A Practical One-Pot Synthesis of Soluble Hexa-*peri*-hexabenzocoronene and Isolation of Its Cation-Radical Salt

Rajendra Rathore* and Carrie L. Burns

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

rajendra.rathore@marquette.edu

Abstract: A simple and practical synthesis of soluble hexa-*peri*-hexabenzocoronene (**HBC**) from readily available hexaphenylbenzene (**HPB**) is described. In this simple procedure, the substitution of the free para positions of the propeller-shaped **HPB** with *tert*-butyl groups and the oxidative cyclodehydrogenation to planar **HBC** is achieved in a one-pot reaction using ferric chloride both as a Lewis acid catalyst and as an oxidant in excellent yields. The ready availability of **HBC** allows the isolation of its pure cation-radical salt using a variety of chemical oxidants such as antimony pentachloride and triethyloxonium and nitrosonium hexachloroantimonate salts.

Polycyclic aromatic hydrocarbons (PAH) have found extensive usage as building blocks for the preparation of materials that can be used as molecular devices such as conductors, ferromagnets, wires, liquid crystalline materials, and other electronic and optoelectronic devices.[1] Although Clar[2] in his classical papers in the early 1960s suggested that "fully benzenoid" hexa-*peri*-hexabenzocoronene (**HBC**) should possess exceptional thermal and photochemical stability, the study of this novel PAH was pursued hitherto owing to its insolubility in most organic solvents. Recently, Müllen and co-workers[3] have prepared a variety of soluble derivatives of hexa-*peri*-hexabenzocoronene (and its higher homologues) by substitution of its free para positions with either long alkyl chains or with bulky *tert*-butyl groups to prevent graphite-like stacking. The preparation of these hydrocarbons is generally achieved either by cyclotrimerization of diarylacetylenes or Diels−Alder reaction between tetraarylcyclopentadienone and diarylacetylene followed by oxidative cyclodehydrogenation.[3b] Unfortunately, appropriately substituted diarylacetylene and tetraarylcyclopentadienone, required for these procedures, are generally prepared by multistep synthetic procedures.

Our continued interest in organic molecules that yield stable cation-radical salts[4] and their extensive usage as aromatic oxidants in a variety of electron-transfer catalyzed (ETC) organic and organometallic transformations[5] prompted us to seek an inexpensive and simple synthesis of a soluble derivative of hexa-*peri*-hexabenzocoronene (**HBC**) from readily available hexaphenylbenzene (**HPB**). Accordingly, we now report the development of a simple procedure in which the substitution of the free para positions of the propeller-shaped hexaphenylbenzene with *tert*-butyl groups and the oxidative cyclodehydrogenation to planar **HBC** is achieved in a one-pot reaction using ferric chloride both as a Lewis acid catalyst and as an oxidant in excellent yields, eq 1.
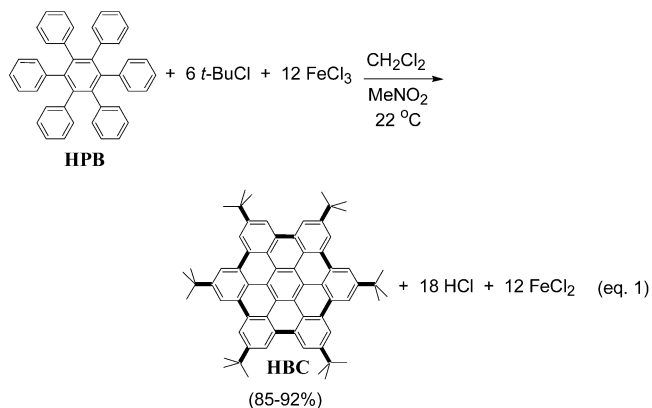
The ready availability of the soluble **HBC** allowed the isolation of its highly robust cation-radical salts (**HBC**[•+]) in pure form using different chemical oxidants such as $SbCl_5$, $NO^+SbCl_6^-$, and triethyloxonium hexachloroantimonate.[4b]

