o-Carborane-assisted Lewis acidity enhancement of triarylboranes[†]

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The introduction of an o-carborane cage into the triarylborane significantly enhances the Lewis acidity of the boron atom leading to large increase in fluoride ion affinity.

Triarylboranes have recently attracted great attention in the fields of dihydrogen activation,¹⁻⁴ catalytic polymerization,⁵⁻⁷ and anion sensors⁸⁻¹¹ due to their high Lewis acidity. Efforts to enhance their Lewis acidity have thus been the focus of research interest in such applications. For this purpose, the introduction of electron-withdrawing groups into the triarylboranes, which involves the use of perfluorinated arenes, 12,13 cationic substituents $^{13-19}$ or metal chelation, 20,21 is actively being investigated. While the first approach is the most straightforward and effective, this method may adversely affect the stability in ambient air conditions, the anion selectivity, and the compatibility with a Lewis basic medium in proportion to the increasing Lewis acidity, rendering the use of triarylboranes limited in many applications. In contrast, the latter two methods utilize the attachment of electronwithdrawing substituents at the peripheral positions of aryl moieties to afford the enhanced Lewis acidity while retaining the steric protection of the boron center by ortho-methyl groups.

Bearing in mind that the Lewis acidity is governed by the stability of the vacant p-orbital on the boron atom which contributes largely to the LUMO of triarylboranes, the effective stabilization of the boron orbital is necessary to attain high Lewis acidity in the boron center. In this regard, we have become interested in closo-C₂B₁₀H₁₂ carborane as a novel substituent on the triarylboranes because the carborane not only constitutes an electron deficient cage, but also possesses high stability.²² Although the carborane attached on an aryl group is generally regarded as an electron-withdrawing group like halogens,²³ its electronic effects on the Lewis acidity have not been clearly disclosed. Thus, it will be intriguing to investigate whether the electronic properties of the carborane cage would directly lead to the stabilization of the vacant p-orbital of the boron atom and whether the extent of such stabilization could be comparable to that of usual electronwithdrawing groups. In this report, we provide a novel type of



Scheme 1 Reagents and conditions: (i) n-BuLi, ether, -78 °C. (ii) Mes₂BF, ether, 25 °C. (iii) KF/18-crown-6, toluene, 25 °C.

highly Lewis acidic triarylboranes bearing a peripheral o-carborane cage, and describe their fluoride binding properties to account for the enhanced Lewis acidity in conjunction with computational studies.

The reaction between the lithium salts derived from 1-bromo-4-(2-R-o-carboran-1-yl)benzene (R = Ph (1a), Me (1b)^{24,25} and the dimesitylboron fluoride (Mes₂BF) in ether afforded the o-carborane substituted triarylboranes $[1-(Mes_2B)-4-(2-R-o-carboran-1-yl)benzene]$ (R = Ph (1), Me (2)) as a white solid (Scheme 1).†

The identity of 1 and 2 has been fully characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction methods. While the ¹H and ¹³C NMR spectra show the expected resonances corresponding to the 2-R-o-carborane and the Mes₂B moieties, the ¹¹B NMR signals detected in the two regions of δ 74 ppm and δ -2--10 ppm confirm the presence of a trigonal planar boron center and of o-carboranyl boron atoms, respectively. The crystal structures of 1 (Fig. 1, left)[‡] and 2 (Fig. S3 in the ESI)† further reveal the trigonal planar geometry $\left(\sum_{(C-B-C)} = 360.0^{\circ} \text{ for both 1 and 2}\right)$ around the boron atom of the triarylborane moiety and the o-carborane cage appended to the triarylborane. As similarly noted in the triarylboranes possessing the ortho-methyl groups, compounds 1 and 2 are also air- and moisture-stable.

Prior to investigation of the fluoride binding properties of 1 and 2, compound 1 was converted into a fluoride adduct. Treatment of 1 with KF in the presence of 18-crown-6 in toluene cleanly led to the potassium salt of $[1F]^-$ (Scheme 1). Besides the ¹¹B resonances attributed to the boron atoms of the o-carborane cage, which appears in a region similar to that of 1, the ¹¹B NMR signal detected at δ 5.0 ppm and the ¹⁹F NMR signal at δ –177 ppm collectively confirm the formation of four-coordinate triarylfluoroborate, thus indicating the binding of fluoride to the boron atom of the triarylborane

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Fig. 1 Crystal structures of 1 (left) and $[1F]^-$ (right) (30% thermal ellipsoid). The H-atoms and $[K(18-crown-6)]^+$ were omitted for clarity.

moiety. The crystal structure of $[1F]^-$ determined from the X-ray diffraction study (Fig. 1, right) is also in good agreement with the spectroscopic data.

