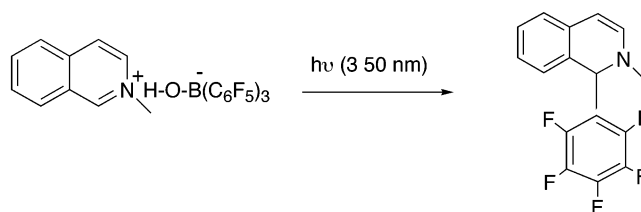# *JOC*Article

Pentafluorophenyl Transfer: A New Group-Transfer Reaction in Organoborate Salts

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Irradiation of isoquinolinium hydroxytris(pentafluorophenyl)borate, **1**, and phenanthridium hydroxytris(pentafluorophenyl)borate, **2**, in either CH_2Cl_2 or CH_3CN resulted in C_6F_5 transfer to the isoquinolinium and phenanthridium cations, generating 2-methyl-1-(2,3,4,5,6- pentafluorophenyl)-1,2-dihydroisoquinoline, **3**, and 2-methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydrophenanthridine, **4**, respectively. In addition, photogeneration of $H_2O \cdot B(C_6F_5)_3$ resulted from **1**. Photogeneration of $C_6F_5-C_6F_4H$ from $HO-B(C_6F_5)_3^-$ and of $C_6H_5-C_6F_4H$ from $C_6H_5-B(C_6F_5)_3^-$ was discovered.

Introduction

Boranes such as BX_3, RBX_2, and R_2BX (X = F, Cl, Br, OTF) are important Lewis acids used in organic synthesis, though their high-moisture sensitivity and instability make them difficult to handle. It has recently been demonstrated that tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) is a strong Lewis acid, comparable to BF_3,[1] that is relatively stable and not particularly moisture sensitive. Recently, this compound has been used in various synthetic transformations such as the hydrosilation of alcohols,[2] enones,[3] carbonyl compounds,[4] and imines;[5,6] the stereoselective transformation of epoxides;[7,8] the allylstannation of aromatic aldehydes;[9,10] the allylation of secondary benzyl acetates;[11] the cleavage of aryl and alkyl ethers with hydrosilanes,[12–14] aldol reactions,[15,16] and ring-opening reactions of nonactivated aziridines.[17] In addition, it has been reported to be a superior catalyst in the synthesis of optically active SiO-containing polymers.[18]

Organoboranes react readily with a variety of nucleophiles to form the corresponding tetravalent tetrahedral borate complexes.[19] Just as borohydride is a source of hydride (H^-), organoborate anions serve as sources of nucleophilic alkyl groups (1) and represent mild alternatives to Grignard and organolithium reagents.[20–22] They

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may also undergo single-electron transfer (2) in both thermal and photochemical reactions. Direct photochemical processes are limited to aryl and unsaturated borates because borates are transparent to UV light longer than 220 nm only. The direct photolysis of tetraarylborates (Ar_4B^-) was first studied by Williams and co-workers,[23] and the photoinduced single-electron transfer from aryl borates to neutral acceptors as well as to cation acceptors is well-known.[24,25] Electron transfer to positively charged acceptors can either be by an intermolecular[26] or an intramolecular reaction.[26-28] Schuster showed that carbocyanine alkyltriphenylborates undergo electron transfer, yielding an alkyl radical and triarylborane if the anion/cation is assembled as a tight ion pair.[29] As a result of these studies, the alkyltriphenylborates are probably best known as free-radical initiators for vinyl photopolymerization[30] but they are also potential sources of Lewis acids. Kochi first reported intramolecular alkyl transfer from alkyltriphenylborates to pyridinium, quinolinium, and isoquinolinium cations.[27] However, phenyl-radical formation was not indicated by his studies, and phenyl-group transfer has not been observed in any aryl borates before.

A particular advantage of tetrakis(pentafluorophenyl)-borate is that, unlike the alkylaryl borate anions, it is hard to oxidize (E_{ox} = 2.3 V vs SCE).[31] Therefore, electron transfer from tetrakis(pentafluorophenyl)borate is unlikely to most electron acceptors (e.g., cyanine).[31] Because of its nonnucleophilic nature, the tetrakis(pentafluorophenyl)borate anion is widely used as a counterion in photoacid generators, some of which are commercial.[32,33] Tris(pentafluorophenyl)borane is also used extensively as an activator in Ziegler–Natta (Z/N) polymerization.[34-37] It therefore becomes an objective to examine photochemical routes to it because there are no known photochemical Z/N polymerization processes.

