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Aluminum Chloride Activation of Chloro-Boronsubphthalocyanine: a Rapid and Flexible Method for Axial Functionalization with an Expanded Set of Nucleophiles

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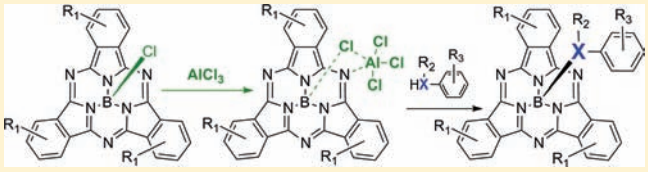
Supporting Information

ABSTRACT: We have developed a process whereby chloro-boronsubphthalocyanine (Cl-BsubPc) and other BsubPcs are activated to reaction with oxygen, sulfur, and nitrogen based nucleophiles by treatment with aluminum chloride under mild conditions. This allows for the scope of atoms chemically bound to the boron atom to be expanded beyond those derived from the traditional oxygen and carbon based nucleophiles. The successful formation of thiophenoxy and phenylamino derivatives of BsubPc was confirmed spectroscopically and by X-ray crystallography of single crystals. We have proposed a detailed mechanism for this process based on experimental observation and NMR spectroscopy (^{1}H, ^{11}B, and ^{27}Al) which involves formation of a complex between a halo-BsubPc and $AlCl_3$ (which we denote BsubPc(Cl)·Al(Cl′)$_3$). Our observations indicate that the action of phenol on BsubPc(Cl)·Al(Cl′)$_3$ does not involve direct reaction at the boron atom; rather phenol first reacts at the aluminum atom along the way to the formation of a new intermediate complex BsubPc(OPh)·Al(O′Ph)$_3$. The consequence is that the rate of this process is independent of the nature of the starting BsubPc. Cl-BsubPc and Br-BsubPc as well as BsubPcs with peripheral substitutents all react to form their respective phenoxy derivatives at the same rate. Quenching of BsubPc(OPh)·Al(O′Ph)$_3$ with a Lewis base ultimately produces a new bond between the phenol nucleophile and the boron atom of the BsubPc.



INTRODUCTION

Boronsubphthalocyanine (BsubPc) pigments and dyes are robust polycyclic aromatic systems currently being used in a broad spectrum of applications.[1] Recently there has been increased interest in the study of BsubPc derivatives because of their unique bowl-shaped structure,[2] their intense orange fluorescence,[3] their intense magenta color (ε = 50,000–90,000 L M^{-1} cm^{-1}),[4] their organic semiconducting properties,[5] and their selective ion sensing capability.[6] In the past 30 years, the synthetically accessible structural variants of BsubPc have largely been a result of variation around the periphery of the BsubPc ligand achieved through the use of substituted phthalonitriles as starting materials (Figure 1). In contrast, structural variation resulting from the displacement of the labile axial halide in halo-BsubPcs has been limited to reaction with oxygen[7−10] and carbon[11,12] based nucleophiles. In many cases the displacement requires lengthy reaction times and/or elevated temperatures.[13] Still, such axial substitutions have been shown to allow for the formation of BsubPc-oligothiophene hybrids[11c] and for the control of the solid state arrangement of BsubPcs.[14] The mechanism for the displacement of the axial halide is complex but is generally thought to be S_N1 in nature when oxygen nucleophiles are used; simple phenol affects the transformation whereas phenoxylate does not and the presence of base (to sequester the produced HX) shows little effect on conversion and in many cases is known to degrade the BsubPc.[15] It is generally accepted that "peripheral donor groups increase the rates and the yields of substitution, probably by stabilization of an eventual positive charge on the boron atom";[1] as a corollary, electron withdrawing groups should slow reaction rates by reducing the molecules' ability to stabilize a reactive charged state.

Clearly changing the chemical structure of the BsubPc ligand for the sole purpose of affecting reaction rates is undesirable, so we sought out methods to enhance the reactivity of the axial boron-halide bond in a general way. The aim was to allow for milder reaction conditions in a facile and inexpensive manner without degradation of the BsubPc ligand. One option would be to make use of the other halides. While Cl-BsubPcs are common, both F-BsubPcs[16] and Br-BsubPcs[3,8a] are thought to have different reactivities relative to Cl-BsubPc (Br-BsubPc being faster) although no kinetic data exists in the literature. Our experience with Br-BsubPc are that it readily hydrolyzes to hydroxy-BsubPc (HO-BsubPc) at ambient conditions over a

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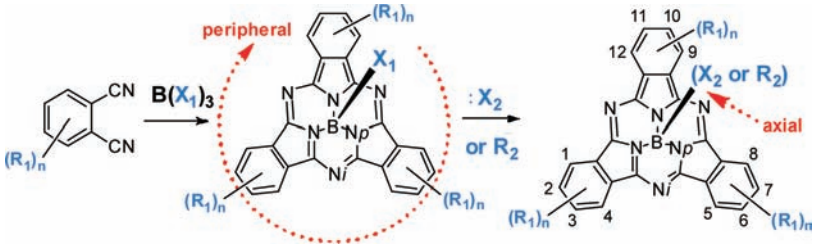

Figure 1. Generalized synthetic scheme to BsubPcs functionalized in the axial position. Peripheral positions are numbered, axial positions are indicated, and imine (N*i*) and pyrrole (N*p*) nitrogens are indicated.

