Anion binding by multidentate Lewis acids: a DFT study†

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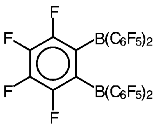
Density functional studies of model tribora-macrocyclic Lewis acids indicate extremely strong binding of the methyl anion, which in some cases exceeds that of $B(C_6F_5)_3$. In addition anion selectivity for the fluoride ion is implied by binding energies *ca.* 200 kJ mol^{-1} greater than those of other halides.

The formation of donor/acceptor complexes exploiting the well known Lewis acidic nature of organo-boranes and -alanes has been the subject of much recent research interest.[1] In part, this stems from the role of species such as MAO or $B(C_6F_5)_3$ as hydride or alkide abstractors in the generation of highly active cationic olefin polymerisation catalysts.[2] In such cases the activity and stability of catalysts are known to be strongly dependent on the extent of interactions between the cationic transition metal species and the anionic donor/acceptor complex.[3] Attempts have been made to manipulate the nature and strength of ion pairing interactions in solution, for example through the use of sterically more encumbered Lewis acids.[4] An alternative to the manipulation of the steric environment about the Lewis acidic centre is the incorporation of additional acceptor sites within a multidentate framework. By analogy with classical chelating agents such species offer the possibility for even stronger anion binding and the greater delocalisation of negative charge. Recently several groups have investigated this approach using bifunctional Lewis acids such as **1**.[5] A logical extension of this strategy is the development of macrocyclic multidentate Lewis acids. Classical macrocyclic donor ligands are well noted for the formation of exceptionally stable metal complexes and for slow dissociation kinetics.[6] In addition, by the incorporation of acceptor sites into a medium-sized cyclic structure ring strain is released on anion binding *via* the pyramidalization of planar boron centres.



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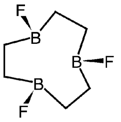

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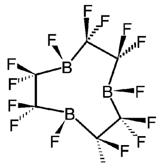

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This work explores the nature of two such model compounds, 1,4,7-trifluoro-1,4,7-triboracyclononane **2** and perfluoro-1,4,7-triboracyclononane **3**, and their complexes with a number of anions (H^-, F^-, Cl^-, Br^-, CH_3^-). To facilitate quantitative interpretation of the results, the binding energy of tris(pentafluorophenyl)borane **4** with CH_3^- has also been computed at the same level of theory. Although there are some recent density functional studies of simple mono-functional boranes (BH_3 or BF_3) and their complexes with neutral Lewis bases,[7] studies of anion binding to boranes (either mono- or poly-functional) are limited to a recent high-level study of complexes of BH_3 with PH_2^-, OH^- and Cl^-,[8] and a semi-empirical investigation of anion complexes of macro-bi- and -tri-cyclic boranes.[9]

The geometries of **2**, **3** and their various donor–acceptor complexes were optimized at the Hartree-Fock level using 3-21G and 6-31+G* basis sets (Fig. 1 and 2) (see also ESI†). The minimum energy geometries for F^-, Cl^-, and Br^- complexes with both macrocyclic Lewis acids **2** and **3** feature symmetrical binding of the anion to all three boron centres (see Tables 1 and 2). For hydride anion, however, three different BH distances are observed in the minimum energy structure. The H^- anion bridges two boron centres in near symmetrical fashion {r(B–H) = 1.429, 1.414 Å for [**2**·H]$^-$; 1.351, 1.364 Å for [**3**·H]$^-$}, but interacts minimally with the third boron atom {r(B···H) = 2.668 Å for [**2**·H]$^-$; 2.813 Å for [**3**·H]$^-$}. Such a geometry is unsurprising given the small size of the hydride anion, the μ_2- bonding mode for bridging hydrogen atoms being far more common than the face-capping μ_3-mode in polyhedral boron hydrides, for example. BH distances can be compared to those determined by X-ray diffraction for hydride complexes of bidentate Lewis acids {*e.g.* with 'hydride sponge' $[1,8\text{-}(Me_2B)_2C_{10}H_6{\cdot}H]^-$, r(B–H) = 1.20(5), 1.49(5) Å and $[(HBC_4H_8)_2{\cdot}H]^-$, r(B—H) = 1.28(2), 1.31(2) Å}.[11] In general the closest BH contacts for [**2**·H]$^-$ and [**3**·H]$^-$ are somewhat longer (*ca.* 5–10%) than those determined experimentally. Conceivably this may reflect the anomalous shortening found for E–H bonds determined by X-ray diffraction, as the B···B distances to be spanned by the hydride 'ligand' in both the macrocyclic and bidentate complexes are very similar (2.473 and 2.535 Å for the macrocyclic complexes; 2.480 and 2.544 Å for the bidentate species).

