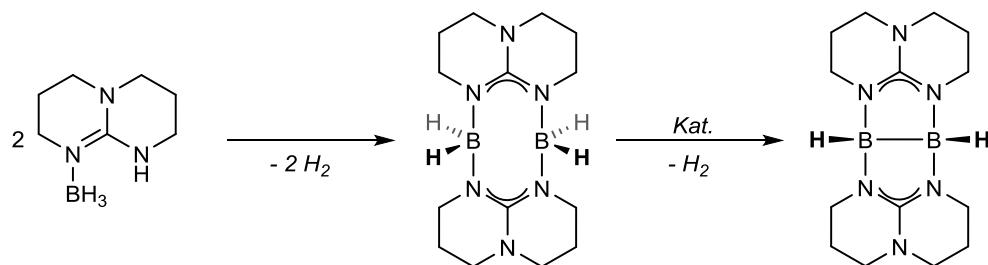


Group 13 hydrides

Borane, stabilized by the bicyclic guanidine hppH, undergoes a thermal B-N dehydrocoupling reaction to give the diborane $[H_2B(hpp)]_2$. Catalytic B-B dehydrocoupling gives in high yield $[HB(hpp)]_2$ with a direct B-B bond. We tested several catalysts to find the optimal conditions. With the best catalysts, we achieve complete transformation to $[HB(hpp)]_2$ at 110 °C in less than 40 min.



The $[HB(hpp)]_2$ molecule has a rich chemistry, that we are currently developing in three directions: coordination chemistry, oxidative insertion into the B-B bond and hydride substitution, and synthesis of cationic boron hydrides (see Figure 1).

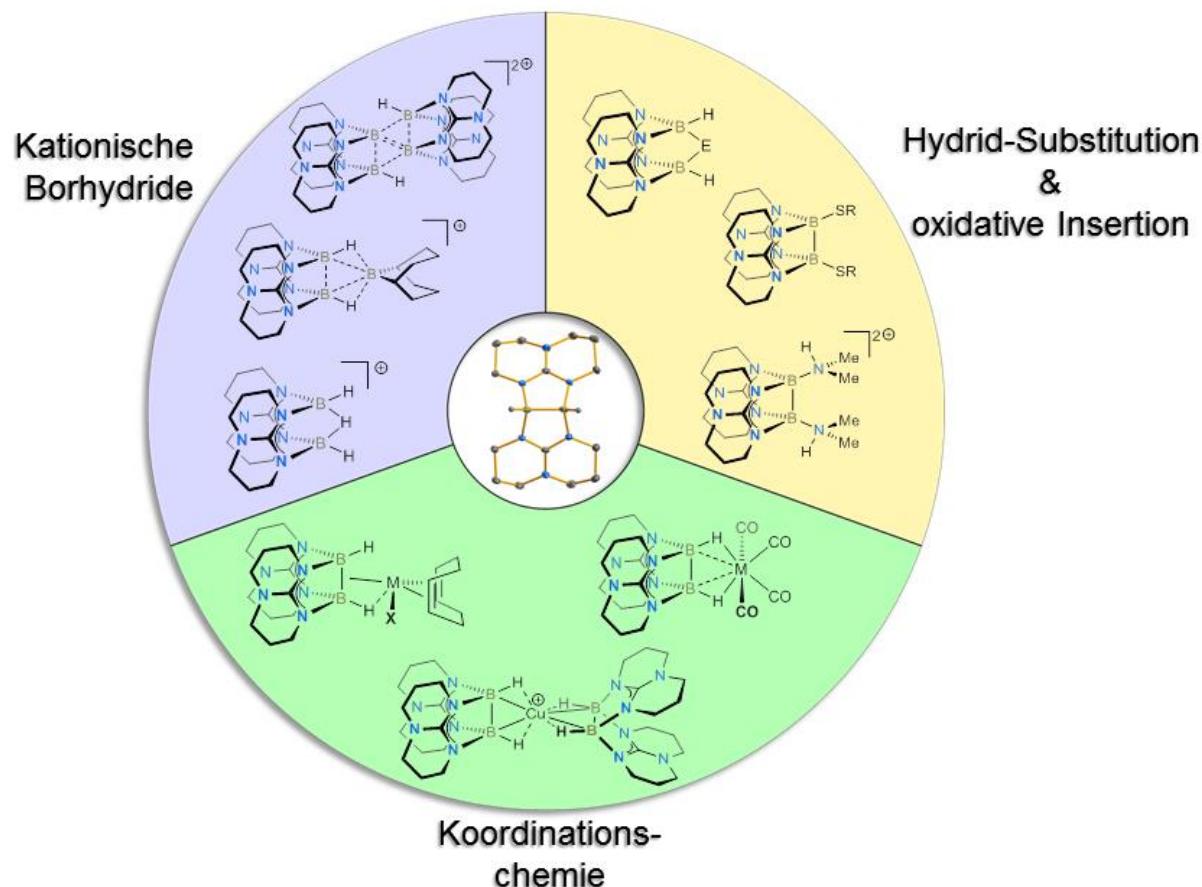


Figure 1 (designed by Arne Wagner)