period of months when stored outside of a glovebox[3,17] This makes it impractical for use as a starting material in industrial synthesis or exploratory research of BsubPcs by negating the benefits of process scale up (i.e., having a large supply on hand which can be used over a period of time or after a period of time). Boron dipyrrins, first described in 1937[18] many decades before BsubPcs in 1972,[19] are structurally similar to BsubPc, and thus their chemistry presents a rich resource to aid in the exploration of potential new chemistry for BsubPcs. Boron dipyrrins are formed by the complexation of dipyrrin with boron trifluoride producing HF and leaving two residual boron−fluorine bonds. These bonds are hydrolytically stable and robust; as a result, chemical transformations of the B−F bonds are relatively limited. In 2007, however, Tahtaoui et al. found Lewis acids (aluminum chloride inter alia) to complex with boron dipyrrins (specifically 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY)) activating the stable boron−fluorine bond, causing a rapid displacement upon addition of phenols[20] while requiring stochiometric quantities of the Lewis acid similar to Friedel−Crafts chemistry.[21]

Herein we outline a process which begins with the formation of a complex when Cl-BsubPc (and other selected halo-BsubPcs) is/are treated with aluminum chloride. Once this complex is formed a rapid reaction with phenol (or other selected nucleophiles) is observed, which on quenching with a Lewis base, yields the desired BsubPc derivative. Our experimental evidence suggests that the role of aluminum chloride in this process is not to simply activate the halogen-boron bond to reaction with nucleophiles (as is the case for BODIPYs mentioned above[20]) nor does it facilitate the formation of $BsubPc^{+}$[22] as a prelude to reaction with a nucleophile. Our investigation suggests that the mechanism is more complexed. Nonetheless, this process shows high utility, rapid reactivity which is independent of the choice of nucleophiles or halo-BsubPc (among those selected for this study), and uses a readily available, inexpensive, and industrially practical reagent: aluminum chloride.

Concurrent with our study, Guilleme et al. have shown that the chloride of Cl-BsubPc can also be extracted with a halophilic reagent (silver triflate, AgOTf) to form boronsubphthalocyanine-triflate (TfO-BsubPc) in situ which can be further functionalized with a variety of nucleophiles.[23] Their approach requires a 1−2 h reaction to form the reactive TfO-BsubPc, displays sensitivity to peripheral substitution, and uses silver triflate in reagent quantities, a salt derived from a precious metal.

RESULTS AND DISCUSSION

The process began with the preparation of a dispersion of 20 mg/mL of Cl-BsubPc (or Br-BsubPc or other BsubPc derivative) in chlorobenzene which appeared deep pink/red in appearance (specific solubility of Cl-BsubPc in chlorobenzene is 0.2 mg/mL[4]). Next, 1.5 equiv of aluminum chloride was added which immediately resulted in a color change of the solution to deep blue (Figure 2). The solution/mixture was

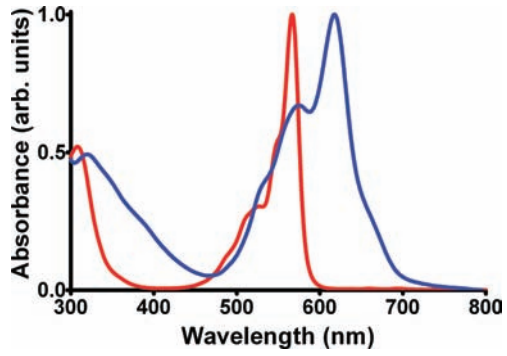

Figure 2. Absorption spectra of Cl-BsubPc (1a, red), and its complex with $AlCl_3$ ($BsubPc(Cl)\cdot Al(Cl')_3$, blue).

then stirred at 60 °C to aid dissolution. After complete evolution of the blue color (approximately 20−40 min) 5 equiv of phenol was added to the reaction mixture while a temperature of 60 °C was maintained. Samples were taken as a function of time and quenched using a Lewis base (DMF or pyridine). Analysis by HPLC showed rapid conversion to phenoxy-BsubPc (PhO-BsubPc, compound **2**) by comparison to a genuine sample. Complete conversion was achieved after 1 h (Figure 3). Conventional workup procedures were used at this point. In this case the samples were filtered through a plug of basic alumina and the solvent was removed by rotary evaporation. We did not observe a difference in the rate of reaction when Br-BsubPc or selected other BsubPcs were used in place of Cl-BsubPc (Figure 3a). If residual water was present HO-BsubPc was formed. This can be avoided by conducting the process in a glovebox or by prudently drying glassware and solvents prior to use and operating under a positive pressure of argon outside of a glovebox. No indication of the formation of ring expanded products such as metal free phthalocyanine or chloro-aluminumphthalocyanine was seen. Slower and stalled conversions were observed when reducing the amount of the phenol to 1.1 or 0.5 equiv (stalled at 86% and 38% conversion respectively in under 1 h, Figure 3b). We found that dichloromethane and chloroform are also useable as solvents in this process although the former precludes heating the reaction to 60 °C (in this case complete conversion at room temperature was achievable in 6−8 h). The use of higher amounts of Cl-BsubPc (100 mg/mL for example) retarded the rate of reaction presumably because of a mass transfer and/or

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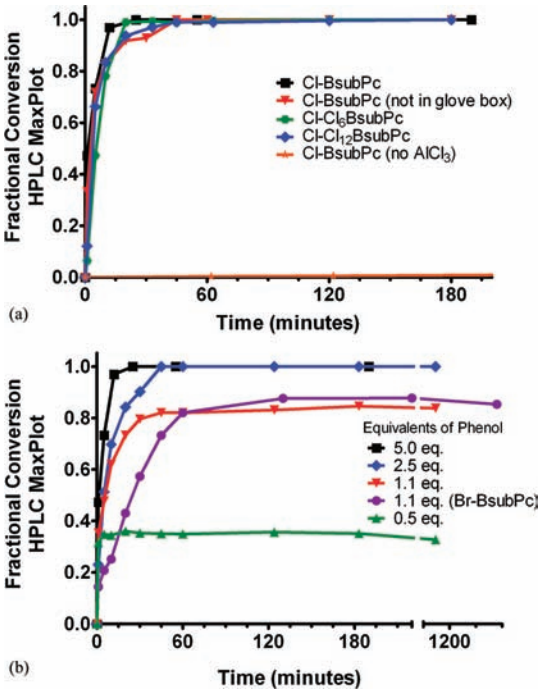


Figure 3. (a) Conversion of halo-BsubPc to PhO-BsubPc as a function of time in the presence of 1.5 equiv of $AlCl_3$ and 5 equiv of phenol (as indicated). Conversion of Cl-BsubPc to PhO-BsubPc without $AlCl_3$ is given for comparison; (b) Conversion of Cl-BsubPc to PhO-BsubPc (or Br-BsubPc as indicated) as a function of time in the presence of 1.5 equiv of $AlCl_3$ and varying equiv of phenol.