Our interest in photoreactions of isoquinolinium salts results from attempts to photochemically generate polyolefins from simple olefin monomers and prepolymers. A photo-Z/N polymerization might be achieved by generating an active cocatalyst in the presence of an activatable organometallic compound following irradiation (Scheme 1).

Results and Discussion

Tris(pentafluorophenyl)borane, a commonly used cocatalyst in Z/N polymerization, is widely recognized for its superior catalytic properties.[2-18] So, its photogenesis takes on added importance. Irradiation of a pyridinium, a quinolinium, or an isoquinolinium alkyltriphenylborate leads to efficient alkyl transfer to the cation affording nucleophilic adducts[27] and triphenylborane in quantitative yields. The basic questions we addressed were: can tetrasubstituted pentafluorophenylborate salts be oxidized using light, and if one finds that they can, does one generate tris(pentafluorophenyl)borane? Unfortunately, attempts to synthesize *N*-methylisoquinolinium methyl-tris(pentafluorophenyl)borates failed, likely because of the instability of the compound. The presence of the trace water in $B(C_6F_5)_3$ yielded, instead, salts containing hydroxytris(pentafluorophenyl)borate (Figure 1).

Upon irradiation at 350 nm in degassed CH_2Cl_2 or CH_3-CN, **1** yields 2-methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydroisoquinoline (**3**) (48%, $\phi = 0.21$) presumably as a result of C_6F_5 transfer to the isoquinolinium cation. Because **3** is unstable on silica, the compound was only partially purified by evaporating solvent after irradiation and extraction with diethyl ether. The structure was confirmed using GC/MS, ^1H NMR, and ^{19}F NMR. The water adduct $H_2O \cdot B(C_6F_5)_3$ may also be observed from its ^{19}F NMR.[38] Moreover, because $H_2O \cdot B(C_6F_5)_3$ is slightly acidic (pK_a = 8.4 in acetonitrile),[38] its formation can be detected with acid–base indicators. Carrying out the photoreaction in the presence of quinaldine red (QR) resulted in bleaching of its absorption at 520 nm, and a concomitant growth of the absorption at 350 nm (due to protonated QR) was observed.[39] When irradiated, **1** also catalyzed the photopolymerization of either tri(ethyleneglycol)divinyl ether (DVE-3) or cyclohexene oxide.

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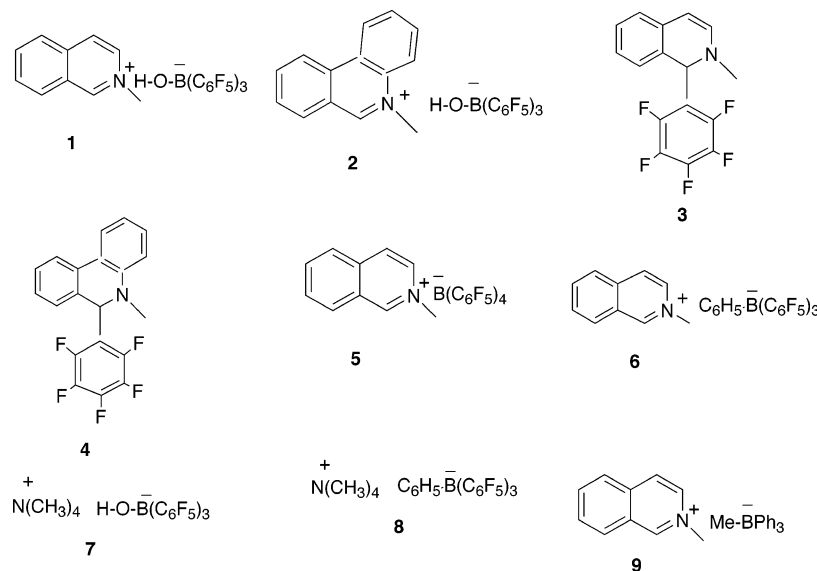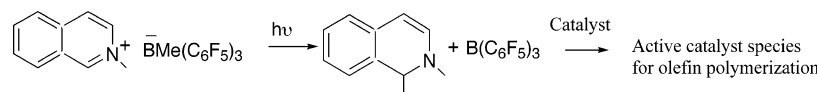(39) Ren, K.; Malpert, J. H.; Li, H.; Gu, H.; Neckers, D. C. *Macromolecules* **2002**, *35*, 1632.