Sulphur inserts oxidatively into the B-B bond. Since the reaction proceeds slow, one could see several electron transfer intermediates. The reaction mixture darkens with time, and the colors resemble those of a sunrise (see Figure 1, which was made by Nikola Schulenberg for the cover page of *Eur. J. Inorg. Chem.*). At the end the color fades.

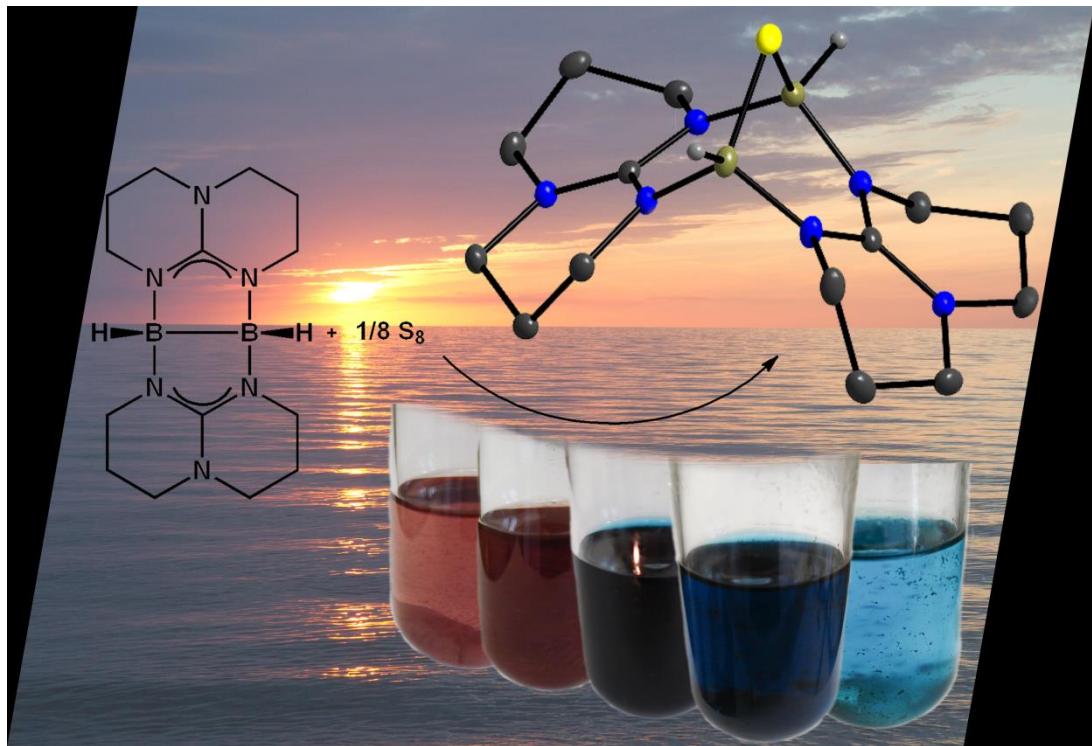
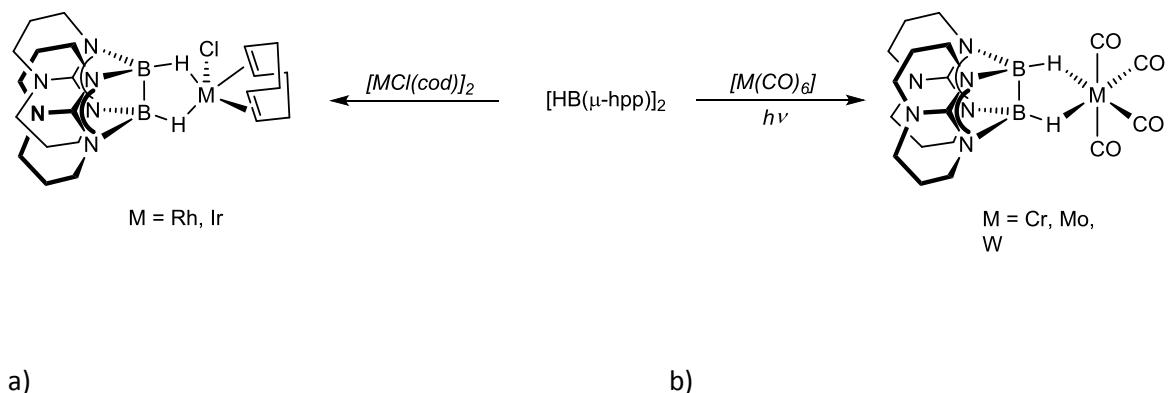


Figure 2 (designed by Dr. Nikola Schulenberg)

The $[\text{HB}(\text{hpp})]_2$ molecule is a good ligand, and we prepared several complexes.