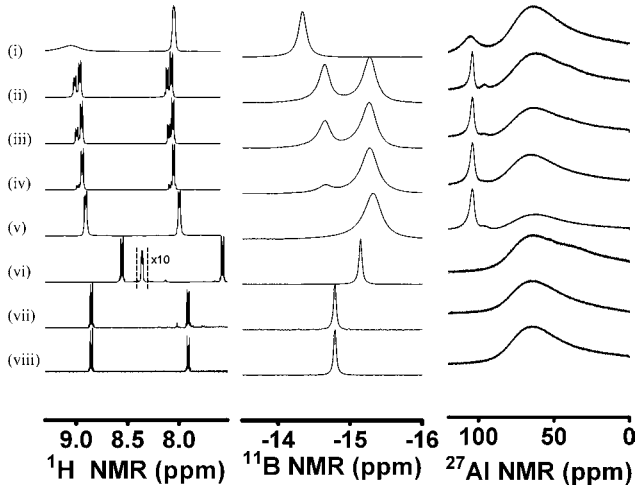


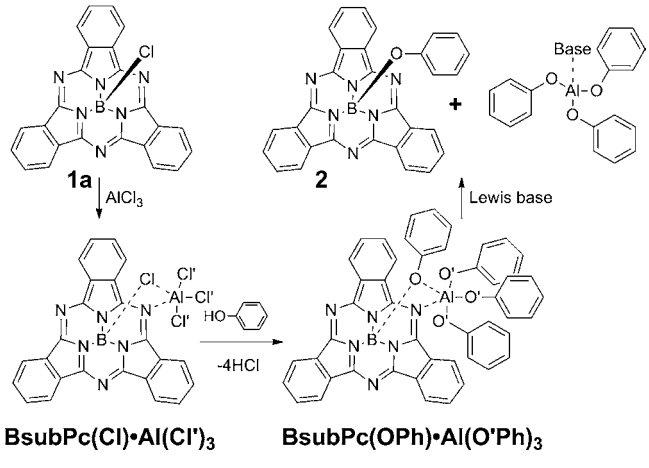
Figure 4. Stacked plot of ^1H, ^{11}B, and ^{27}Al NMR showing the steps though a typical reaction sequence (Scheme 1): (i) after stirring Cl-BsubPc and 1.5 equiv of aluminum chloride in $CDCl_3$; (ii) 30 min, (iii) 90 min, (iv) 210 min, and (v) 16 h after the addition of 5 equiv of phenol; (vi) after quenching with excess pyridine (the section between 8.4 and 8.3 is reduced by a factor or 10 because of a large peak from pyridine); (vii) after filtering through a plug of basic alumina and rotary evaporation; and (viii) a reference spectra of PhO-BsubPc.

solubility limitations of both Cl-BsubPc and PhO-BsubPc in chlorobenzene (0.2 mg/mL and 2.7 mg/mL respectively[4]).

Owing to the rapid formation of a deep blue colored solution on addition of $AlCl_3$ to Cl-BsubPc a complex must be formed between the two constituents. To elucidate the nature of this complex as well as the remaining mechanism of the reaction occurring during this process we conducted a spectroscopic investigation of the process. ^1H, ^{11}B, and ^{27}Al NMR were performed during the course of a typical reaction of Cl-BsubPc (**1a**) with $AlCl_3$ and phenol in $CDCl_3$ (20 mg/mL) at 40 °C (Figure 4). On addition of $AlCl_3$ to Cl-BsubPc, ^{27}Al NMR showed a *broad* resonance at δ = 105 ppm (Figure 4i, the other broad resonance present in the ^{27}Al spectrum is due to aluminum present in the NMR sample tube glass). The position of this resonance is commonly a characteristic of an anionic $AlCl_4^-$.[24] Indeed, we also acquired the ^{27}Al NMR spectrum of the ionic liquid 1-ethyl-3-methylimidazolium tetrachloroaluminate (CAS# 80432-05-9) which contains the $AlCl_4^-$ anion and indeed it also shows a *sharp* resonance at δ = 104 ppm (doublet, J = 24.80 Hz). However, if $AlCl_4^-$ anion is present then it must have been formed by abstraction of the chloride from Cl-BsubPc resulting in the presence of the corresponding positively charged $BsubPc^+$ species. ^{11}B NMR does not suggest this to be the case. We observed a ^{11}B resonance at approximately δ = −14.3 ppm (Figure 4i) which is shifted by approximately +1 ppm from what might be expected from Cl-BsubPc itself[25] (see Supporting Information) and significantly different from the calculated ^{11}B resonance of $BsubPc^+$ of δ = +7.4 ppm.[22a] Given the lack of spectroscopic evidence for the presence of cationic $BsubPc^+$ and the *broad* ^{27}Al NMR resonance we must conclude that the resonance in the ^{27}Al spectrum is in fact indicative of tetra-coordinated aluminum rather than the $AlCl_4^-$ anion itself. This is consistent with the observation that the sharpness (or line-width) of an ^{27}Al resonance is proportional to its symmetry.[26] We can then ultimately conclude that the action of Lewis acidic $AlCl_3$ on Cl-BsubPc results in the formation of an intermediate species whereby the aluminum complexes to a location close to the Lewis basic imine nitrogen (see N*i* in Figure 1) of Cl-BsubPc while simultaneously the chloride of Cl-BsubPc interacts with the aluminum of $AlCl_3$ to form a complex as illustrated (Scheme 1) which we will denote as $BsubPc(Cl)\cdot Al(Cl')_3$ (where Cl and Cl′ are used to differentiate chlorides originating from Cl-BsubPc and $AlCl_3$ respectively).