FIGURE 1. Structures of borate salts studied and photoproducts **3** and **4**.

SCHEME 1.   Photogeneration of a Cocatalyst

That $H_2O \cdot B(C_6F_5)_3$ acted as a cationic initiator was confirmed by mixing $H_2O \cdot B(C_6F_5)_3$ (0.05 wt % of the monomer) with DVE-3 and cyclohexene oxide at room temperature. A highly exothermic polymerization of both (DVE-3) and cyclohexene oxide ensued.

$C_6F_6 - C_6F_5$ and $C_6F_5 - C_6F_4D$ were observed in trace amounts when either **1** or **2** was irradiated at 350 nm in degassed CD_2Cl_2. $C_6F_5 - C_6F_4H$, observed from irradiation in CH_2Cl_2, was not observed in CH_3CN, suggesting that the more reactive solvent CH_2Cl_2 participates in product formation.

Because one suggested route to the photoproducts formed from either **1** or **2** might involve $C_6F_5^-$, we attempted, though unsuccessfully, to trap this anion. Thus, irradiation of **1** in either 4-chlorobenzaldehyde or methyl vinyl ketone yielded no addition products, strongly suggesting that no trappable free C_6F_5 was formed. In contrast, irradiation of **1** in butylacrylate (0.05 wt % of the monomer) at 350 nm almost immediately produced poly(butylacrylate). Though we did observe that oxygen interferes with C_6F_5 transfer, radical trapping experiments were not successful. A proposed mechanism is shown in Scheme 2.

Under similar irradiation conditions, **2** in CH_3CN produces 2-methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydrophenanthridine (**4**) (76%, $\phi = 0.47$). As expected, **5** was photostable under our experimental conditions because of the high oxidation potential of the anion.

Evidence for Electron Transfer. A. Oxidation Potentials of Organoborates. We must presume C_6F_5 transfer occurs via an initial electron transfer from the borate to the *N*-methylisoquinolinium cation, similar to electron-transfer reactions in alkyltriphenylborate salts.[24–28] Though the oxidation potential of the HOB-$(C_6F_5)_3^-$ is unknown and fluorination of phenyl groups inherently causes a substantial increment in oxidation

SCHEME 2.   Proposed Mechanism for the Photodecomposition of 1
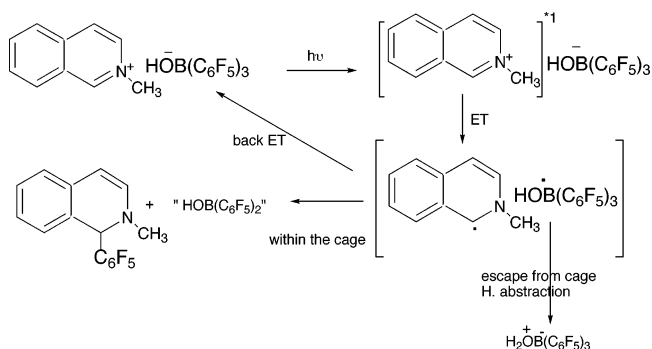
potential (e.g., E_{ox} of $B(C_6F_5)_4^- = 2.3$ eV vs SCE),[31] the direct measurement of the oxidation potentials of borates using electrochemical methods gives irreversible waves that are not thermodynamically meaningful. Electron-transfer quenching of excited electron acceptors (fluorescers) with known reduction potentials and singlet energies, on the other hand, produces systems from which the oxidation potentials of electron donors can be calculated using the Rehm–Weller equation (eq 1).[40] A partial

$$\Delta G_{et} = E_{ox}(D/D^{+\bullet}) - E_{red}(A^{-\bullet}/A) - E^* + Ze^2/\epsilon a \quad (1)$$

potential bracket was provided, in that addition of $[(CH_3)_4N]^+[HOB(C_6F_5)_3]^-$ (**7**) failed to quench the fluorescence of pyrene and 9,10-dimethylanthracene.

The physical parameters of **1** are given in Table 1. Because the Coulombic energy, $Ze^2/\epsilon a$, is 0.06 for acetonitrile, by substituting the highest known E_{ox} for organoborates (2.3 eV, $B(C_6F_5)_4^-$), the ΔG for the electron

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TABLE 1. Physical Parameters of 1

λ_{emiss} (nm) (S)[a]	ϕ_F	E_s (eV)	τ_F (ns)	E_{red} (eV)[b]	λ_{emiss} (nm) (T)[c]	E_T (eV)
376	0.4	3.48	11 ± 1	1.08	521	2.55

[a] S: singlet state. [b] vs SCE.[27] [c] T: triplet state.