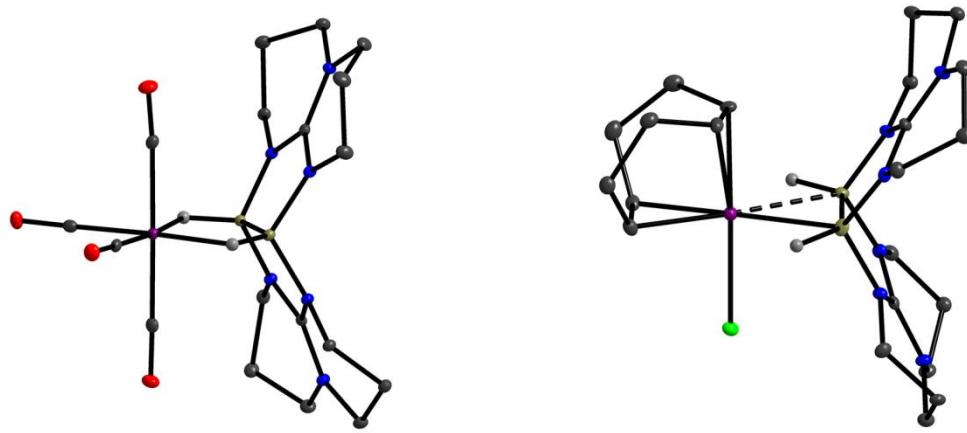
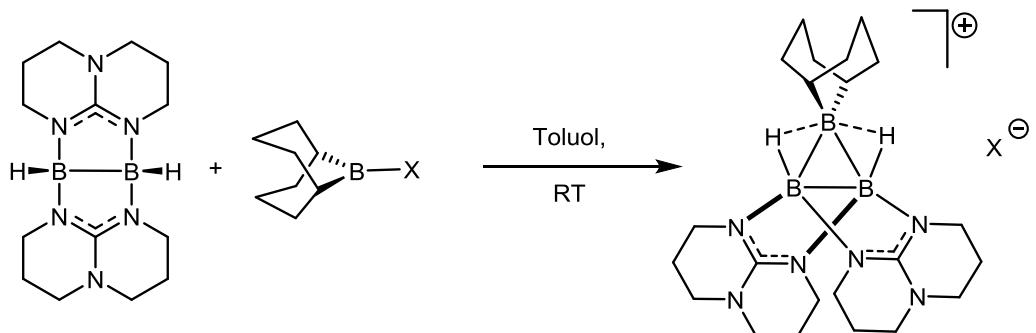
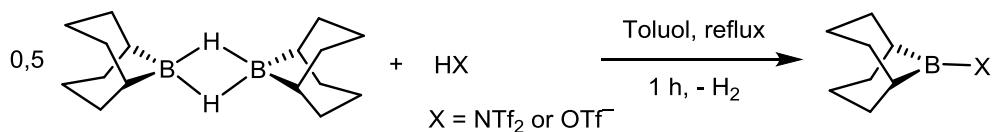


Figure 3. Structures of two complexes with $[\text{HB}(\text{hpp})]_2$ as ligand. a) $[\text{Cr}\{\text{HB}(\text{hpp})_2\}(\text{CO})_4]$, b) $[\text{Rh}(\text{cod})\{\text{HB}(\text{hpp})\}_2\text{Cl}]$.