The formation of the $BsubPc(Cl)\cdot Al(Cl')_3$ complex is corroborated by the ^1H NMR spectrum which shows that the BsubPc ^1H resonances associated with the outer hydrogen atoms (H2, H3, H6, H7, H10, H11; see Figure 1 for

Scheme 1. Proposed Mechanism of Cl-BsubPc Activation to Reaction with Nucleophiles by Treatment with Aluminum Chloride



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numbering) are slightly shifted downfield by +0.9 ppm to δ = 8.04−8.06 ppm. The resonances of the bay hydrogen atoms (H1, H4, H5, H8, H9, H12) are significantly broadened on addition of $AlCl_3$ and appear at δ = 9.05 ppm which is shifted significantly downfield from the corresponding resonances for Cl-BsubPc itself (δ = 7.95−7.97 ppm and 8.90−8.92 ppm; Supporting Information, Figure S1). We conclude that the significant broadening of the resonances associated with the bay hydrogens is further indication that the BsubPc(Cl)·Al(Cl′)$_3$ complex rests within the bay of the BsubPc through an interaction with the Lewis basic imine nitrogens (Scheme 1). Our attempts to grow crystals of the BsubPc(Cl)·Al(Cl′)$_3$ complex were unsuccessful, although we were able to obtain a blue/green glassy precipitate during a few attempts.

On addition of phenol several observations can be made. The first is that on addition of 5 equiv of phenol ^{11}B NMR indicates that there is formation of two distinct complexes during the first 30 min which completely convert to one distinct species between 210 min to 16 h (Figure 4ii−Figure 4v). In each complex the ^{11}B nucleus is progressively shielded from the initial BsubPc(Cl)·Al(Cl′)$_3$ complex indicating reaction with phenol. Second, ^{27}Al NMR does not show a difference in the position of the ^{27}Al resonance on additional of phenol over the same time scale indicating the persistence of tetra-coordinated aluminum (δ = 105 ppm). The resonance is however significantly sharpened.

We can then suppose that on addition of phenol to the process the BsubPc(Cl)·Al(Cl′)$_3$ complex reacts quickly with the initial equivalents of phenol discriminately and rapidly (under 30 min) at the Cl′ position first (the chloride bound to Al) forming BsubPc(Cl)·Al(O′Ph)$_3$ followed by reaction at the Cl position relatively slowly (started at 30 min and completed at approximately 120 min) to form BsubPc(OPh)·Al(O′Ph)$_3$ (Scheme 1).

The supposition that phenol reacts discriminately at the aluminum center is further supported by the observation that upon addition of 5 equiv of phenol, we observed a lack of difference in the observed rates of formation of the phenoxy derivative of each of Cl-BsubPc, Br-BsubPc, Cl−Cl$_6$BsubPc, and Cl−Cl$_{12}$BsubPc (Figure 3a). This is in contrast to the observation that under standard conditions (without $AlCl_3$) reaction of this list of derivatives with phenol shows a differential reactivity relative to each other presumably because of a difference in the polarization of the B−Cl bond.[17] This is also in contrast to the observations of Guilleme et al. who have observed when TfO-BsubPc was generated in situ and reacted there was also a difference in reactivity with different peripheral substituents.[23] Each of these observations which are contrary to previous observations are further indications that the action of $AlCl_3$ on Cl-BsubPc produces an intermediate complex BsubPc(Cl)·Al(Cl′)$_3$ rather than simply enhancing the formation of BsubPc$^+$ in the S_N1-type mechanism which is typical for phenoxylation of halo-BsubPcs[1] and supposed for TfO-BsubPc.[23]

Finally, after complete formation of the BsubPc(OPh)·Al(OPh′)$_3$ complex (Scheme 1), the addition of a common Lewis base (we have used both pyridine and DMF in this case) effects its rearrangement to quantitatively give PhO-BsubPc (Figure 4vi). The ^{1}H and ^{11}B NMR resonances of the quenched sample are significantly shifted upfield; however, we have confirmed this is due only to the large portion of pyridine present in the sample (a ^{1}H NMR spectrum of PhO-BsubPc in the presence of large amounts of pyridine is illustrated in Supporting Information, Figure S1). Upon addition of pyridine, ^{27}Al NMR shows the disappearance of the resonance at δ = 105 ppm characteristic of the tetra-coordinated aluminum species (Figure 4vi). After a workup by filtration through a plug of basic alumina and then rotary evaporation, a final ^{1}H and ^{11}B NMR proves an identical match to a genuine sample of PhO-BsubPc (Figures 4vii and 4viii, respectively).

We should also note that 5.0 equiv of phenol is not required to facilitate the complete conversion of PhO-BsubPc. We have found that only 2.5 equiv of phenol is required (Figure 3b). Below 2.5 equiv of phenol a plateau in conversion occurs. For example, upon addition of 1.1 equiv of phenol conversion from Cl-BsubPc (or Br-BsubPc) to PhO-BsubPc stalls at 86% (Figure 3b). Following our supposition above, addition of 1.1 equiv of phenol would lead to the formation of a complex BsubPc(Cl)·Al(Cl′)$_{1.9}$(OPh′)$_{1.1}$. Given that quenching of this complex does produce PhO-BsubPc, the act of quenching must give rise to the migration of the phenoxy fragment from the aluminum to the boron atom. If this migration is merely statistical, one might expect the formation of ∼25% of PhO-BsubPc on quenching. Given that it yields 86% PhO-BsubPc indicates a preference to form the stronger B−O bond of PhO-BsubPc over reforming the B−Cl bond of Cl-BsubPc, although this preference is clearly not absolute in this case.

