

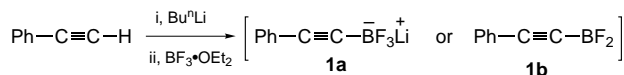
Reaction of an alkynyllithium reagent with boron trifluoride: the structure of a likely intermediate in alkynyl anion chemistry

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Lithium phenylacetylide reacts with 1 equiv. of $\text{BF}_3 \cdot \text{OEt}_2$ in thf–toluene to yield both a thf adduct of tris(phenylacetylido)borane **2**, which is probably the true intermediate in $\text{RC}\equiv\text{CLi}/\text{BF}_3$ -promoted alkynyl anion chemistry, and LiBF_4 , products which are considered to form *via* sequential LiF elimination from previously proposed acetylidoborate intermediates; complex **2** is the first structurally characterised tris(alkynyl)borane and in the solid state it forms an unusual hydrogen-bonded dimer.

The value of organometallic nucleophilic addition to imines¹ has been limited in the past by the poor reactivity of the latter as acceptors,² and by their propensity for enolisation in the presence of, for example, organolithium species.³ While initial attempts at activating imines towards nucleophilic addition of organometallic reagents involved the use of organocopper–boron trifluoride complexes⁴ it was subsequently reported that supposed *in situ* generation of alkynylborane/borate species⁵ led to β -aminoacetylenes from aldimines.⁶ More recent work has incorporated the use of similar *in situ* boron-containing intermediates in the synthesis of allenes from *N*-aziridinylimines.⁷ In each case, however, the existence of the alkynylborane/borate intermediate was assumed, the presumption being that lithium phenylacetylide⁸ reacted with 1 equiv. of $\text{BF}_3 \cdot \text{OEt}_2$ to yield either the monophenylacetylidoborate, **1a**, or, following the elimination of lithium fluoride, the monophenylacetylidoborane, **1b** (Scheme 1). An unexplained anomaly was that the subsequent nucleophilic addition reactions gave higher yields in the presence of 2 or, better, 3 equiv. of **1a/b**.



Scheme 1

We have investigated and now report on the actual species obtained from reacting a 1 : 1 mixture of a lithium acetylide with $\text{BF}_3 \cdot \text{OEt}_2$. They are not the intermediates **1a/b** suggested previously (Scheme 1). They do, however, explain the preference for excess intermediate to be present during subsequent reaction with amide,⁵ aldimine,⁶ or *N*-aziridinylimine.⁷ Thus, reaction of *in situ* generated lithium phenylacetylide with just 1 equiv. of $\text{BF}_3 \cdot \text{OEt}_2$ in thf–toluene affords, as one of the products, an air-stable mono-thf adduct of tris(phenylacetylido)borane **2**,[†] the X-ray crystal structure of which has been determined.[‡] A search of the Cambridge Crystallographic Database shows that **2** is not only the first structurally characterised tris(acetylido)borane, but that it is also the first acetylidoborane structure to incorporate an O-donor molecule. It exists as a hydrogen-bonded dimer in the solid state (Fig. 1), the boron centres having distorted tetrahedral geometries, with the fourth coordination site being occupied by the oxygen of the thf [mean C–B–C 114.2(2)°, mean O–B–C 104.1(2)°]. Unsurprisingly, at 1.633(3) Å, the observed B–O distance is rather longer than any previously observed in three-coordinate monoacetylidoborane structures containing direct B–O linkages.¹¹ Both the B–C [mean 1.580(4) Å] and C≡C [mean 1.209(3) Å] distances show close agreement with those in other

(*i.e.* mono and bis) acetylidoboranes. Dimerisation *via* hydrogen bonding is seemingly a new feature in the solid state for acetylidoborane structures. The relevant interaction is between the adduct O-centre and the *m*-aromatic proton on a phenylacetylide ligand in an adjacent borane monomer. This results in the formation of a 16-membered ring, incorporating an O...C hydrogen bonding distance¹² of 3.46(1) Å.

Notwithstanding the structure of **2**, obtained from the 1 : 1 reaction of $\text{Ph}-\text{C}\equiv\text{C}-\text{Li}$ and $\text{BF}_3 \cdot \text{OEt}_2$ in thf, NMR studies show that the bulk product is a co-crystalline mixture. While ¹H and ¹³C NMR spectra of the product were consistent with the observed structure of **2**, ¹¹B NMR spectroscopy in Me_2SO yielded only a first-order quintet at $\delta -0.75$. At 1.1 Hz, coupling was identical to that demonstrated by the quartet observed in the ¹⁹F spectrum at $\delta -147.59$ and accorded with previously observed ¹J_{11BF} coupling for the tetrafluoroborate anion.¹³ Confirmation that LiBF_4 , **3**, was present in the isolated crystals came from the observation of a very sharp singlet at $\delta -0.11$ in the ⁷Li spectrum in Me_2SO , suggesting the presence of $[\text{Li}(\text{Me}_2\text{SO})_4]^+$.