Thus, to a solution of readily available hexaphenylbenzene[6] (1.6 g, 3 mmol) and *tert*-butyl chloride (2.9 mL, 27 mmol) in dichloromethane (100 mL) was added slowly a solution of anhydrous ferric chloride (9.7 g, 60 mmol) in nitromethane (60 mL) at 22 °C while a slow stream of argon was bubbled through the solution to remove gaseous hydrochloric acid formed in the reaction (see eq 1). The reaction mixture immediately took on a red coloration that intensified to a dark red color with further additions of ferric chloride solution during a 30 min period. The highly colored solution was stirred for 3 h and poured in methanol (200 mL). The bright yellow precipitate thus formed was filtered and washed repeatedly with cold methanol. An ^{1}H NMR spectrum of the crude precipitate (2.19 g, yield: 85%) showed the char-

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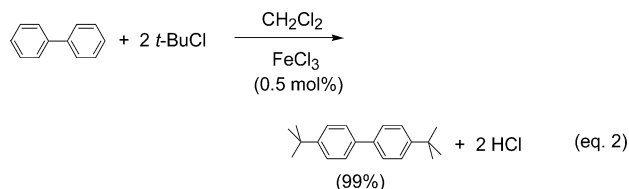(5) (a) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A., Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371. (b) Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 6072. (c) Blackstock, S. C.; Selby, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12155. (d) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (e) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114. (f) Yoshida, K. *Electrooxidation in Organic Chemistry. The Role of Cation Radicals as Synthetic Intermediates*; Wiley: New York, 1984.
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acteristic singlets at 9.31 ppm (*peri* hydrogens) and 1.83 ppm (*tert*-butyl groups) in a 2:9 ratio and thus confirmed the formation of **HBC**[7] in greater than 95% purity. The crude product can be further purified by column chromatography using silica gel and an ethyl acetate−hexanes mixture as eluent.

The yield and purity of the **HBC** produced above was further improved by heating a solution of hexaphenylbenzene (3.2 g, 6 mmol) and *tert*-butyl chloride (5.8 mL, 54 mmol) in dichloromethane (200 mL) with a few drops of a stock solution of anhydrous ferric chloride (19.4 g, 120 mmol) in nitromethane (120 mL) at 40 °C for 3 h. The red solution was cooled to room temperature, and remaining ferric chloride solution was then added dropwise (∼30 min.). The resulting dark-red reaction mixture was worked up as above to afford **HBC** as a yellow powder (4.9 g, 95%); see the Experimental Section.

The success of this efficient transformation in eq 1 stems from the fact that a nearly quantitative yield of 4,4′-di-*tert*-butylbiphenyl can be obtained by a reaction of biphenyl/*tert*-butyl chloride in dichloromethane in the presence of a catalytic amount of ferric chloride (∼0.5 mol %) at 22 °C (eq 2).[8]

$$\text{biphenyl} + 2\ t\text{-BuCl} \xrightarrow[\substack{\text{FeCl}_3 \\ (0.5\ \text{mol}\%)}]{\text{CH}_2\text{Cl}_2} \text{4,4'-di-}tert\text{-butylbiphenyl} + 2\ \text{HCl} \quad \text{(eq. 2)}$$

(99%)

The highly efficient *tert*-butylation of biphenyl using ferric chloride as a catalyst is accompanied by a vigorous evolution of hydrochloric acid gas and is completed within minutes. [***Caution:*** Note that a large-scale reaction (>50 mmol) in eq 2 should be carried out by a dropwise addition of a solution of ferric chloride in dichloromethane with rapid stirring to prevent a violent evolution of gaseous hydrochloric acid.] However, when we attempted to isolate the intermediate hexakis(4-*tert*-butylphenyl)benzene by a reaction of hexaphenylbenzene and *tert*-butyl chloride in the presence of a catalytic amount of ferric chloride, it produced a mixture of partially *tert*-butylated products together with hexakis(4-*tert*-butylphenyl)benzene[7] (∼30%) and traces of cyclized **HBC**s. The hexakis(4-*tert*-butylphenyl)benzene contaminated with traces of **HBC** (<1%) can be isolated by repeated crystallization from a dichloromethane−methanol mixture. This observation coupled with the good isolated yield of fully *tert*-butylated **HBC** in eq 1 suggested that the *tert*-butylation could occur even after oxidative cyclodehydrogenation of partially *tert*-butylated **HBC**s.