To further support our observations and our proposed mechanism two additional experiments were performed. Each experiment is designed to show the formation of an intermediate complex which on quenching results in migration of a molecular fragment from the aluminum atom to the boron atom concurrent with the formation of a stronger bond to boron than existed in the starting material. In the first, we intercepted our process after the reaction of Br-BsubPc with 1.5 equiv of $AlCl_3$ (60 °C, chlorobenzene, 3 h). The result was the formation of a deep blue solution. We quenched the resulting BsubPc(Br)·Al(Cl)$_3$ complex with a Lewis base (pyridine) without addition of phenol. The workup was as described above. The result was complete conversion of Br-BsubPc to Cl-BsubPc which was confirmed by ^{1}H NMR (Supporting Information, Figure S2) and HR MS (EI, calcd for 430.0905, found 430.0904, Supporting Information, Figure S3); MS confirming the absence of Br-BsubPc again indicating the formation of a stronger B−Cl bond over reforming the weaker B−Br bond in this case absolutely and without forming a statistical mixture.

In the second experiment, while not exactly the equivalent of initiating the reaction with the phenoxylated aluminum complex BsubPc(OPh)·Al(O′Ph)$_3$ (Scheme 1), we treated Br-BsubPc with 1.5 equiv of Al(OPh)$_3$ at 60 °C in chlorobenzene (3 h). The result was a color change of the solution which was not as dramatic a change as is seen with $AlCl_3$ (likely because of the lower Lewis acidity of Al(OPh)$_3$). Subsequent treatment of the intermediate complex BsubPc(Br)·Al(OPh)$_3$ with a Lewis base (pyridine) resulted in the color reverting back to the standard magenta/purple color characteristic of BsubPcs and the complete formation of PhO-BsubPc (workup was as described above, absence of Br-BsubPc and conversion to PhO-BsubPc confirmed by ^{1}H NMR (Supporting Information, Figure S2) and HR MS (EI, calcd for 488.1557, found 488.1559, Supporting Information, Figure S4)). Again a statistical mixture is not formed and formation of the stronger B−O bond is favored over reforming the weaker B−Br bond. Each of these two experiments further corroborate our proposed mechanism shown in Scheme 1 and the idea that

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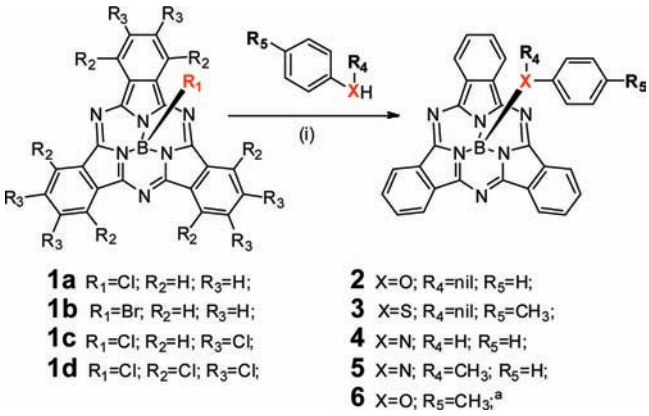
the phenoxy molecular fragment of PhO-BsubPc does indeed come about by migration from the aluminum atom to the boron atom on quenching with a Lewis base when less than 5 equiv of phenol are used.

Because we are interested in accessing BsubPc derivatives with new molecular fragments in the axial positions through reaction with new nucleophiles, we attempted to use our process conditions with *p*-thiocresol, aniline, and *N*-methylaniline in place of phenol. We had previously attempted to directly react these nucleophiles with Cl-BsubPc under conventional reaction conditions[5c,17] without any success; in the case of *p*-thiocresol, complete discoloration was observed thereby indicating the decomposition of the BsubPc unit and in the case of aniline and *N*-methylaniline, no reaction was observed. Each observation is in line with that recently reported by Guilleme et al.[23] Yet, using the process conditions described herein, conversion of Cl-BsubPc was achieved forming 4-methylthiophenoxy-boronsubphthalocyanine (**3**, Scheme 2), *N*-phenyl-amino-boronsubphthalocyanine (**4**, Scheme 2) and *N*-phenyl-*N*-methyl-amino-boronsubphthalocyanine (**5**, Scheme 2) respectively. Each reaction took between 2 h and 8 h to complete after addition of the nucleophile depending on the nucleophile. Compound **3** was then purified by sequential Kauffman column chromatography on silica and then standard basic alumina with dichloromethane as eluent with an isolated yield of 44%. Compounds **4** and **5** were isolated by flash chromatography using basic alumina and dichloromethane, followed by precipitation from a tetrahydrofuran (THF) solution into pentane. Final purification was achieved by sublimation to 210 °C with isolated yields of 30% and 77% respectively. Crystals suitable for X-ray diffraction of **3** and **5** were obtained by slow vapor diffusion of heptane into chloroform, unambiguously identifying their respective structures (Figure 5 and Figure 6). Selected crystallographic information is given in Table 1 and complete crystallographic data is given in the Supporting Information accompanying this Article.

The crystal structure of compound **3** presents the first example of a crystal structure where a B−S bond is attached to a BsubPc. We have previously synthesized and crystallized the exact analogue to compound **3** containing oxygen (**6**, Scheme 2)[14a] thus allowing the comparison of the molecular geometry changes on introduction of the heavier sulfur atom to the structure (Table 1). As would be expected, the B−S bond is longer at 1.923(3) Å as compare to a B−O bond length of 1.436(2) Å. Similarly the S−C bond is longer at 1.776(2) Å compared to 1.386(2) Å. The B−S−C bond angle was significantly smaller at 99.2(1)° compared to 115.6(1)° for B−O−C. What was unexpected was a difference in the bowl depth of the BsubPc ligand. Bowl depth is defined by the distance between a line intersecting the boron atom which is perpendicular to the plane defined by C2|C3|C6|C7|C10|C11 (see numbering in Figure 1). For compound **3** it was significantly shorter (2.515 Å compared to 2.707 Å) than for compound **6** indicating that the presence of sulfur has the effect of flattening the bowl of the BsubPc ligand in the solid state. We also noted a 5 nm red-shift (to 566 nm) in the absorption spectrum of **3** relative to **6** in toluene possibly indicating the flattening of the bowl of BsubPc also happens in solution.

