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Synthesis of N-heterocyclic carbene-stabilized catecholatoborenium 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-BCl}_2][\text{X}] (\text{NHC} = (\text{R}_2\text{C})_2(\text{NR})_2\text{C}; \text{I}) \text{ or } \text{Pr} = \text{Pr} ^{\prime} = \text{H}; 2: \text{R} = \text{Pr} ^{\prime} = \text{Me}; 3: \text{R} = \text{Bu} ^{\prime} = \text{H}; \text{X} = \text{AlCl}_4 ^- \text{or } \text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_2\text{Li}) \text{could be replaced with a catecholato moiety to produce } [\text{NHC-Bcat}][\text{X}]. \text{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, hydrosilylation, haloboration, halosilylation, hydrosilation, hydrogenation and Diels-Alder reactions.\textsuperscript{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)\textsuperscript{2a-d,3a,b,6b} and substituent X elimination by A from neutral L-BR\textsubscript{2}X adducts (route b).\textsuperscript{2e-3c-g,4,6,7} Other examples include spontaneous bromide extrusion as a result of sterically/electronic factors or THF activation, as well as substituent protonation of the corresponding neutral boranes.\textsuperscript{2d,3s} Borenium cations containing one or two halo/hydrido substituents \([\text{L-Br}_2\text{X}]^+ (\text{X} = \text{H} \text{or } \text{halogen}) \text{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.\textsuperscript{2d,3b,4} In this work, we wish to communicate the synthesis of several NHC-stabilized catecholatoborenium 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.\textsuperscript{2m} For the current report three of these borocations \([\text{NHC-BCl}_2][\text{X}] (\text{NHC} = (\text{R}_2\text{C})_2(\text{NR})_2\text{C}; \text{I}) \text{ or } \text{Pr} = \text{Pr} ^{\prime} = \text{H}; 2: \text{R} = \text{Pr} ^{\prime} = \text{Me}; 3: \text{R} = \text{Bu} ^{\prime} = \text{H}; \text{X} = \text{AlCl}_4 ^- \text{or } \text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_2\text{Li}) \text{were subjected to ligand exchange with either catechol (cat-H\textsubscript{2}) or lithium catecholate (cat-Li\textsubscript{2}, Scheme 2). According to } ^{1}B \text{NMR spectroscopy all dichloroborenium cations (\text{cat} between 47 and 52 ppm for [NHC-BCl] + species) completely reacted with 1 equiv of either source of catecholate to yield the target catecholate products (\text{cat} 26-29 ppm for [NHC-Bcat] + species) but with different degrees of purity and stability (see below). The identities of \([\text{1Bcat}][\text{AlCl}_4], [\text{2Bcat}][\text{AlCl}_4] \text{and } [\text{3Bcat}][\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_2\text{Li}] \text{were also realized by single crystal X-ray diffraction (Figure 1).}\)\textsuperscript{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\textsubscript{cat} bond lengths (1.375(2) and 1.377(4) \text{Å} for \([\text{1Bcat}]^+; 1.382(3) \text{and } 1.375(3) \text{Å} \text{for } [\text{2Bcat}]^+; 1.377(4) \text{and } 1.372(4) \text{Å for } [\text{3Bcat}]^+\) and \(\text{O1-B1-E2 bond angles (113.04(15), 112.35(18) \text{and } 114.2(3)^{\circ} \text{for } [\text{1Bcat}]^+, [\text{2Bcat}]^+ \text{and } [\text{3Bcat}]^+, \text{respectively) are also in a good agreement with other borenium cations containing a catecholato ligand.\textsuperscript{2d,3b,4,5} Even though the angles between the planes of the NHC and catecholate fragments vary from about 16\textdegree \text{for both } [\text{2Bcat}]^+ \text{and } [\text{3Bcat}]^+ \text{to 81.4}^{\circ} \text{for } [\text{3Bcat}]^+, \text{there is no evidence for } \pi\text{-bonding from the NHC to } \text{the central boron as the B-C bond distances (1.557(2), 1.560(3) and 1.567(4) \text{Å for } [\text{1Bcat}]^+, [\text{2Bcat}]^+ \text{and } [\text{3Bcat}]^+, \text{respectively for these compounds are virtually identical.}}\)\textsuperscript{9} The reaction between \([\text{1BCl}_2][\text{AlCl}_4] \text{or } [\text{2BCl}_2][\text{AlCl}_4], \text{containing close interion contacts (see Figure 1 for the visual depiction of analogous interion contacts),\textsuperscript{2m} and cat-H\textsubscript{2}/cat-Li\textsubscript{2} showed no counterion interference according to } ^{11}B \text{and } ^{27}Al \text{NMR spectroscopy.}\textsuperscript{10} \text{These observations were somewhat surprising considering counterion dependence on the reactivity of similar cationic systems.}\textsuperscript{3b,11} \text{the analogous ligand exchange using } [\text{3BCl}_2][\text{AlCl}_4]\text{.}
and the observed anion interference for the Gutmann-Beckett method involving these two borocations (see below). In fact, the target reactions between [3BCl][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. However, the identities of these species could not be established without a reasonable doubt. 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.

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 [3BCl][B(3,5-Cl₂-C₆H₃)₃]. 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 catecholate 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. As mentioned before, this was not the case with the reaction mixtures containing AlCl₄⁻ suggesting that the presence of this non-innocent anion(s) provided more protection for the electron deficient boron centre with respect to the system containing [B(3,5-Cl₂-C₆H₃)₃]-. Recrystallizing the non-volatile part of the [3BCl][B(3,5-Cl₂-C₆H₃)₃]/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.

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 distances) dramatically decreased from 3.44 and 3.92 Å for the [1BCl][AlCl₄] and [2BCl][AlCl₄], respectively, to 3.23 and 3.51 Å for the corresponding catecholate compounds. Additionally, the ligand exchange involving the Bu-substituted NHC (3, Scheme 2) resulted in the shortening of the average distance between the central boron and the nearest methyl groups of the Bu 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 catecholate ligand to solely cause the close contact discrepancy among the borocations. Thus, these structural changes suggested greater electron depletion at the boron centre 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(π) bonding for [HNC-Bcat]⁺ with respect to the analogous Cl→B(π) bonding for [HNC-BCl]⁺ which would lead to a conclusion that solid-state packing effects were the major contributor for these particular solid state observations.
In order to shed some light on this particular issue we attempted a series of reactions between both dichloro- and catecholatoboreni-
um cations, stabilized by 1 and 2, and triethylphosphine oxide (Et3PO) as described by the Gutmann-Beckett method.14 Unfortu-
nately, according to the 27Al and 31P NMR spectroscopic measure-
ments the addition of Et3PO, regardless of the added amount, to these borocatonic systems suggested that the phosphine oxide’s binding preference was in fact the aluminium 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 borocat/ Et3PO systems.10 This anion interference could be explained by the hard-
soft acid-base concept described for phosphinium 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 borenum cations [NHC-BCl3]+ could be exchanged for the cate-
cholato 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 borocatonic as both intra- (for [3Bcat]+) and inter-ion (for [1Bcat][AlCl4] and [2Bcat][AlCl4]) distances decreased with the ligand substitution. Unfortunately, the Gutmann-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)3]+ 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.

ACKNOWLEDGMENT

We thank A*STAR (grant # 1220703062) for financial support.

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