The ready preparation of soluble **HBC** in multigram quantities prompted us to evaluate its electron-donor properties as follows. The electron-donor strength of **HBC** was evaluated by electrochemical oxidation at a platinum electrode as a 2×10^{-3} M solution in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluoro-
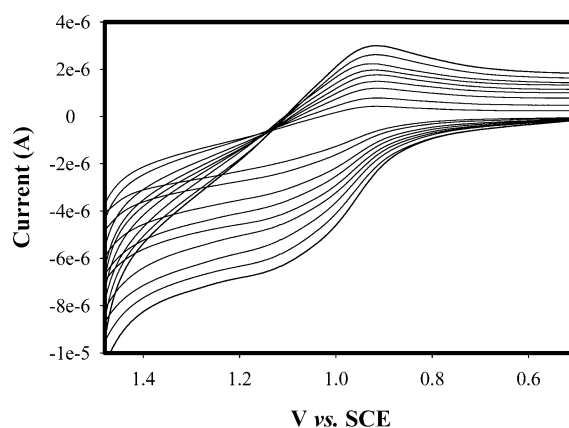

FIGURE 1. Cyclic voltammogram of 2×10^{-3} M **HBC** in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at 22 °C at scan rates between 25 and 400 mV s^{-1}.

phosphate (TBAH) as the supporting electrolyte. The reversible cyclic voltammogram (CV) obtained at scan rates between 25 and 400 mV s^{-1} (see Figure 1) showed anodic/cathodic peak current ratios of $i_a/i_c = 1$ at ambient temperatures. The calibration of the CV peaks with ferrocene provided the reversible oxidation potential $E_{1/2} = 1.00 \pm 0.01$ V vs SCE of **HBC**. Moreover, a quantitative evaluation of the CV peak currents with added (equimolar) ferrocene (as an internal standard) revealed that the reversible cyclic voltammogram of **HBC** corresponded to transfer of less than one electron. Such a discrepancy in the observed current in the CV peaks of **HBC** as compared to ferrocene arises due to its larger size and lower diffusional rate constant as compared to ferrocene.[9]

To confirm that **HBC** does undergo a reversible 1-electron transfer, we carried out its oxidation (or chemical coulometry) using stable cation-radical salts (such as **CRET** and **MB**)[10,11] as 1-electron oxidants with reversible reduction potentials that differ by only 40 mV.

	CRET$^{•+}$	**MB**$^{•+}$	
E_{red}^o	1.11	1.15	(V *vs.* SCE)
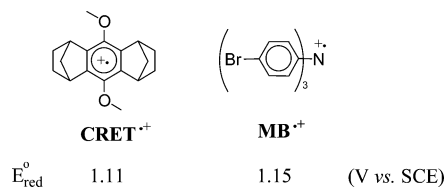
Thus, Figure 2 shows the spectral changes attendant upon the reduction of 5.2×10^{-5} M magic blue cation radical **MB**$^{•+}$ [λ_{max} (log ϵ) = 728 nm (4.45)] by an incremental addition of 6.3×10^{-3} M **HBC** to its cation radical **HBC**$^{•+}$ in dichloromethane at 22 °C. The presence of well-defined isosbestic points at λ_{max} = 585 and 768 nm in Figure 2 established the uncluttered character of the electron transfer.