The X-ray determined structure of compound **5** has two independent molecules in the unit cell showing an axial B−N bonding distance of 1.508(3) Å and 1.532(3) Å, similar to those recently described by Guilleme et al.[23] The independent molecules are joined by a single molecule of water despite the dry solvents being used. The water is hydrogen bound to one of the nitrogen atoms of the BsubPc ligand of each molecule. In this case the bowl of the BsubPc ligand in each molecule was also flattened compared to that of **6**, and similarly its absorption maximum is shifted by 3 nm to 564 nm in toluene. However we cannot clearly attribute the flattening of the bowl of BsubPc to a contribution of the nitrogen (in place of oxygen), the *N*-methyl group, or the unique crystal structure. Exhaustive attempts to crystallize **4** were all unsuccessful.

Scheme 2. Reaction of halo-BsubPc (1a−d) Yielding Their Respective Axially Substituted BsubPc (Compounds 2−5)[a]



[a]Conditions: (i) 1.5 equiv of $AlCl_3$, 5 equiv of phenol, thiophenol, aniline, or *N*-methylaniline, chlorobenzene, 60 °C. [a] − Compound **6**: 4-methyphenoxy-BsubPc is included for reference and was prepared as detailed in ref 14a.

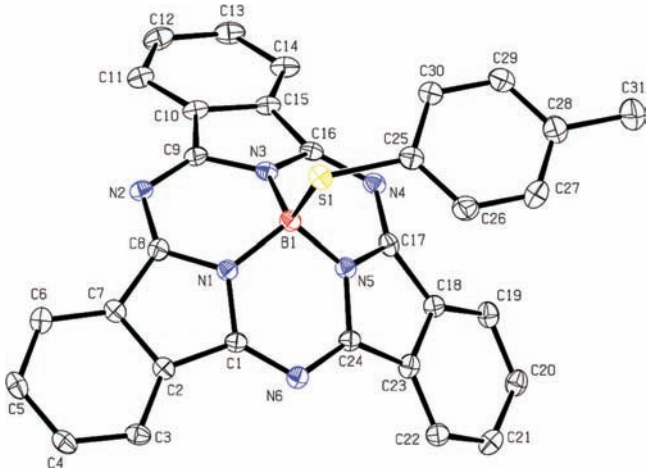


Figure 5. Thermal ellipsoid plot of compound **3** at a 35% probability level. Hydrogen atoms have been omitted for clarity.

CONCLUSION

In summary, we have outlined a new and rapid process to obtain a variety of BsubPc derivatives with unique molecular fragments in the axial position. Using a readily available and inexpensive reagent, aluminum chloride ($AlCl_3$), we have been able to show a rapid and low temperature (less than 60 °C) method to produce PhO-BsubPcs in at least three solvents (chlorobenzene, chloroform, and dichloromethane). This method can also be used to access a wider range of molecular

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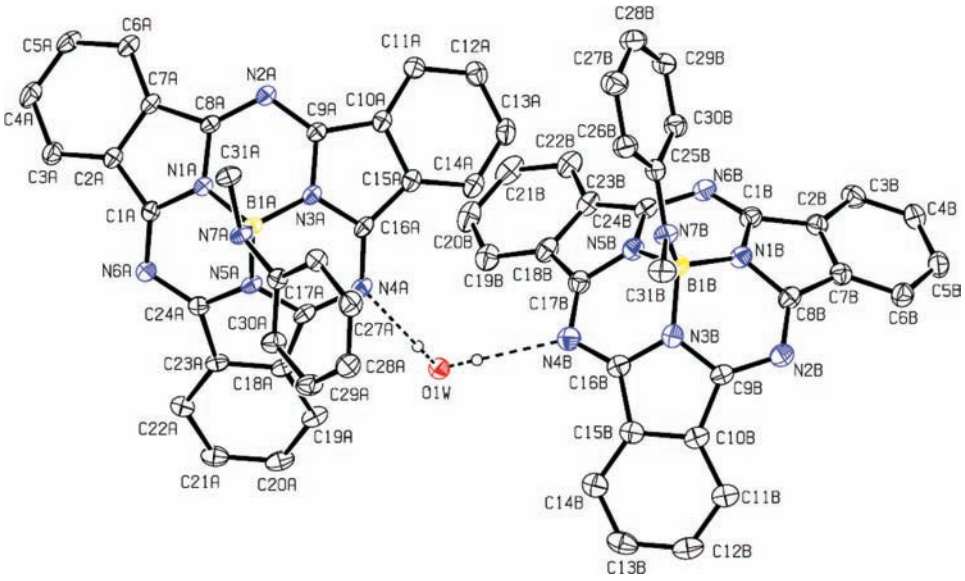

Figure 6. Thermal ellipsoid plot of compound **5** at a 35% probability level. Hydrogen atoms have been omitted for clarity.

fragments based on nitrogen and sulfur for BsubPcs (from their respective nucleophiles).