TABLE 2. Transient Absorption Data for 1, 5, and 9 in CH₃CN[a]

| compound	kinetics at (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
1	440	12	450	3500
	360	440		
5	440	16		
	360			
9	440	10		3000
	360	88		3300

[a] τ_1 = rise time, τ_2 = decay time of the first component, and τ_3 = decay time of the second component.

transfer from borate to the singlet excited state of the cation becomes $\Delta G_{et} = 2.3 + 1.08 + 0.06 - 3.48 = -0.04$ eV. Because the photoactivities of **1** and **2** are much higher than that of **5**, it is possible that E_{ox} of $HOB(C_6F_5)_3^-$ is less than 2.3 eV, and electron transfer from $HOB(C_6F_5)_3^-$ to the *N*-methylisoquinolinium cation can be anticipated. This was confirmed by fluorescence quenching of **1** by $[NBu_4]^+[HOB(C_6F_5)_3]^-$ (**7**). Addition of **7** to **1** caused no shifts in the absorption spectrum of **1**, indicating there is no ground-state complex formation. Because the emission spectrum of **1** did not shift upon the addition of **7**, exciplex formation was also excluded. It is known that cyanine borates exist as solvent separated ion pairs in solvents with higher dielectric constants. Hence, we conclude that a change in the proportion of **1** is associated as the ion pair facilitates electron transfer and this leads to the quenching of fluorescence.

The bimolecular quenching rate constant K_q is related to the Stern−Volmer constant (K_{sv}) according to the equation $K_{sv} = K_q\tau_0$ where τ_0 is the lifetime of the fluorescer in the absence of a quencher. Fluorescence quenching of **1** was studied by the addition of varying concentrations of **7** to the compound **1** (10^{-5} mol/L solution in acetonitrile). The K_{sv} was found to be 3860.7 M^{-1}. Substituting values for K_{sv} and τ_0 (11 ± 1 ns, Table 1), we estimated K_q ($K_q = 3.51 \times 10^{11}$ M^{-1} S^{-1}) to be above the diffusion rate limit in acetonitrile, 2×10^{10} M^{-1} S^{-1}.[41]

B. Nanosecond Transient Absorption Experiments. Nanosecond laser-flash photolysis (excitation 355 nm) of **1** and model compounds (**5** and **9**) was carried out in dry, oxygen-free CH₃CN. Compound **5** was photostable, whereas **9** underwent rapid photoreaction, yielding the corresponding adducts via photoinduced electron transfer.[27] Comparison of the absorption spectra and kinetics of **1** with those of **5** and **9** may suggest whether electron transfer from the $HOB(C_6F_5)_3^-$ to the corresponding cation takes place. Three peaks at 360, 440, and 590 nm were observed in the case of **1** and **9**, and the 360 nm peak was absent in **5** (Supporting Information).

Kinetic data for **1**, **5**, and **9** at 440 and 360 nm are summarized in Table 2. The rise time at 440 nm was more or less the same for **1**, **5**, and **9** (10−16 ns) and close to the 355 nm excitation laser-pulse width (7−8 ns). The

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SCHEME 3. Photoinduced Electron-Transfer Reaction in 9
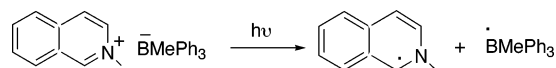
transient signal at 360 nm formed with different rise times. In compound **9**, the peak at 360 nm formed faster (in less than 100 ns) and could not be easily separated from the peak at 440 nm. However, in **1**, the decay time of the initial peak at 440 nm was measured (450 ns) and a concomitant growth of the peak at 360 nm was observed. In **5**, although a transient absorption at 440 nm growing in within 16 ns was present, the fit of its kinetic trace did not yield the decay time. In **1** and **9**, the peak at 360 nm was quenched by oxygen. At the same time, oxygen did not affect the signals at 440 nm.

