Synthesis of N-heterocyclic carbene-stabilized catecholoborenium cations by ligand substitution

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Supporting Information Placeholder

ABSTRACT: Ligand substitution is not a common procedure for the preparation of different borenium cations. This work demonstrates that the chloride ligands of several NHC-stabilized dichloroborenium cations $[\text{NHC}\cdot\text{BCl}_2][\text{X}]$ ($\text{NHC} = (\text{R}'\text{C})_2(\text{NR})_2\text{C}$; **1**: $\text{R} = \text{'Pr}$, $\text{R}' = \text{H}$; **2**: $\text{R} = \text{'Pr}$, $\text{R}' = \text{Me}$; **3**: $\text{R} = \text{'Bu}$, $\text{R}' = \text{H}$; $\text{X} = \text{AlCl}_4$ or $\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_4$) could be replaced with a catecholato moiety to produce $[\text{NHC}\cdot\text{Bcat}][\text{X}]$. According to single crystal X-ray analyses this particular ligand exchange enhanced Lewis acidity of the target borocations with respect to the dichloro precursors.

Tricoordinate boron cations, also known as borenium cations, are becoming very versatile reagents and catalysts for a wide variety of organic transformations including borylation, hydroboration, haloborylation, hydrosilylation, hydrogenation and Diels Alder reactions.¹⁻⁸ Two of the most prominent approaches for the synthesis of these borocations are included in Scheme 1 and involve substituent X displacement by a neutral donor (L) in the presence of an abstracting agent (A, route a)^{2a-d,3a-b,6b} and substituent X elimination by A from neutral $\text{L}\cdot\text{BR}_2\text{X}$ adducts (route b).^{2e-q,3c-g,4,6a,7} Other examples include spontaneous bromide extrusion as a result of steric/electronic factors or THF activation, as well as substituent protonation of the corresponding neutral boranes.^{2d,r,s} Borenium cations containing one or two halo/hydrido substituents $[\text{L}\cdot\text{BX}_2]^+$ ($\text{X} = \text{H}$ or halogen) could potentially be used for ligand substitution offering another synthetic approach (route c, Scheme 1). There are, however, only a handful of reports dealing with this particular methodology including unsuccessful attempts to exchange the bromide substituents of a pyridine-stabilized borenium cation.^{2d,f,3b,c} In this work, we wish to communicate the synthesis of several NHC-stabilized catecholoborenium cations by reacting the corresponding dichloroborenium cations with 1 equiv of catechol or lithium catecholate.

Results and Discussion

Recently, our group examined synthetic viability of a series of NHC-stabilized dichloroborenium cations in the presence of several different counterions.^{2m} For the current report three of these borocations ($[\text{NHC}\cdot\text{BCl}_2][\text{X}]$; $\text{NHC} = (\text{R}'\text{C})_2(\text{NR})_2\text{C}$; **1**: $\text{R} = \text{'Pr}$, $\text{R}' = \text{H}$; **2**: $\text{R} = \text{'Pr}$, $\text{R}' = \text{Me}$; **3**: $\text{R} = \text{'Bu}$, $\text{R}' = \text{H}$; $\text{X} = \text{AlCl}_4$ or $\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_4$) were subjected to ligand exchange with either catechol (cat-H_2) or lithium catecholate (cat-Li_2 , Scheme 2). According to ¹¹B NMR spectroscopy all dichloroborenium cations (δ_{B} between 47 and 52 ppm for $[\text{NHC}\cdot\text{BCl}_2]^+$ species) completely reacted with 1 equiv of either source of catecholate to yield the

Scheme 1. The most common preparatory methods for the synthesis of borenium cations (routes a and b), and the methodology explored in this report (route c).

L: = neutral donor substituents such as carbenes, amines, pyridines etc.

X = H, halides, OMe, etc.

R = H, halides, alkyl, aryl, alkoxy, etc.