We have proposed a mechanism by which this transformation occurs which is supported by observation and NMR spectroscopy (^{1}H, ^{11}B, and ^{27}Al). The mechanism involves formation of an intermediate complex BsubPc(Cl)·Al(Cl′)$_3$ by which aluminum chloride complexes with Cl-BsubPc. The subsequent addition of a phenol results in the formation of another immediate complex BsubPc(OPh)·Al(OPh′)$_3$ which upon quenching with a Lewis base results in the formation of a new bond between the selected nucleophile and the boron atom of the BsubPc. We also present experimental evidence which suggests that the reaction of phenol occurs at the aluminum atom first. This observation is further supported by the reaction of $AlCl_3$ and $Al(OPh)_3$ with Br-BsubPc producing Cl-BsubPc and PhO-BsubPc, respectively. The consequence is that this process does not show the sensitivity to peripheral BsubPc substitution that other processes do as the polarization or chemical environment of the halo-B bond is not of significance. Other nucleophiles such as *p*-thiocresol, aniline, and *N*-methylaniline yield their respective BsubPc derivatives, despite being entirely unreactive under conventional/standard axial substitution conditions.

The aim of our group is to use this new process to rapidly access an ever expanding set of molecular fragments for the axial position of BsubPc. We have shown that changes in the axial fragment can affect the physical (including electronic) properties[3,4,27] and solid state arrangements of BsubPcs.[14] Such effort is both warranted and timely as BsubPcs are materials of current interest for application in the fields listed above.[1−6]

EXPERIMENTAL SECTION

Methods and Materials. Pyridine, *N*,*N*-dimethylformamide (DMF), acetonitrile, and phenol were purchased from Caledon Laboratories Ltd. and used as received. Chlorobenzene was obtained from Caledon Laboratories Ltd. and purified and stored in a Pure Solv solvent purification system prior to use. Aluminum chloride, *p*-thiocresol, aniline, and *N*-methylaniline were obtained from Sigma Aldrich Canada. All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 MHz system in deuterated chloroform ($CDCl_3$) purchased from Cambridge Isotope Laboratories which was used as received. All ^{1}H NMR spectra where referenced to an internal standard of 0.05% TMS. All crystal structures were collected using computer-controlled KappaCCD system and an Oxford Cryostream variable temperature apparatus. All ultraviolet−visible (UV−vis) spectroscopy was performed using PerkinElmer Lambda 1050 with a 10 mm path length for solution phase samples. High pressure liquid chromatography (HPLC) analysis was conducted using a Waters 2695 separation module with a Waters 2998 photodiode array and a Waters 4.6 mm ×100 mm SunFire C_{18} 3.5 μm column. HPLC grade acetonitrile and DMF were eluted at 0.6 mL/min during operation at a composition of 80:20, respectively. Mass spectrometry was performed on a Waters GC Time-of-Flight mass spectrometer with an electron ionization probe and accurate mass determination.

Phenoxylation of Boronsubphthalocyanines (Compounds 1a−d). The conversion of compounds **1a−d** to their phenoxylated derivative was observed using the following conditions. BsubPc (**1a**: 0.100 g, **1b**: 0.221 g, **1c**: 0.148 g, **1d**: 0.196 g) was combined with aluminum chloride (1.5 equiv) and chlorobenzene (21.5 L chlorobenzene/mol BsubPc (∼20 g BsubPc/L chlorobenzene); molar concentration kept constant) in a 20 mL scintillation vial inside a glovebox. The contents were stirred at 60 °C temperature for between 30 min until complete evolution of the blue color was achieved. Then 5 (2.5, 1.1 or 0.5) equiv of phenol (**1a**, **1c**, **1d**: 0.109 g; **1b**: 0.048 g) were added. The contents were stirred for another 5 h at which point 1 mL of pyridine was added to the reaction mixture and allowed to stir for 5 min. Each reaction was monitored by HPLC. The products of each reaction were not isolated.

Chloro-boronsubphthalocyanine (Compound 1a). Synthesized as previously reported.[4,10c]

Bromo-boronsubphthalocyanine (Compound 1b). Synthesized as previously reported.[9a]

Chloro-hexachloroboronsubphthalocyanine (Compound 1c). Synthesized as previously reported.[27]

Chloro-dodecachloroboronsubphthalocyanine (Compound 1d). Cl-**Cl$_{12}$BsubPc** was synthesized by adapting the method of Zyskowski and colleagues.[10c] 220 mL of 1,2-dichlorobenzene was added to 11.047 g of tetrachlorophthalonitrile in a 500 mL three-neck round-bottom flask. 100 mL of 1.0 M solution of BCl_3 in heptane was added. The mixture was then heated, and the heptane was removed through distillation using a short-path condenser. After distillation the flask was heated at reflux (180.5 °C) for 1.5 h. A positive pressure of argon was maintained throughout the experiment. The products were then cooled, and the solvent was removed by rotary evaporation. Next, the dry solid was placed in a cellulose thimble and extracted with methanol and then petroleum ether, each for 20 h in a Soxhlet

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Table 1. Relevant Crystallographic and Selected Geometrical Parameters for Compounds 3, 5, and 6

	3	5		6[a]
chemical formula	$C_{31}H_{19}BN_6S$	$C_{31}H_{20}BN_7{\cdot}0.5(H_2O)$		$C_{31}H_{19}BN_6O$
formula mass	518.39	502.25		502.33
crystal system	monoclinic	triclinic		triclinic
a/Å	10.3506(4)	11.5120(3)		10.1555(3)
b/Å	22.6651(9)	11.7673(3)		10.9258(4)
c/Å	10.7047(3)	19.3022(5)		11.7215(4)
α/deg	90.00	72.9030(14)		86.3530(17)
β/deg	102.582(2)	81.8810(12)		78.496(2)
γ/deg	90.00	75.8510(13)		66.9870(18)
unit cell volume/Å^3	2450.99(15)	2416.61(11)		1172.88(7)
temperature/K	150(1)	150(1)		150(1)
space group	$P21/c$	$P\bar{1}$		$P\bar{1}$
no. of formula units per unit cell, Z	4	4		2
no. of reflections measured	14105	42414		14448
no. of independent reflections	5356	11050		5309
R_{int}	0.0496	0.0641		0.0441
final R_1 values ($I > 2\sigma(I)$)	0.0548	0.0578		0.0465
final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1312	0.1392		0.1138
final R_1 values (all data)	0.1004	0.1131		0.0651
final $wR(F^2)$ values (all data)	0.1583	0.1638		0.1264
goodness of fit on F^2	1.019	1.038		1.058
B-R_4 bond length (Å)	1.923(3)	1.508(3)	1.532(3)	1.436(2)
R_4-C bond length (Å)	1.776(2)	1.426(3)	1.407(3)	1.386(2)
B-R_4-C bond angle (deg)	99.2(1)	119.8(2)	123.5(2)	115.6(1)
bowl depth (Å)	2.515	2.556	2.631	2.707