At room temperature, ¹¹B NMR spectroscopy of the bulk product in Me_2SO failed to yield any signal attributable to **2**. Studies were therefore undertaken in alternative media. Whereas treatment of the co-crystalline product (**2/3**) with Me_2SO yielded a solution, ¹¹B NMR spectroscopy demonstrated that the necessity to filter the suspension afforded in $[\text{C}_6\text{H}_6]_2$ prior to spectral analysis reflected the complete failure of the tetrafluoroborate component to dissolve. Accordingly, the ¹¹B NMR spectrum at room temp. now showed no quintet, but rather a broad signal attributable to **2** (δ *ca.* 0.03, $\Delta\nu_{1/2} = 450$ Hz). Complete dissolution of **2/3** was afforded by $[\text{C}_6\text{H}_8]_2$ thf, yielding both the tetrafluoroborate quintet ($\delta -1.18$) with a slightly expanded ¹J_{BF} coupling (1.8 Hz), and a broad, high-field signal (δ *ca.* -7.32 , $\Delta\nu_{1/2} = 340$ Hz), the relative integrations suggesting a 1.25 : 1 ratio of **2** to **3**.

Spectroscopic evidence points, therefore, not only to the elimination of LiF from **1a**, yielding **1b** in the first instance, but also to the subsequent addition of LiF to an unreacted boron

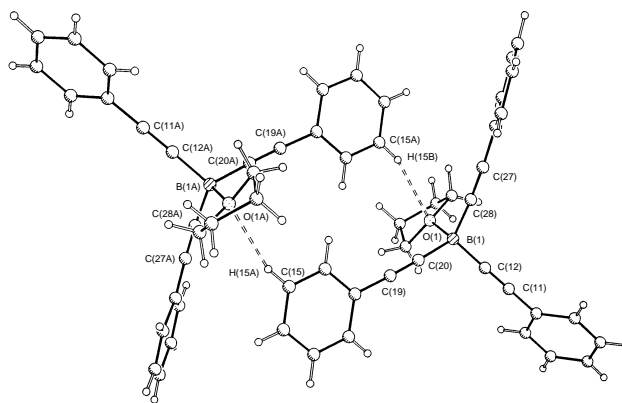
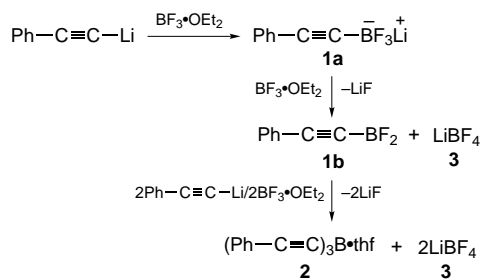
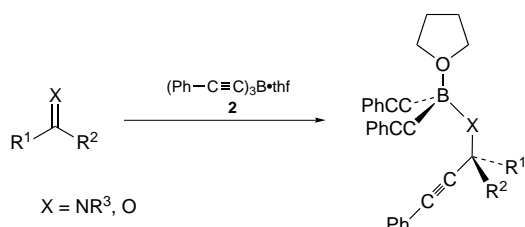


Fig. 1 Dimeric structure of **2**; hydrogen bonding between thf and a *m*-aromatic proton yields a 16-membered ring



Scheme 2

trifluoride molecule, generating **3**. Furthermore, it appears that **1b** is attacked by **2** further equiv. of lithium phenylacetylide, eliminating LiF each time and ultimately giving **2** (Scheme 2). It is also apparent that an explanation of the favourability of utilising **2** or **3** equiv. of the supposed acetylidoborate/borane intermediate (**1a,b**) in subsequent nucleophilic addition chemistry is then at hand. Thus, the true alkynyl anion intermediate, **2**, contains not one, but three phenylacetylido-ligands. The implication is that one phenylacetylido-ligand is relatively active with respect to subsequent nucleophilic behaviour while the other two are largely inactive. This can be rationalised in terms of the sterically congested intermediate species resulting from the addition of **2** across just one carbonyl,⁵ imine⁶ or *N*-aziridinyimine (Scheme 3).⁷