A = abstracting agent such as AlCl_3 , $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, $\text{Na}[\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_4]$, $[\text{SiEt}_3][\text{CB}_{11}\text{H}_6\text{Br}_6]$, etc.

target catecholato products (δ_{B} 26-29 ppm for $[\text{NHC}\cdot\text{Bcat}]^+$ species) but with different degrees of purity and stability (see below). The identities of $[\mathbf{1Bcat}][\text{AlCl}_4]$, $[\mathbf{2Bcat}][\text{AlCl}_4]$ and $[\mathbf{3Bcat}][\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_4]$ were also realized by single crystal X-ray diffraction (Figure 1).⁹ At this point it is noteworthy that the target ligand exchange did not result in any significant structural changes for the “NHC·B” fragments including the B-C bond distances. The B-O_{cat} bond lengths (1.375(2) and 1.377(2) Å for $[\mathbf{1Bcat}]^+$; 1.382(3) and 1.375(3) Å for $[\mathbf{2Bcat}]^+$; 1.377(4) and 1.372(4) Å for $[\mathbf{3Bcat}]^+$) and O1-B1-O2 bond angles (113.04(15), 112.35(18) and 114.2(3)° for $[\mathbf{1Bcat}]^+$, $[\mathbf{2Bcat}]^+$ and $[\mathbf{3Bcat}]^+$, respectively) are also in a good agreement with other borenium cations containing a catecholato ligand.^{2d,3b,d,5} Even though the angles between the planes of the NHC and catecholate fragments vary from about 16° for both $[\mathbf{1Bcat}]^+$ and $[\mathbf{2Bcat}]^+$ to 81.4° for $[\mathbf{3Bcat}]^+$, there is no evidence for π -bonding from the NHC to the central boron as the B-C bond distances (1.557(2), 1.560(3) and 1.567(4) Å for $[\mathbf{1Bcat}]^+$, $[\mathbf{2Bcat}]^+$ and $[\mathbf{3Bcat}]^+$, respectively) for these compounds are virtually identical.

The reaction between $[\mathbf{1BCl}_2][\text{AlCl}_4]$ or $[\mathbf{2BCl}_2][\text{AlCl}_4]$, containing close interion contacts (see Figure 1 for the visual depiction of analogous interion contacts),^{2m} and $\text{cat-H}_2/\text{cat-Li}_2$ showed no counterion interference according to ¹¹B and ²⁷Al NMR spectroscopy.¹⁰ These observations were somewhat surprising considering counterion dependence on the reactivity of similar cationic systems^{3h,11}, the analogous ligand exchange using $[\mathbf{3BCl}_2][\text{AlCl}_4]$

Scheme 2. The general synthetic procedure.

and the observed anion interference for the Gutmann-Beckett method involving these two borocations (see below). In fact, the target reactions between [3BCl₂][AlCl₄] and either source of catecholate initially resulted in the formation of at least two additional boron- and one aluminum-containing products as observed by ¹¹B and ²⁷Al NMR spectroscopy. Besides the usual signals for [3Bcat]⁺ (δ_B 29 ppm) the ¹¹B spectrum also contained peaks at around δ_B 2 and 22 ppm, while the usual signal for AlCl₄⁻ (δ_{Al} 103 ppm) was accompanied by a signal at around δ_{Al} 90 ppm in the ²⁷Al NMR spectrum.¹⁰ However, the identities of these species could not be established without a reasonable doubt.¹² Adventitious amounts of water were thought to be responsible for at least the presence of the boron containing species as the intensity of the signal at δ_B 22 ppm increased when the reaction mixtures were left in solution.¹⁰

Figure 1. Molecular structures for [1Bcat][AlCl₄] (left), [2Bcat][AlCl₄] (middle) and [3Bcat][B(3,5-Cl₂-C₆H₃)₄] (right) drawn at 50% probability level. For [1Bcat][AlCl₄] and [2Bcat][AlCl₄] interion close contacts have also been included. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for [1Bcat][AlCl₄]: B1-C1 1.557(2), B1-O1 1.375(2), B1-O2 1.377(2), C1-N1 1.351(2), C1-N2 1.353(2), B1...Cl1 3.310, B1...Cl3# 3.157, O1-B1-O1 113.04(15), N1-C1-N2 106.77(14); [2Bcat][AlCl₄]: B1-C1 1.560(3), B1-O1 1.382(3), B1-O2 1.375(3), C1-N1 1.354(3), C1-N2 1.356(2), B1...Cl3 3.806, B1...Cl4# 3.207, O1-B1-O1 112.35(18), N1-C1-N2 106.85(16); [3Bcat][B(3,5-Cl₂-C₆H₃)₄]: B1-C1 1.567(4), B1-O1 1.377(4), B1-O2 1.372(4), C1-N1 1.350(4), C1-N2 1.345(4), O1-B1-O1 114.2(3), N1-C1-N2 108.0(2).