To determine the fluoride ion affinity of 1 and 2, UV-vis titrations were carried out. Compounds 1 and 2 feature a low-energy absorption band at 322 nm (log $\varepsilon = 4.09$ for 1 and 4.05 for 2) in THF which is quenched upon addition of incremental amounts of fluoride (Fig. S6 and S7†). Remarkably, the binding constants estimated from the 1:1 binding isotherms exceed the measurable range ($K > 10^7 \text{ M}^{-1}$) for both 1 and 2.

Since we note that the fluoride binding constant of Mes₃B (3) is equal to $3.3(\pm 0.5) \times 10^5 \text{ M}^{-1}$ in THF (Fig. S7†),¹⁰ this result indicates that the *o*-carborane cage significantly enhances the fluorophilicity of the boron atom of 1 and 2. To provide a more quantitative measure of the fluoride ion affinity, the titrations were carried out in a more competitive medium of THF–H₂O (9/1 vol.). As shown in Fig. 2a, the fluoride complexation by 1 does occur in THF–H₂O (9/1 vol.) with the binding constant of $5.0(\pm 0.3) \times 10^3 \text{ M}^{-1}$. The similar *K* value of $7.7(\pm 0.3) \times 10^3 \text{ M}^{-1}$ is also obtained for 2 (Fig. S12†). Comparison of these *K* values with that of 3 ($K = 1(\pm 0.3)$)²⁶ reveals the drastic increase of fluorophilicity

of **1** and **2** by 3 orders of magnitude. Furthermore such binding constants are even larger than that found in the neutral bidentate B/Hg Lewis acid $[1-\{Mes_2B\}-8-\{(2,6-Me_2-4-Me_2NC_6H_2)Hg\}C_{10}H_6]$ ($K = 1.3(\pm 0.1) \times 10^2 \text{ M}^{-1}$)¹⁷ under the same conditions.

To get more insight into the effect of the o-carborane cage, we compared the fluoride binding constants of a series of *para*-substituted triarylboranes, *i.e.* Mes₂B(4-R-C₆H₄) (R = F (4); H (5); Me (6)) (Fig. S8-S10⁺). The titration results indicate that the K values are in order of $\mathbf{1} \approx \mathbf{2} (K > 10^7 \text{ M}^{-1}) >$ $4 (5.0 \times 10^7 \text{ M}^{-1}) > 5 (5.0 \times 10^6 \text{ M}^{-1}) > 6 (2.5 \times 10^6 \text{ M}^{-1}) \text{ in}$ THF, which is in good agreement with the inductive electronic effect of the substituents being in parallel with their Hammett constants.^{23,27} For better discrimination between the binding constant of 4 and those of 1 and 2, the fluoride binding constant of 4 was further measured in THF-H₂O (9/1 vol.). The titration result confirms that the fluoride binding constants of 1 and 2 are higher than that of 4 ($K = 3.3(\pm 0.1) \times 10^1 \text{ M}^{-1}$ in THF-H₂O 9/1 vol.) by 2 orders of magnitude (Fig. 2b). These results thus suggest that the high fluoride ion affinity of 1 and 2, which in turn indicates the increased Lewis acidity of the boron atom, is ascribable to the introduction of the o-carborane cage at the aryl moiety of the triarylboranes.



Fig. 2 Spectral changes in the UV-vis absorption of a solution of (a) $\mathbf{1}$ (4.04×10^{-5} M) and (b) $\mathbf{4}$ (4.38×10^{-5} M) in THF–H₂O (9/1 vol.) upon addition of a Bu₄NF (0–9.20 × 10⁻⁴ M for 1 and 0–3.27 × 10⁻² M for 4). The insets show the absorbance of the solution of 1 and 4 at 322 and 314 nm, respectively, as a function of [F⁻] (\blacksquare). The thin lines correspond to the binding isotherm calculated with $K = 5.0 \times 10^3$ M⁻¹ for 1 and 3.3 × 10¹ M⁻¹ for 4.