Furthermore, a plot of the depletion of **MB**$^{•+}$ (i.e., decrease of the absorbance at 728 nm) and formation of **HBC**$^{•+}$ (i.e., increase in the absorbance at 840 nm) against the increments of added **HBC** (inset Figure 2)

(7) NMR spectral data of the **HBC** obtained herein were identical to that reported for the hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (**HBC**) prepared by a multistep procedure; see: Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 1834.
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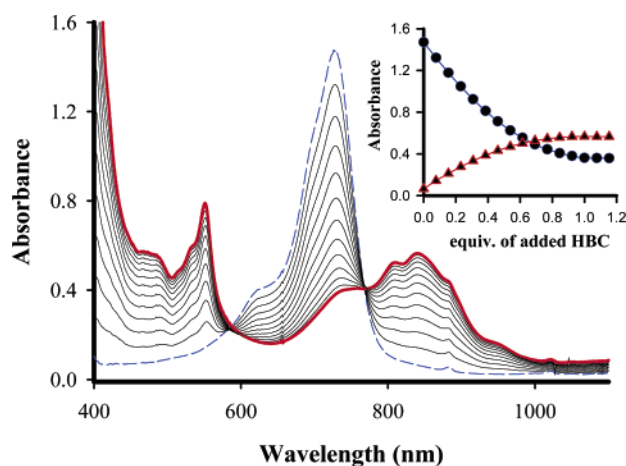
FIGURE 2. Spectral changes upon the reduction of 1.5×10^{-4} M **MB**$^{\bullet+}$ (---) by incremental addition of 1.2×10^{-3} M **HBC** to **HBC**$^{\bullet+}$ (−) in dichloromethane at 22 °C. Inset: A plot of depletion of absorbance of **MB**$^{\bullet+}$ (circles, monitored at 728 nm) and an increase of the absorbance of **HBC**$^{\bullet+}$ (triangles, monitored at 840 nm) against the equivalent of added **HBC**.

established that **MB**$^{\bullet+}$ was completely consumed after the addition of 1 equiv of **HBC**; the resulting highly structured absorption spectrum of **HBC**$^{\bullet+}$ [λ_{max} (log ϵ) = 551 (4.18), 753 (sh), 810 (sh), 840 (4.04), and 882 (sh) nm][12] remained unchanged upon further addition of neutral **HBC** (i.e., eq 3).

$$\mathbf{MB^{\bullet+}} + \mathbf{HBC} \rightarrow \mathbf{HBC^{\bullet+}} + \mathbf{MB} \qquad (3)$$

A similar coulometric titration of **CRET** cation radical with neutral **HBC** yielded **HBC**$^{\bullet+}$ quantitatively (see the Experimental Section).

It is noteworthy that the red **HBC**$^{\bullet+}$ obtained in eq 3 is highly persistent at room temperature and did not show any decomposition during a 24 h period at 22 °C. The high stability of the **HBC**$^{\bullet+}$ allowed the isolation of its crystalline salt as follows. Thus, a treatment of a solution of **HBC** with antimony pentachloride (SbCl$_5$) in anhydrous dichloromethane at −78 °C immediately resulted in a dark red solution (vide infra) from which the microcrystalline salt [**HBC**$^{\bullet+}$ SbCl$_6^-$] was isolated, by precipitation using hexanes, in nearly quantitative yield according to the stoichiometry in eq 4.[13]

$$2\ \mathbf{HBC} + 3\ \text{SbCl}_5 \rightarrow 2\ \mathbf{HBC^{\bullet+}}\ \text{SbCl}_6^- + \mathbf{SbCl_3}\ \ (4)$$

In a similar vein, **HBC**$^{\bullet+}$ SbCl$_6^-$ was also prepared in >95% yields from reaction with either triethyloxonium hexachloroantimonate salt[13] or nitrosonium hexachloroantimonate[4b] (see the Experimental Section). The highly colored **HBC**$^{\bullet+}$ SbCl$_6^-$ salt obtained by the above procedures was found to be extremely robust and can be recrystallized readily from a dichloromethane solution by a slow diffusion of toluene at −20 °C. The purity of the

(12) A monomeric cation-radical **HBC**$^{\bullet+}$ has not been prepared heretofore. However, Müllen and co-workers[7] have recently isolated a dimeric (**HBC**)$_2^{\bullet+}$ salt at −30 °C by electrocrystallization for which no spectral data were reported.