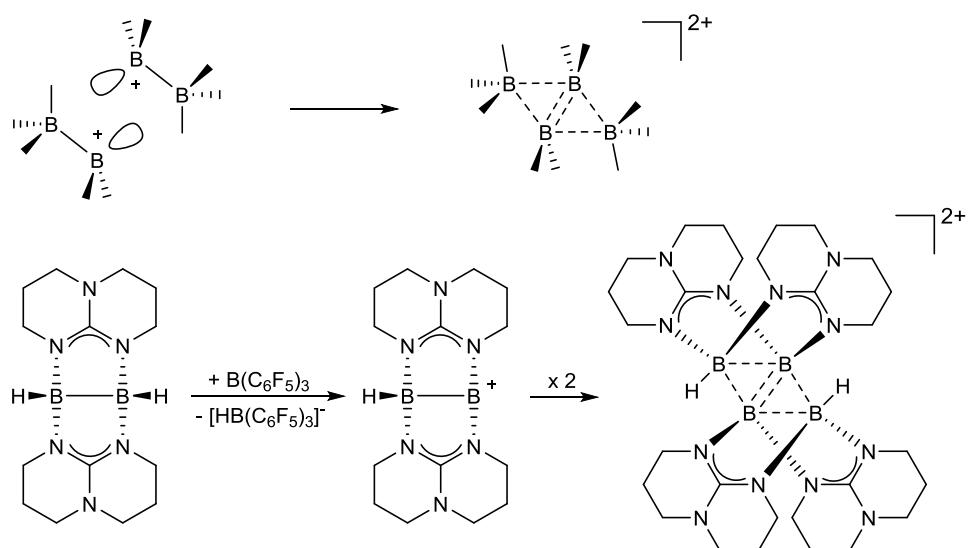
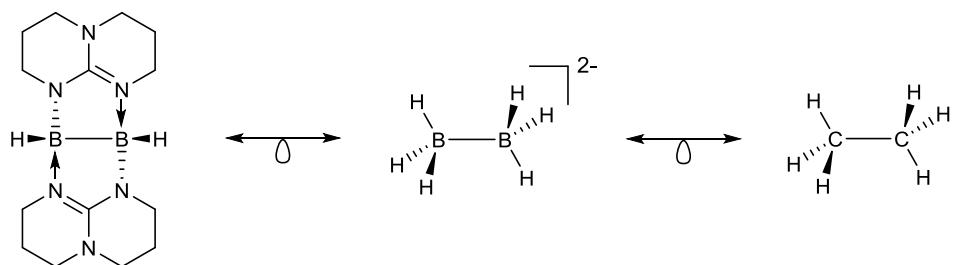
Interestingly, the complexes could be grouped in two classes: Complexes in which the electrons of the B-B bond are involved in metal-ligand bonding (late-transition metals), and those in which bonding predominantly involves the hydrides (earlier transition metals). Late-transition metals activate the B-B bond (see the parameters accumulated in the Table).

	M	H	$\text{B}-\text{B}$	H	M	H	$\text{B}-\text{B}$	H			
			$d(\text{B-B})$ / Å		$v(\text{B-H})$ / cm^{-1}		$\delta(^1\text{H}\{ ^{11}\text{B}\})$ / ppm		$\delta(^{11}\text{B})$ / ppm		$^1J(\text{B-H})$ / Hz
$[\text{HB}(\text{hpp})]_2$			1.772(3)		2272 2249		2.17		-1.14		-
$[\text{Cr}\{\text{HB}(\text{hpp})\}_2(\text{CO})_4]$			1.739(3)		2010		-4.84		-8.76		55
$[\text{Mo}\{\text{HB}(\text{hpp})\}_2(\text{CO})_4]$			1.742(4)		2018		-2.91		-7.65		64
$[\text{W}\{\text{HB}(\text{hpp})\}_2(\text{CO})_4]$			1.748(7)		2041		-3.26		-7.73		63
$[\text{Rh}(\text{cod})\{\text{HB}(\text{hpp})\}_2\text{Cl}]$			1.810(6)		2258		2.09		-7.59		54
$[\text{Ir}(\text{cod})\{\text{HB}(\text{hpp})\}_2\text{Cl}]$			1.835(8)		2282		0.67		-4.69		90
$[\text{ZnCl}_2\{\text{HB}(\text{hpp})\}_2]$			1.834(4) 1.841(4)		2180 2152		3.36		-8.61		70
$[\text{ZnBr}_2\{\text{HB}(\text{hpp})\}_2]$			1.834(4) 1.851(6)		2175		3.35		-7.93		72
$[\text{ZnMe}_2\{\text{HB}(\text{hpp})\}_2]$			1.805(4)		2219		3.32		-1.75		-

Addition of BR_2^+ to the $[\text{HB}(\text{hpp})]_2$ molecule gives a B_3 triangle featuring a closed B-B-B three-centre-two-electron bond.



The $[\text{HB(hpp)}]_2$ molecule is isolobal to $\text{B}_2\text{H}_6^{2-}$ and also to the ethane molecule. Curiously, hydride abstraction with $\text{B}(\text{C}_6\text{F}_5)_3$ is followed by dimerization to give the tetraborane dication $[\text{B}_4(\text{hpp})_4\text{H}_2]^{2+}$ with a four-centre-four-electron bond.