Numerous attempts to isolate pure [3Bcat][AlCl₄] by recrystallization were also unsuccessful. Apart from the initial absence of the signals at δ_B 2 and 22 ppm similar observation were made when the target ligand exchange was performed using [3BCl₂][B(3,5-Cl₂-C₆H₃)₄]. However, when cat-H₂ was used and after complete consumption of this particular dichloro precursor it was necessary to remove all volatiles in order to prevent substantial decomposition of the catecholato product. If the volatiles were not removed several unidentified boron-containing species were detected by ¹¹B NMR spectroscopy whose formation was possibly due to the presence of the HCl byproduct.¹⁰ As mentioned before, this was not the case with the reaction mixtures containing AlCl₄⁻ suggesting that the presence of this non-innocent anion(s)^{2m} provided more protection for the electron deficient boron centre with respect to the system containing [B(3,5-Cl₂-C₆H₃)₄]. Redissolving the non-volatile part of the [3BCl₂][B(3,5-Cl₂-C₆H₃)₄]/cat-H₂ reaction mixture in fresh DCM did not, however, prevent gradual formation of the boron-containing species identified by the δ_B signal at 22 ppm.¹⁰

These last observations implied that the catecholato-for-chloride replacement resulted in less stable/more reactive borocations especially for the [3Bcat]⁺ systems. In fact, the solid state analysis of [1Bcat][AlCl₄] and [2Bcat][AlCl₄] provided evidence for more Lewis acidic, and possibly more reactive, boron centres in the target products with respect to the dichloro precursors. The average values for the interion close contacts (B...Cl_(anion)) dramatically decreased from 3.44 and 3.92 Å for [1BCl₂][AlCl₄] and [2BCl₂][AlCl₄], respectively, to 3.23 and 3.51 Å for the corresponding catecholato compounds. Additionally, the ligand exchange involving the ^tBu-substituted NHC (**3**, Scheme 2) resulted in the shortening of the average distance between the central boron and the nearest methyl groups of the ^tBu substituents by almost 0.1 Å (Figure 2). It is also very difficult to envision that the chloride ligands are drastically more sterically demanding than the catecholato ligand to solely cause the close contact discrepancy among the borocations. Thus, these structural changes suggested greater electron depletion at the boron centre^{3e} after the ligand substitution which is consistent with the relative electronegativity values for O (3.44) and Cl (3.16). On the other hand, one would expect a greater degree of O→B(p_z) π-bonding for [HNC·Bcat]⁺ with respect to the analogous Cl→B(p_z) bonding for [NHC·BCl₂]⁺¹³ which would lead to a conclusion that solid-state packing effects were the major contributor for these particular solid state observations.

Figure 2. The distances (in Å) between the boron centre and the nearest methyl groups of the ^tBu substituents for [3Bcat]⁺ (left) and [3BCl₂]⁺ (right).

In order to shed some light on this particular issue we attempted a series of reactions between both dichloro- and catecholoborenum cations, stabilized by **1** and **2**, and triethylphosphine oxide (Et₃PO) as described by the Gutmann-Beckett method.¹⁴ Unfortunately, according to the ²⁷Al and ³¹P NMR spectroscopic measurements the addition of Et₃PO, regardless of the added amount, to these borocationic systems suggested that the phosphine oxide's binding preference was in fact the aluminum centre of the counterion. This was confirmed by examining ²⁷Al and ³¹P NMR spectra of AlCl₃/Et₃PO mixtures which revealed the presence of virtually identical signals as observed for the borocation/Et₃PO systems.¹⁰ This anion interference could be explained by the hard-soft acid-base concept described for phosphonium cations.¹⁵ Thus, the Gutmann-Beckett method could not be used to determine whether the target ligand exchanged resulted in more Lewis acidic systems as suggested by the solid state analysis.

In summary, we have demonstrated that the chloro substituents of borenium cations [NHC·BCl₂]⁺ could be exchanged for the catecholato ligand using either cat-H₂ or cat-Li₂. The target cationic moieties were identified by multinuclear NMR, ES-MS and single crystal X-ray diffraction. The solid state analysis suggested increased electron deficiency at the newly synthesized borocations as both intra- (for [3Bcat]⁺) and inter-ion (for [1Bcat][AlCl₄] and [2Bcat][AlCl₄]) distances decreased with the ligand substitution. Unfortunately, the Guttmann-Beckett method was inconclusive for this purpose due to the anion interference. It was nevertheless postulated that this diminished electron density at the boron centre might have been the leading cause for the solution-state instability of [3Bcat]⁺ especially towards HCl when [B(3,5-Cl₂-C₆H₃)₄]⁻ was present as the counterion.

ASSOCIATED CONTENT

Supporting Information

General synthetic procedures, crystallographic data as well as copies of multinuclear NMR.

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Notes

The authors declare no competing financial interests.

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