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crystalline **HBC**$^{\bullet+}$ was determined by iodometric titrations[14] and was found to be of greater than 99% purity.

In summary, we have developed an efficient one-pot procedure for the preparation of soluble hexa-*peri*-hexabenzocoronene from readily available hexaphenylbenzene and have shown that its stable cation-radical salt can be isolated in pure form. We are presently attempting to obtain suitable single crystals of the pure **HBC**$^{\bullet+}$ SbCl$_6^-$ and its cocrystallization with neutral π-donors of varying donor strength such as substituted benzenes, naphthalenes, triphenylenes, and pyrenes for X-ray crystallographic studies and for the evaluation of their solid-state properties.

Experimental Section

Hexaphenylbenzene was prepared according to the literature procedure.[6] Nitrosonium hexachloroantimonate was prepared from a reaction of SbCl$_5$ and NOCl in dichloromethane at −78 °C, and the resulting salt was recrystallized from a dichloromethane−hexanes mixture and stored in an inert-atmosphere glovebox. Triethyloxonium hexachloroantimonate, antimony pentachloride, ferric chloride, *tert*-butyl chloride, anhydrous dichloromethane, and nitromethane were used as received.

Hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (HBC). In a three-neck round-bottomed flask equipped with a dropping funnel and an argon inlet and outlet adapter (for bubbling argon through the solution) were placed hexaphenylbenzene (3.2 g, 6 mmol), *tert*-butyl chloride (5.8 mL, 54 mmol), and anhydrous dichloromethane (200 mL). A few drops of a stock solution of anhydrous ferric chloride (19.4 g, 120 mmol) in nitromethane (120 mL) were added to the above solution, and the resultant mixture was heated at 40 °C for 3 h while argon was bubbled through the solution. Then, the reaction mixture was cooled to room temperature, and the remaining ferric chloride solution was added dropwise during a 30 min period. The resultant dark-red solution was stirred for 2 h at room temperature and was poured into methanol (400 mL). A yellow precipitate formed immediately and was filtered and washed repeatedly with cold methanol (3 × 25 mL) to afford 4.9 g of **HBC** of greater than 95% purity as judged by ^{1}H NMR spectroscopy. The crude **HBC** was further purified by column chromatography on silica gel using an ethyl acetate−hexanes (1:9) mixture as eluent: yield 4.74 g (92%); mp >320 °C (hexanes) (lit.[7] mp >300 °C); UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ) 345 (4.88), 362 (5.19), and 389 (4.74) nm; ^{1}H NMR (CDCl$_3$) δ 1.83 (s, 54H), 9.31 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 32.66, 36.33, 118.72, 120.28, 123.76, 130.19, 148.52; FAB Mass *m/z* 858 (M$^+$), 858 calcd for C$_{66}$H$_{66}$. Anal. Calcd for C$_{66}$H$_{66}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.74.

Hexakis(4-*tert*-butylphenyl)benzene. In a three-neck round-bottomed flask equipped with a dropping funnel and an argon inlet and outlet adapter (for bubbling argon through the solution) were placed hexaphenylbenzene (3.2 g, 6 mmol), *tert*-butyl chloride (5.8 mL, 54 mmol), and anhydrous dichloromethane (200 mL). A solution of anhydrous ferric chloride (50 mg) in nitromethane (0.5 mL) was added to the above solution, and the resultant mixture was heated at 40 °C for 3 h while argon was bubbled through the solution. Workup as above afforded a mixture of *tert*-butylated products (4.1 g). Chromatographic separation using silica gel and hexanes as eluent produced pure hexakis(4-*tert*-butylphenyl)benzene (1.5 g): yield