[a]Compound **6**: 4-methyphenoxy-BsubPc from ref 14a.

extraction apparatus. The solid was then placed in a vacuum oven at 50 °C overnight. Cl-**Cl_{12}BsubPc** was used without further purification in the subsequent steps. Yield 6.344 g (purity 92%, HPLC maxplot). HRMS exact mass calcd for $C_{24}BCl_{13}N_6$, 843.6141; found 843.6127.

4-Methylthiophenoxy-boronsubphthalocyanine (Compound 3). Cl-BsubPc (0.300 g, 6.97×10^{-4} mol) was combined with *p*-thiocresol (0.288 g, 3.48×10^{-3} mol, 5 equiv), aluminum chloride (0.139 g, 1.05×10^{-3} mol, 1.5 equiv), and chlorobenzene (15 mL) in a 20 mL scintillation vial inside a glovebox. The contents were stirred at 60 °C temperature for 2 h after which 3 mL of pyridine was added to the reaction mixture and allowed to stir for 5 min. The reaction mixture was subsequently poured onto a bed of standard basic alumina after which it was isolated by sequential Kauffman column chromatography, first on standard basic alumina and then on standard silica with dichloromethane as eluent in each case. The solvent was removed by rotary evaporation yielding 0.160 g of a dark purple solid (44%, 99+% pure HPLC maxplot and ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.24 (3H, s), 6.05−6.08 (2H, d), 6.67−6.70 (2H, d), 7.92−7.89 (6H, m), 8.80−8.83 (6H, m). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si): δ 21.28, 122.38, 128.76, 129.35, 139.99, 130.34, 131.12, 134.37, 150.45 HRMS (positive) exact mass calcd for $C_{31}H_{19}BN_6S$, 518.1475; found 518.1485. UV−vis$_{toluene}$ λ_{max}: 566 nm. Crystals of suitable quantity for X-ray diffraction were grown by slow vapor diffusion of heptane into chloroform.

***N*-Phenylamino-boronsubphthalocyanine (Compound 4).** Cl-BsubPc (0.300 g, 6.97×10^{-4} mol) was combined with aniline (0.32 mL, 3.48×10^{-3} mol, 5 equiv), aluminum chloride (0.139 g, 1.05×10^{-3} mol, 1.5 equiv), and chlorobenzene (15 mL) in a 20 mL scintillation vial inside a glovebox. The contents were stirred at 60 °C temperature for 8 h after which 3 mL of pyridine was added to the reaction mixture and allowed to stir for 5 min. The reaction mixture was subsequently purified by flash chromatography through a plug of standard basic alumina with dichloromethane and the solvent. Removal of the dichloromethane by rotary evaporation yielded an oily red/pink fluid. Next, the oil was redissolved in 1 mL of tetrahydrofuran, precipitated with pentane, and filtered yielding a red/purple powder. Residual volatile impurities were next removed by sublimation at 210 °C (100 mg, yield 30%, 99+% pure by HPLC maxplot). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 5.02 −5.06 (2H, d), 6.27−6.32 (1H, t), 6.69−6.73 (2H, t), 7.88−7.91 (6H, m), 8.83−8.86 (6H, m), ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si): δ 113.77, 116.40, 122.02, 128.85, 129.72, 130.88, 144.24, 151.69. HRMS (positive) exact mass calcd for $C_{30}H_{18}BN_7$, 487.1717; found 487.1728. UV−vis$_{toluene}$ λ_{max}: 564 nm.

***N*-Phenyl-*N*-methyl-amino-boronsubphthalocyanine (Compound 5).** Cl-BsubPc (0.300 g, 6.97×10^{-4} mol) was combined with aniline (0.32 mL, 3.48×10^{-3} mol, 5 equiv), aluminum chloride (0.139 g, 1.05×10^{-3} mol, 1.5 equiv), and chlorobenzene (15 mL) in a 20 mL scintillation vial inside a glovebox. The contents were stirred at 60 °C temperature for 8 h after which 3 mL of pyridine was added to the reaction mixture and allowed to stir for 5 min. The reaction mixture was subsequently filtered through a plug of silica with dichloromethane, and the solvent was removed by rotary evaporation yielding an oily red/pink fluid. Next, the oil was redissolved in 1 mL of tetrahydrofuran, precipitated with pentane and filtered yielding a red/purple powder. Residual volatile impurities were next removed by sublimation at 210 °C yielding gold crystals (268 mg, yield 77%, 99+% pure by HPLC Maxplot). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.06 (3H, s), 5.44−5.47 (2H, d), 6.50−6.55 (1H, t), 6.71−6.75 (2H, t), 7.87−7.90 (6H, m), 8.81−8.84 (6H, m), ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si): δ 32.07, 119.31, 119.71, 122.07, 128.02, 129.66, 130.81, 147.78, 151.55, HRMS (positive) exact mass calcd for $C_{31}H_{20}BN_7$, 518.1873; found 518.1991. UV−vis$_{toluene}$ λ_{max}: 564 nm. Crystals of suitable quantity for X-ray diffraction were grown by slow vapor diffusion of heptane into chloroform.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplementary figures; ^{1}H and ^{13}C NMR spectra for compounds **3**, **4** and **5**; and detailed crystallographic data for compounds **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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