The BCl distances in [**2**·Cl]$^-$ and [**3**·Cl]$^-$ (2.654 and 2.329 Å, respectively) are also somewhat longer than those found in the chloride complex of the bidentate Lewis acid 'chloride sponge', $[1,8\text{-}(Cl_2B)_2C_{10}H_6{\cdot}Cl]^-$ [1.86(1)–2.10(1) Å].[12] In this case, however this reflects the significantly longer B···B distance to be spanned by the Cl^- ligand {3.373 and 3.311 Å for the macrocyclic complexes compared to 3.055 Å for $[1,8\text{-}(Cl_2B)_2C_{10}H_6{\cdot}Cl]^-$}. Comparison with the structure of the known $B_2F_7^-$ ion shows a similar trend for the fluoride complexes of **2** and **3**.

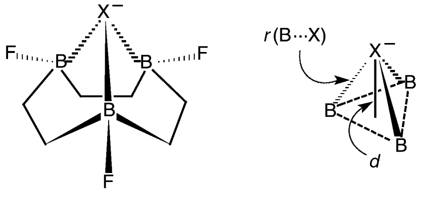

Fig. 1 Definitions of parameters defining the macrocyclic complex geometries.

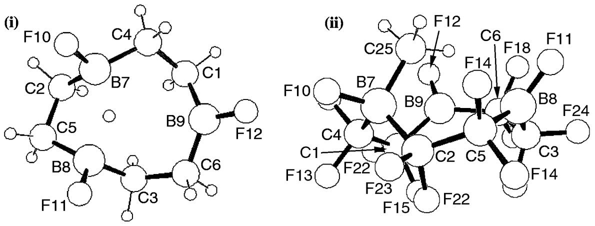

Fig. 2 HF/6-31+G* optimized geometries of (i) [**2**·H]$^-$ and (ii) [**3**·CH_3]$^-$.

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† Electronic supplementary information (ESI) available: geometry optimization details and results of calibration calculations. See http://www.rsc.org/suppdata/cc/b0/b007544m/

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Table 1 HF/6-31+G(d) calculated geometrical parameters for complexes of anions with macrocyclic Lewis acids **2** and **3**

	2			**3**		
Lewis base	$r(\mathrm{B}\cdots\mathrm{X})$/Å	d^a/Å	F–B–X/°	$r(\mathrm{B}\cdots\mathrm{X})$/Å	d^a/Å	F–B–X/°
H^-	1.429, 1.414, 2.668	—	—	1.351, 1.364, 2.813	0.413	—
F^-	1.832	0.721	101.9	1.805	0.516	103.8
Cl^-	2.654	1.803	99.7	2.329	1.330	103.4
Br^-	2.857	2.062	98.6	2.445	1.491	104.0
CH_3^-	1.659, 3.276, 3.221	—	—	1.651, 2.984, 3.016	—	—

[a] The perpendicular distance of the anion from the mean plane of the three boron acceptor atoms, as defined in Fig. 1.

