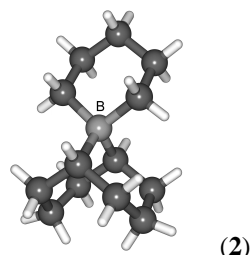
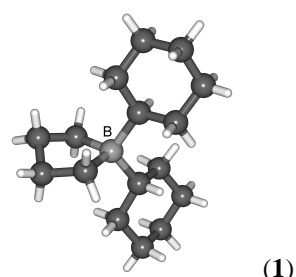


## Organoborates as Potential Anions for Novel Ionic Liquids

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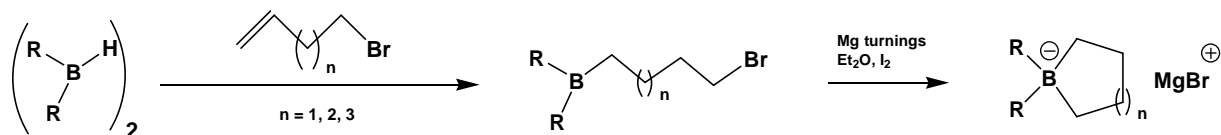


(1)

(2)

The synthesis of new ionic liquids, free from labile fluoride, is one of the most important developments for their application as 'green' solvents. Room-temperature ionic liquids usually consist of nitrogen-containing organic cations, most commonly N,N'-dialkylimidazolium and N-alkylpyridinium, and weakly coordinating inorganic anions (AlCl<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, etc.). We have been preparing ionic liquids with unsymmetrical organoborates as the anions.

The use boron containing compounds covers a vast range of applications: organic synthesis, catalysis, medicine, materials, polymers, etc. While working in this field, our group has discovered a convenient, easy and versatile synthesis for tetraalkylcycloborates,<sup>1</sup> which may be exploited as organic anions for designing novel ionic liquids. It involves hydroboration of unsaturated substrates and formation of Grignard reagents and leads to the preparation of novel classes of compounds. By simply modifying the alkyl chain length it is possible to vary the size of the heterocycle. For example, by using 4, 5 or 6 carbon atom spacers a facile and unprecedented cyclisation reaction of  $\alpha,\omega$ -Borylbromoalkanes is seen upon treatment with magnesium turnings, forming organocycloborates in high yield. The ring closure reaction occurs via an intra-molecular Grignard rearrangement occurring at the boron centre.



The novel borate-cyclopentanes and -hexanes have been characterised by X-ray crystallography.

**Fig. 1:** The structure of the anion (B-B-dicyclohexylboratacyclopentane) (1) and 1,5-pentadiyl-9-borabicyclo[3.3.1]nonane (2) determined by X-ray crystallography.

Our present work is focusing on exploiting the above organoborates as novel counter-anions for a new class of ionic liquids. The reason for the low melting points of room-temperature ionic liquids is not well understood, although the asymmetry and the dimension of the cation are believed to play a major role.<sup>2</sup> Our new synthesis opens up the possibility of making unsymmetrical organic anions. By varying the alkyl chains in both the anion and cation, it may be possible to fine tune the chemical and physical properties of ionic liquids to improve development in organic, inorganic and organometallic chemistry, along with chemical technology.

<sup>1</sup> H. Braunschweig, G. D'Andola, T. Welton, A. J. White, *Chem Comm.*, in press.

<sup>2</sup> *Ionic Liquids in Synthesis*, P. Wasserscheid, T. Welton (Eds.), Wiley-Vch, 2003.