(14) A solution of **HBC**$^{\bullet+}$ SbCl$_6^-$ (0.119 g, 0.01 M) in dichloromethane was added to a solution containing excess tetra-*n*-butylammonium iodide (1 mmol, 0.1 M) in dichloromethane at 22 °C, under an argon atmosphere to afford a dark brown solution. The mixture was stirred for 5 min and was titrated (with rapid stirring) by slow addition of a standard aqueous sodium thiosulfate solution (0.005 M) in the presence of a starch solution as an internal indicator. Based on the amount of thiosulfate solution consumed (59.3 mL), the purity of the cation radical was determined to be >99%. For a general procedure for iodometric titrations of cation radicals, see: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399.

~30%; mp > 315 °C (ethanol−dichloromethane) (lit.[7] mp >300 °C); ^{1}H NMR (CDCl$_3$) δ 1.12 (s, 54H), 6.68 (d, $J = 8.7$ Hz, 12H), 6.81 (d, $J = 8.7$ Hz, 12H); ^{13}C NMR (CDCl$_3$) δ 31.83, 34.65, 122.79, 130.77, 137.59, 139.88, 146.85. Anal. Calcd for C$_{66}$H$_{78}$: C, 90.98; H, 9.02. Found: C, 90.52; H, 8.94.

4,4′-di-*tert*-Butylbiphenyl. In a 1000-mL conical flask were placed biphenyl (15.4 g, 100 mmol), *tert*-butyl chloride (23.2 mL, 216 mmol), and anhydrous dichloromethane (100 mL). A suspension of anhydrous ferric chloride (80 mg) in dichloromethane (5 mL) was added slowly to the above stirred mixture. An evolution of gaseous hydrochloric acid began immediately and subsided within 5 min. The green mixture was warmed to 40 °C and was stirred for an additional 15 min. The resultant reaction mixture was quenched with methanol (10 mL), washed with water (2 × 50 mL) followed by aqueous sodium bicarbonate (5%, 100 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent and recrystallization from ethanol afforded pure 4,4′-di-*tert*-butylbiphenyl in quantitative yield (27.4 g, 97%): mp 127−128 °C (lit.[8] mp 127−128 °C); ^{1}H NMR (CDCl$_3$) δ 1.41 (s, 18H), 7.50 (d, $J = 8.4$ Hz, 4H), 7.58 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 31.69, 34.80, 125.76, 126.79, 138.28, 149.95; GC−MS *m/z* 266 (M$^+$), 266 calcd for C$_{20}$H$_{26}$.

Cyclic Voltammetry (CV). Cyclic voltammetry was performed on an Epsilon Electrochemical Analyzer. The CV cell was of an airtight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1 mm^2) significantly. The reference SCE electrode (saturated calomel electrode) and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.1−0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate, TBAH) and (2−5) × 10^{-3} M substrate (such as an arene donor) in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV s^{-1}, unless otherwise specified, and were IR compensated. The oxidation potentials ($E_{1/2}$) were referenced to SCE, which was calibrated with added (equimolar) ferrocene ($E_{1/2} = 0.450$ V vs SCE). The $E_{1/2}$ values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.

Preparation of HBC$^{•+}$ SbCl$_6^-$ Using SbCl$_5$. The donor **HBC** (858 mg, 1 mmol) was dissolved in anhydrous dichloromethane (20 mL) under an argon atmosphere in a 100 mL flask equipped with a Schlenk adapter and a rubber septum. The flask was cooled in a dry ice−acetone bath (−78 °C), and a dichloromethane solution of SbCl$_5$ (0.2 M, 7.5 mL) was added slowly with the aid of a Teflon cannula under a flow of argon. The solution immediately turned dark red, and a large amount of microcrystalline material precipitated. The resultant mixture was warmed slowly to −10 °C and was stirred for a further 10 min; anhydrous diethyl ether (50 mL) was added to precipitate the dissolved cation-radical salt. The dark-red precipitate was filtered under an argon atmosphere and washed thoroughly with anhydrous diethyl ether (3 × 10 mL). The microcrystalline **HBC$^{•+}$** SbCl$_6^-$ salt was dried at room temperature (~ 22 °C) in vacuo to afford a fine microcrystalline powder in nearly quantitative yield (1.16 mg, 97%). The purity of the cation-radical salt was determined iodometrically to be greater than 99%.[14]