Earlier, Yagci and co-workers[42] reported that the transient absorption spectrum of the isoquinolinium radical cation had two prominent absorptions at 360 and 640 nm. On the basis of that and the kinetic behavior of the transient absorption in compounds **1**, **5**, and **9**, the transient signal at 440 nm was assigned to the singlet state of the *N*-methylisoquinolinium cation. The 360 nm signal was assigned to the *N*-methylisoquinolinium radical formed as a result of electron transfer from the $HOB(C_6F_5)_3^-$ to the excited cation. Because it is known that irradiation of **9** results in an efficient electron transfer to form an *N*-methylisoquinolinium radical (Scheme 3), we submit that the absorptions at 360 and 440 nm appear simultaneously because of the fast electron-transfer reaction. The 360 nm absorption peak in **1** also indicates the presence of the *N*-methylisoquinolinium radical, confirming that electron transfer takes place between the *N*-methylisoquinolinium cation and the hydroxytris(pentafluorophenyl)borate anion upon irradiation at 355 nm. The absence of 360 nm absorption in **5** suggests that anions with higher oxidation potentials do not undergo electron transfer to yield the *N*-methylisoquinolinium radical.

Irradiation of **6** at 350 nm under oxygen-free conditions in CH₃CN produced $C_6H_5-C_6F_5$, and in CH₂Cl₂, $C_6H_5-C_6F_4H$ was isolated (~2−3%). ¹⁹F NMR confirmed that it was the ortho fluorine that was substituted by hydrogen.[43] The hydrogen atom is thought to result from the solvent, similar to the formation of $C_6F_5-C_6F_4H$ from **1** and **2**. Upon irradiation of **6**, neither biphenyl nor decafluorobiphenyl was observed nor was phenyl transfer observed in any solvent. The cation decomposed giving unidentified products.

The photochemistry of tetraphenylborate salts has been extensively studied,[44,45] and labeling studies show that both phenyl groups of the biphenyl observed in high yield as a photoproduct originate from a single tetraphenylborate.[45] The absence of biphenyl among the products of **6** confirms that the two phenyls originate from one

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SCHEME 4. Mechanism for the Formation of 2,3,4,5-Tetrafluorobiphenyl
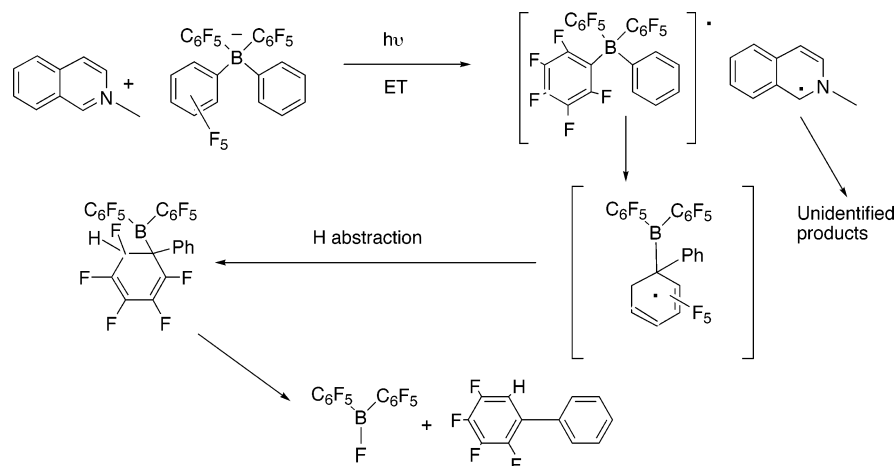
phenyltris(pentafluorophenyl)borate. Considering the position of hydrogen in the biphenyl, we propose the mechanism (Scheme 4) for the formation of 2,3,4,5-tetrafluorobiphenyl from the irradiation of **6**.

To probe the photochemistry of the phenyltris(pentafluorophenyl)borate anion, an oxygen-saturated acetonitrile solution of **8** was irradiated at 254 nm in a Rayonet photoreactor, and the products were isolated using the same procedure as that used to isolate photoproducts in **6**. Irradiation of **8**, unlike **6**, did not result in formation of 2,3,4,5-tetrafluorobiphenyl, and pentafluorobiphenyl was the only product isolated. Direct and electron-transfer-initiated photoreactions of tetraphenylborate have been extensively studied[44] with biphenyl as a major product in both cases. Williams and co-workers suggested the formation of a bridged intermediate (Figure 2) as a result of direct irradiation of
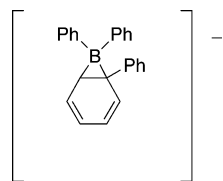

FIGURE 2. Bridged intermediate.