Scheme 3

In conclusion, formation of **2**, the first example of a structurally characterised tris(acetylido)borane, is probably via the sequential elimination of LiF from acetylidoborate precursors (e.g. **1a**). Addition of the eliminated LiF to unreacted boron trifluoride means that formation of **2** is concomitant with that of LiBF₄, **3**, as evidenced by multinuclear NMR spectroscopy. Finally, the fact that **2** is the true intermediate in RC≡CLi/BF₃-promoted alkynyl anion chemistry, rather than **1a** or **1b**, helps to explain the stoichiometries required for efficient subsequent nucleophilic addition reactions.

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Footnotes and References

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† BuⁿLi (1.88 ml, 1.6 M in hexanes, 3.0 mmol) was added to phenylacetylene (0.33 ml, 3.0 mmol) in thf-toluene (5:1 ml) at -78 °C under nitrogen. After stirring for 10 min, BF₃·OEt₂ (0.37 ml, 3.0 mmol) was added and the resultant yellow solution was stirred for a further 10 min at

-78 °C. Warming to room temp. gave a white suspension, which afforded a colourless solution on gentle heating. Storage at +5 °C for three days afforded a colourless co-crystalline mixture of **2** and **3**. Yield (based on ¹¹B NMR spectroscopy and Scheme 2), 61% (**2**) and 16% (**3**), mp 163–164 °C. ¹H NMR [250 MHz, 25 °C, (CD₃)₂SO], δ 7.45–7.35 (m, 15 H, Ph), 3.59 (m, 4 H, thf), 1.76 (m, 4 H, thf). ¹³C NMR (400 MHz, 25 °C, Me₂SO), δ 131.1, 128.5 (*o*-, *m*-Ph), 127.5 (*p*-Ph), 124.7 (*ipso*-C-Ph), 95.3 (≡C-Ph), 67.1, 25.2 (thf). ¹⁹F NMR (235.361 MHz, 25 °C, Me₂SO, CCl₃F δ = 0), δ -147.59 (q, ¹¹BF₄⁻, ¹J_{11BF} 1.1 Hz), -147.53 (br m, ¹⁰BF₄⁻). ⁷Li NMR (155.508 MHz, 25 °C, Me₂SO, PhLi δ = 0), δ -0.11 [s, Li(Me₂SO)₄⁺]. ¹¹B NMR (128.379 MHz, 25 °C, Me₂SO BF₃·OEt₂ δ = 0), δ -0.75 (qnt., BF₄⁻, ¹J_{BF} 1.1 Hz); (C₆D₆, BF₃·OEt₂ δ = 0), δ ca. 0.03 (br s, Δν_{1/2} 450 Hz); ([²H₈]thf, BF₃·OEt₂ δ = 0), δ -1.18 (qnt., 1B, ¹J_{BF} 1.8 Hz), ca. -7.32 (br s, 1.25B, Δν_{1/2} = 340 Hz).

‡ Crystal data for **2**: C₂₈H₂₃BO, monoclinic, space group P2₁/n, a = 10.188(4), b = 15.159(3), c = 14.5899(11) Å, β = 104.385(9)°, U = 2182.6(9) Å³, M_r = 386.27, Z = 4, D_c = 1.176 Mg m⁻³, μ(Mo-Kα) = 0.069 mm⁻¹, F(000) = 816. Data were collected by the ω-2θ scan method on a Rigaku AKC5R four-circle diffractometer at 153(2) K using graphite-monochromated Mo-KKα radiation (λ = 0.71069 Å) in the range 5.16 < 2θ < 45.00°, +h, +k, ±l; 3045 reflections of which 2857 were independent (R_{int} = 0.0222) and used in all calculations. The structure was solved using direct methods⁹ and subsequent Fourier difference syntheses and refined¹⁰ by full-matrix least squares on F² with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model. In the final cycles of refinement a weighting scheme of the form w⁻¹ = [σ²(F_o)² + (0.0745P)² + 1.58P], where P = (F_o² + 2F_c²)/3, was employed which produced a flat analysis of variance. Final R(F) = 0.0452 for 2084 reflections with [I > 2σ(I)], wR(F²) = 0.2247 for all data; 271 parameters; goodness of fit = 1.039. Maximum peak and hole in final Fourier difference map 0.238 and -0.197 e Å⁻³ respectively. CCDC 182/562.

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