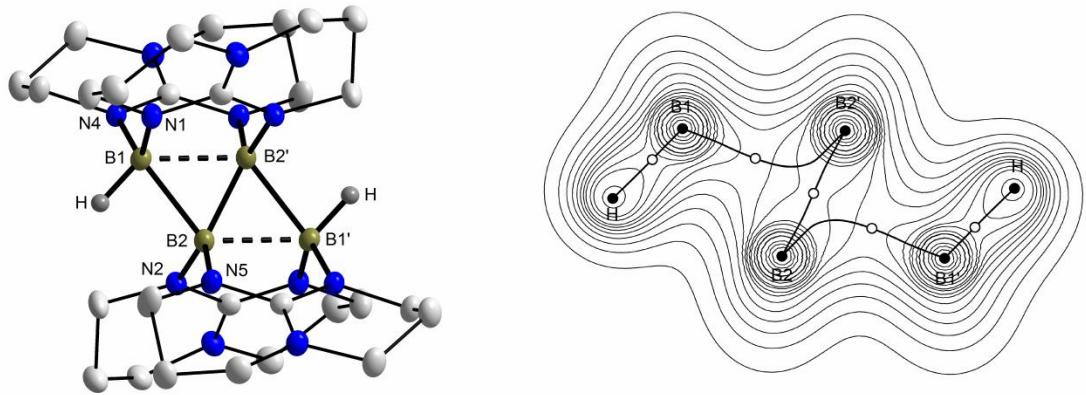


Figure 4. Structure of the tetraborane dication $[B_4(\text{hpp})_4\text{H}_2]^{2+}$.

We are currently trying to use the cationic boron hydrides as building blocks for the construction of (cationic) boron chain polymers.

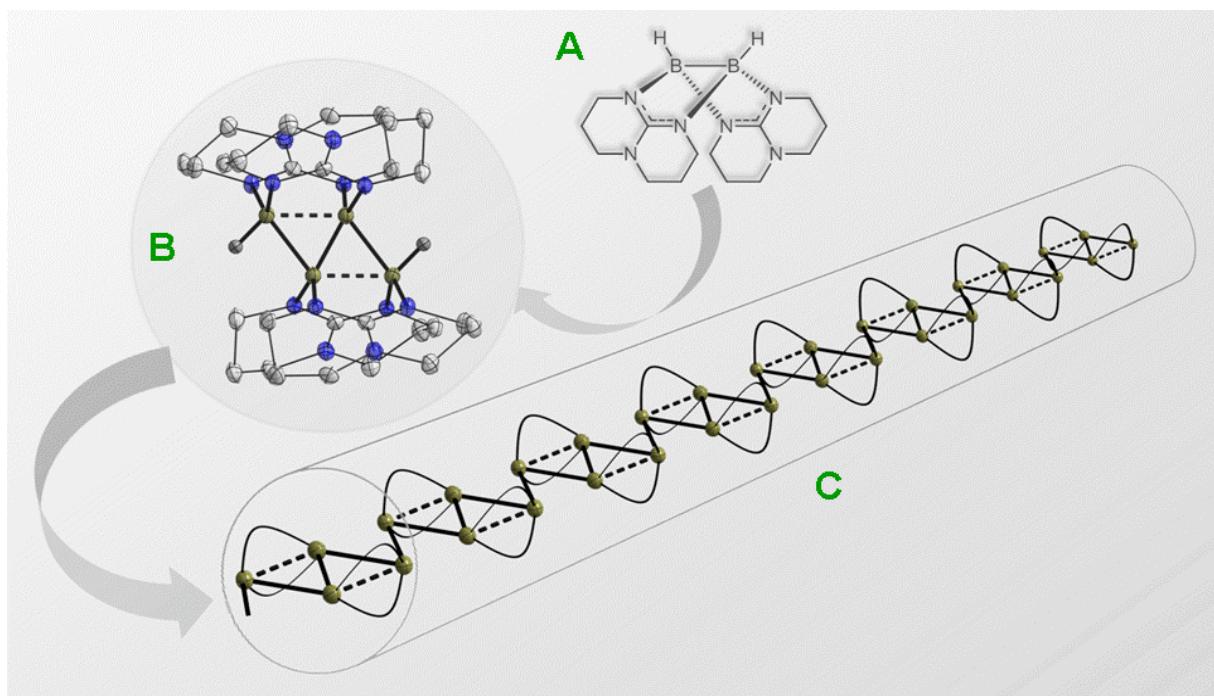


Figure 5 (designed by Sebastian Litters for a press release, Ruprecht-Karls-University Heidelberg)