Fig. 3 HOMO and LUMO of 1 (isovalue = 0.04 a.u.).

To elucidate the increase in the Lewis acidity, the DFT calculations were carried out at the B3LYP/6-31G(d) level of theory. The frontier orbitals of **1** show that while the HOMO is mainly located on the mesityl rings with an orbital contribution of 87%, the LUMO bears a substantial contribution from the *o*-carborane cage (16%), as well as from the empty p-orbital of the boron atom (22%) and the phenylene ring (32%) (Fig. 3). Further inspection of the LUMO indicates that the delocalization occurs through $exo-\pi$ -interaction²⁸ between the tangential p-orbital on the C1 atom of the *o*-carborane cage and the π^* -system of the triarylborane moiety.

More importantly, the LUMO energy level of 1 (-2.10 eV) is found to be substantially lower than that calculated for the LUMO of 4 (-1.63 eV) at the same level of theory, indicating that 1 is much more Lewis acidic than 4 (Fig. S14†). This result is in fact in excellent agreement with the enhanced fluoride ion affinity of 1 and 2. Despite the almost identical compositions of HOMO for 1 and 4, the HOMO level of 1 (-6.19 eV) is also lower than that of 4 (-6.06 eV), implying the strong inductive electron-withdrawing effect of the *o*-carborane cage. However, since the relative stabilization of the LUMO of 1 with respect to 4 is greater than that of the HOMO, it can be suggested that in addition to the inductive effect, the direct contribution of the *o*-carborane cage to the LUMO of 1 is strongly associated with the large stabilization of the LUMO.

In conclusion, the introduction of an *o*-carborane cage into the triarylborane significantly enhances the Lewis acidity of the boron atom. It is suggested that the contribution of the *o*-carborane cage to LUMO coupled with a strong inductive effect leads to the large stabilization of the LUMO of triarylboranes.

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Notes and references

‡ Crystal Data for 1: $C_{32}H_{41}B_{11}$, $M_w = 544.56$, $\lambda = 0.71073$ Å, Monoclinic, $P_{21/c}$, a = 11.3388(7), b = 21.7577(12), c = 13.6469(8) Å, $\alpha = 90.00$, $\beta = 101.822(4)$, $\gamma = 90.00^\circ$, V = 3295.4(3) Å³, Z = 4, $\rho_c = 1.098$ g cm⁻³, $\mu = 0.057$ mm⁻¹, T = 296(2) K, measd reflns = 24356, unique reflns = 5207, $R_{int} = 0.0395$, $R_1 = 0.0519$, $wR_2 = 0.1335$ ($I > 2\sigma(I)$) and GOF = 1.005; For [K-(18-crown-6)][1F]: C₄₅H₆₅B₁₁FKO₆, $M_w = 866.97$, $\lambda = 0.71073$ Å, Monoclinic, Pn, a = 14.5518(5), b = 11.4399(4), c = 15.0625(6) Å, a = 90.00, $\beta = 94.463(2)$, $\gamma = 90.00^{\circ}$, V = 2499.87(16) Å³, Z = 2, $\rho_c = 1.152$ g cm⁻³, $\mu = 0.153$ mm⁻¹, T = 296(2) K, measd reflns = 25774, unique reflns = 6986, $R_{int} = 0.0339$, $R_1 = 0.0769$, $wR_2 = 0.2162$ ($I > 2\sigma(I)$) and GOF = 1.024; For **2**: C₂₇H₃₉B₁₁, $M_w = 482.49$, $\lambda = 0.71073$ Å. Monoclinic, $P2_1/n$, a = 7.9560(4), b = 27.7402(15), c = 13.6954(8) Å, a = 90.00, $\beta = 93.533(3)$, $\gamma = 90.00^{\circ}$, V = 3295.4(3) Å³, Z = 4, $\rho_c = 1.062$ g cm⁻³, $\mu = 0.054$ mm⁻¹, T = 296(2) K, measd reflns = 56299, unique reflns = 6956, $R_{int} = 0.0437$, $R_1 = 0.0597$, $wR_2 = 0.1658$ ($I > 2\sigma(I)$) and GOF = 1.038. CCDC reference numbers **1**, 746 882; [K-(18-crown-6)][1F], 746 881; **2**, 746 883.

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