Table 2 B3-LYP/6-311+G(d)//HF/6-31+G(d) calculated binding energies (E_b) and anion ↔ macrocycle charge transfers (ΔQ) for complexes of anions with macrocyclic Lewis acids **2** and **3**

	2		**3**	
Lewis base	$E_b{}^a$/kJ mol^{-1}	ΔQ	E_b/kJ mol^{-1}	ΔQ
H^-	359.0	0.90	692.3	0.85
F^-	307.9	0.49	595.7	0.60
Cl^-	107.3	0.52	385.4	0.72
Br^-	73.1	0.58	338.9	0.98
CH_3^-	298.3	0.03	555.3	0.09

[a] These include HF/3-21G harmonic thermal corrections (at 298 K) scaled by 0.893.[10]

The binding energies for F^- and Cl^- complexes of macrocycles **2** (307.9 and 107.3 kJ mol^{-1}, respectively) and **3** (595.7 and 385.4 kJ mol^{-1}, respectively) can be compared to values of 265.7 and 141.8 kJ mol^{-1} calculated by Boutalib and coworkers for the corresponding complexes with BH_3 at the G-2 level of theory.[8] For all the anions examined the binding energy is considerably enhanced by perfluorination of the triboramacrocycle. For the smaller anions H^- and F^- extremely high binding energies are observed for the perfluorinated macrocycle (692.3 and 595.7 kJ mol^{-1}). The weaker binding found for complexes of Cl^- and Br^- reflects a poorer size-match selectivity (anion/macrocycle) and the greater B···X distances (2.329 and 2.445 Å, respectively). Fluoride anion recognition is an area of much current interest,[13] and these data imply that [9]aneB$_3$ macrocyclic species have much potential in this regard.

The case of methyl anion binding is intriguing; although a strong overall attractive interaction is found for the symmetrically bound (C_3 symmetry) system, [**3**·CH_3]$^-$, reflected by a binding energy (492.9 kJ mol^{-1}) in excess of that calculated for the analogous complex of $B(C_6F_5)_3$ (*vide infra*), the global minimum for both [**2**·CH_3]$^-$ and [**3**·CH_3]$^-$ features less symmetrical anion binding. In each case, binding of the anion within the cavity is essentially monodentate, featuring a single short B···C distance {1.651 Å for [**3**·CH_3]$^-$} and two other B···C distances long enough to preclude any significant interaction {2.984 and 3.016 Å for [**3**·CH_3]$^-$}. For **3** the binding energy for the methyl anion in this asymmetric mode is found to be 555.3 kJ mol^{-1}; for each complex the less symmetrical C_1 binding geometry is found to be energetically more favourable than the C_3 mode of attachment by at least 60 kJ mol^{-1}.

Given the importance of methyl anion abstraction in the initiation of olefin polymerisation processes, we sought to compare the CH_3^- binding capabilities of **2** and **3** with that of the commonly used Lewis acid **4**. At the B3-LYP/6-311+G*//HF/6-31+G* level with a scaled HF/3-21G vibrational correction, we obtained a binding energy of 472.4 kJ mol^{-1} for [$B(C_6F_5)_3$·CH_3]$^-$, a value which is *ca.* 15% lower than the value found for [**3**·CH_3]$^-$. In terms of binding energies for the methyl anion, the value detailed herein for the perfluorinated macrocycle **3** is the highest absolute value yet to be reported in the literature.‡

In summary the calculations presented here reveal that the macrocycle **3** binds CH_3^- at least as strongly as the 'best' recently synthesised Lewis acids. Although binding of CH_3^- by a Lewis acid is only one step in the generation of the active species from metallocene dimethyl derivatives, other factors such ion pairing interactions are known to be important,[3] this result has clear implications in terms of the design of Lewis acids as activators in olefin polymerisation catalysis. With this in mind we are currently investigating anion binding by a range of multidentate and macrocyclic Lewis acids, including species featuring benzyl backbones which may prove to be more synthetically accessible. The results of these studies will be reported in due course.

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Notes and references

‡ Unpublished work listed in ref. 5 (M. V. Metz, D. J. Schwartz, C. L. Stern, P. N. Nickias and T. J. Marks, *Angew. Chem., Int. Ed.*, 2000, **39**, 1312) indicates that $[(C_6F_4)B(C_6F_5)]_2$ is calculated to have a 10 kcal mol^{-1} stronger affinity for CH_3^- than does $B(C_6F_5)_3$, although no absolute binding energies were given for either species.

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