Preparation of HBC$^{•+}$ SbCl$_6^-$ Using NO$^+$SbCl$_6^-$. A 50 mL flask fitted with a Schlenk adaptor was charged with nitrosonium hexachloroantimonate (183 mg, 0.5 mmol), and a cold solution of **HBC** (430 mg, 0.5 mmol) in anhydrous dichloromethane (20 mL) was added under an argon atmosphere at −10 °C. The solution immediately took on a red coloration, and the red solution was stirred (while slowly bubbling argon through the solution to entrain gaseous NO) for 10 min to yield a dark-red solution of cation radical [**HBC$^{•+}$** SbCl$_6^-$]. The identity of gaseous nitric oxide (NO) produced above was confirmed by UV−vis spectral analysis of the gas, which revealed the characteristic absorbances of NO at $\lambda_{max} = 204$, 214, and 226 nm.[15] The spectrophotometric analysis of the red solution indicated the quantitative formation of [**HBC$^{•+}$** SbCl$_6^-$]. The deep-red solution was carefully layered with dry toluene (30 mL) and placed in a refrigerator (−20 °C). During the course of 3 days, bright-red crystals of the cation-radical salt were deposited which were filtered under argon and dried in vacuo (yield 520 mg, 87%).

Preparation of HBC$^{+•}$ SbCl$_6^-$ Using Triethyloxonium Hexachloroantimonate [Et$_3$O$^+$ SbCl$_6^-$]. A 100-mL flask equipped with a Schlenk adapter was charged with triethyloxonium hexachloroantimonate (657 mg, 1.5 mmol), and a solution of the pure **HBC** (858 mg, 1 mmol) in anhydrous dichloromethane (25 mL) was added under an argon atmosphere at ~0 °C. The heterogeneous mixture immediately took on a red coloration which intensified with time. The dark red mixture was stirred for 2 h to yield a dark red solution of **HBC$^{•+}$**. The dark red solution was cooled to −20 °C in an ice-salt bath, and anhydrous diethyl ether (50 mL) was added to precipitate the dissolved salt. The dark-red precipitate was filtered under an argon atmosphere, washed with diethyl ether (3 × 25 mL), and dried in vacuo. The highly pure cation radical **HBC$^{•+}$** SbCl$_6^-$ was obtained in essentially quantitative yield (1.14 g, 96%) and was photospectrometrically identical to that obtained using above procedures.

General Procedure for the Spectral Titration of [MB$^{•+}$ SbCl$_6^-$] with Neutral HBC. A blue solution of **MB$^{•+}$** SbCl$_6^-$ in dichloromethane (3 mL, 1.5 × 10^{-4} M) was transferred under an argon atmosphere in a 1-cm quartz cuvette equipped with a Schlenk adaptor at room temperature. To this solution was added a dichloromethane solution (1.2 × 10^{-3} M) of **HBC** in 3 μL increments. The UV−vis spectra of the resulting solutions, after the addition of each increment, were recorded at 22 °C (see Figure 2 in the text). Approximately 39 μL of the above **HBC** solution was required to completely reduce the **MB$^{•+}$** cation radical. Note that reduction of **HBC$^{•+}$** (obtained above) with a pinch of zinc dust regenerated the neutral **HBC**, as judged by the UV−vis spectroscopy. A spectrometric titration of **CRET$^{•+}$** with neutral **HBC** in dichloromethane at 22 °C was performed similarly.

JO034271E

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