atm).

ESI 9

Reaction profile for the computed B-Al-hydride shift (B3LYP/cc-pVDZ)



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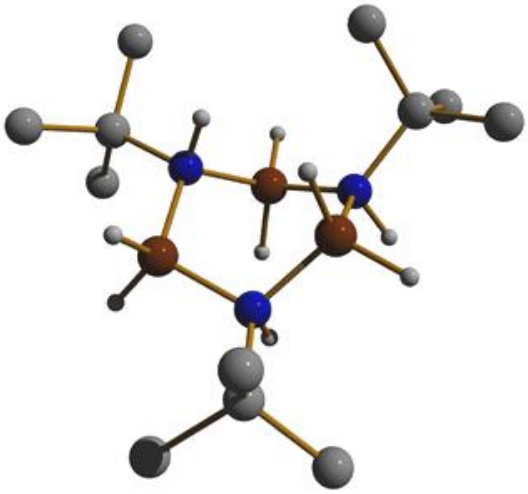
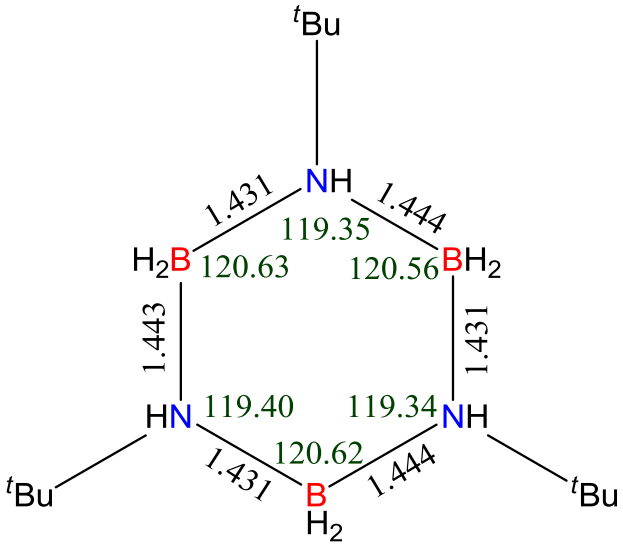
ESI 10

Gas phase geometry optimised structure of [^{t}BuNHBH$_2$]$_3$ (**9**)





Borazane	Observed	Calculated
Average B-N bond length /Å	1.58	1.61
Average N-B-N angle /^{o}	108.6	107.7
Average B-N-B angle /^{o}	111.2	111.1

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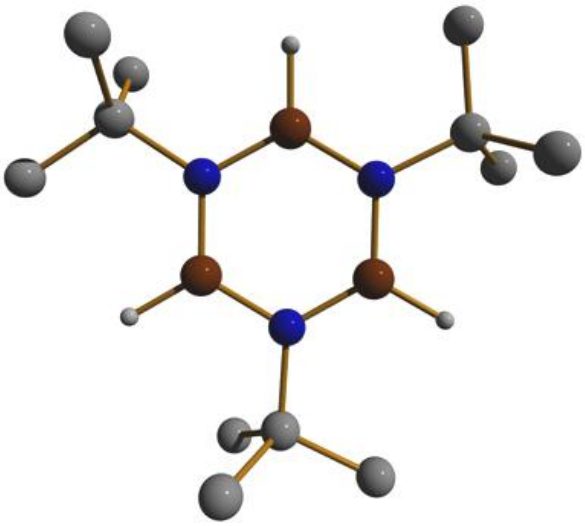
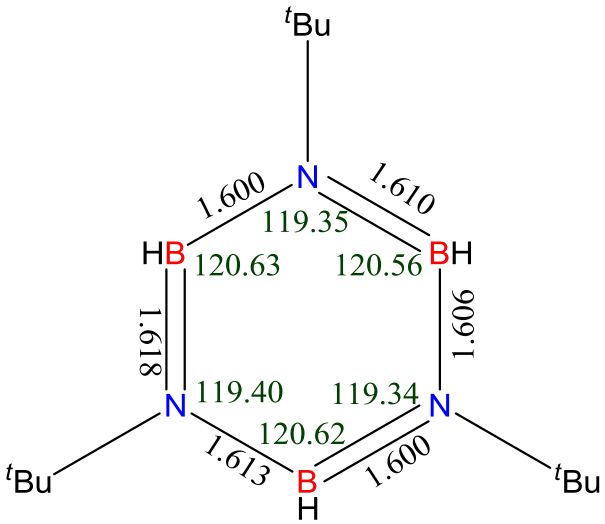
ESI 11

Gas phase geometry optimised structure of [^{t}BuNHBH$_2$]$_3$ (**5**)





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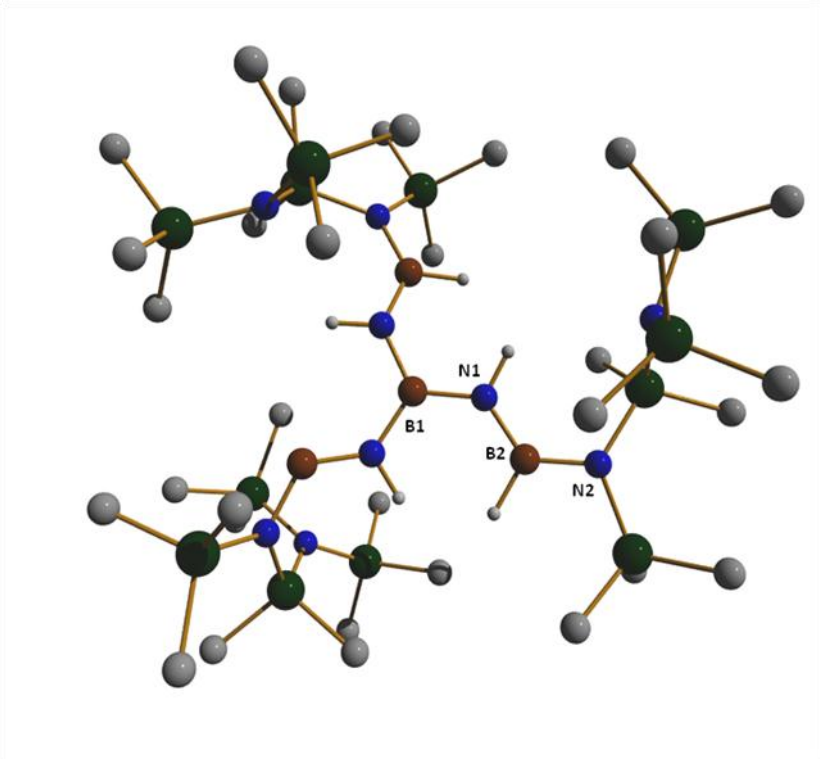
ESI 12

Gas phase geometry optimised structure of [B{NHBH)N($SiMe_3$)Si(Me_2)N($SiMe_3$)$_2$}$_3$] (**10**)



bond	Average bond length /Å		Angle	Average bond angle /°	
	Calculated	Observed		Calculated	Observed
B1-N1	1.453	1.427	N1-B1-N1	120	11.99
N1-B2	1.467	1.435	B1-N1-B2	128.73	128.14
B2-N2	1.448	1.44	N1-B2-N2	126.72	125.84

References:

1. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc., Wallingford CT, 2010;

2. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.