tetraphenylborate.[44b,c] Schuster and co-workers using ^{11}B NMR confirmed the formation of the bridged intermediate and proposed a mechanism for the formation based on di-π-methane rearrangement.[44c] Irradiation of sodium tetraphenylborate in acetonitrile resulted in the appearance of a [11]B signal at −27.3 ppm that was quenched by oxygen to give biphenyl.[44c] Similarly, direct irradiation of **8** in oxygen-free acetonitrile resulted in formation of a single [11]B signal at 4.01 ppm that is also quenched by oxygen to form the pentafluorobiphenyl and ammonim salt of pentafluorodiphenylborinic acid. Hence, the formation of a similar bridged intermediate is proposed in direct photochemical reactions of **8** (Scheme 5). The ammonium salt of pentafluorodiphenylborinic acid was not isolated. It is known that such acids undergo further oxidation.[44c] The difference in the photochemistry of **6** and **7** is that in **6** irradiation of the cation results in electron transfer that leads to different intermediates. Compounds **1**−**8** were stable in air, and their absorption

SCHEME 5. Proposed Mechanism for Photoproduct Formation in 8
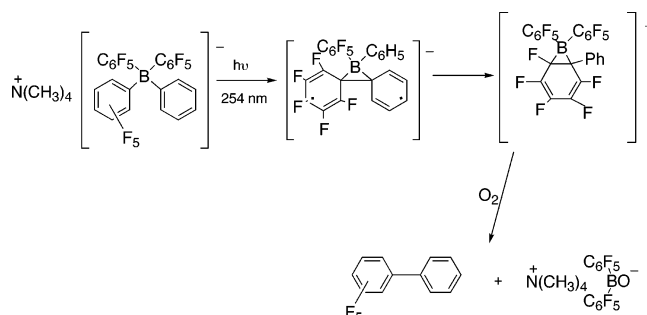
spectra did not change as a result of their being heated at 50 °C for 2 h.

Even the ideal tetrahedral configuration of borate complexes may be distorted by strong interactions between the anion and the cation.[19a] In **1**,[46,47] the hydroxy-tris(pentafluorophenyl)borate moiety is distorted with bond angles O1−B1−C17 of 102.14°, O1−B1−C11 of 114.40°, C17−B1−C11 of 111.38°, O1−B1−C23 of 109.98°, C17−B1−C23 of 114.41°, and C11−B1−C23 of 104.85° (Figure 3). The anion in **1** appears to interact with the isoquinolinium cation through an aromatic C_6F_5 group. The distance of the phenyl group from the isoquinolinium acceptor plane approaches the van der Waals distance (3.39−3.73 Å, Figure 4).

Conclusions

Photolysis of **1** and **2** in CH_2Cl_2 or CH_3CN results in C_6F_5 transfer to generate 2-methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydroisoquinoline and 2-methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydrophenanthridine, respectively. A mechanism based on photoinduced electron transfer is proposed for the C_6F_6 transfer reaction. Electron transfer was confirmed using fluorescence quenching experiments and nanosecond transient spectroscopy. Photoinduced defluorination to generate C_6F_5- C_6F_4H from $HO-B(C_6F_5)_3{}^-$ and $C_6H_5-C_6F_4H$ from C_6H_5-

(46) *Bruker SMART*, version 5.05; Bruker AXS Inc.: Madison, WI, 1999. *SAINT-plus*, version 7.08; Bruker AXS Inc.: Madison, WI, 1999.

(47) Sheldrick, G. M. *SADABS*: *Program for the Empirical Absorption Correctionof Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
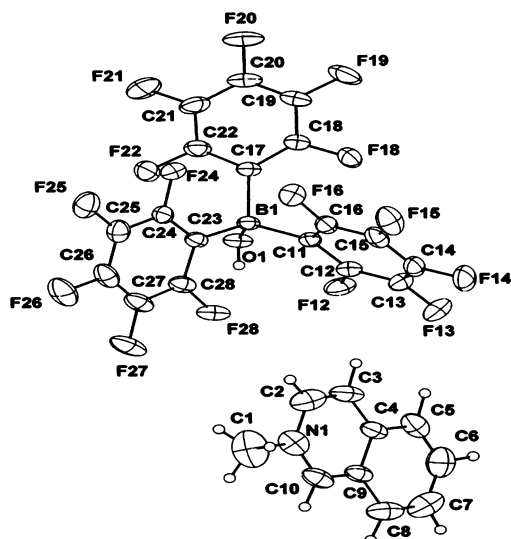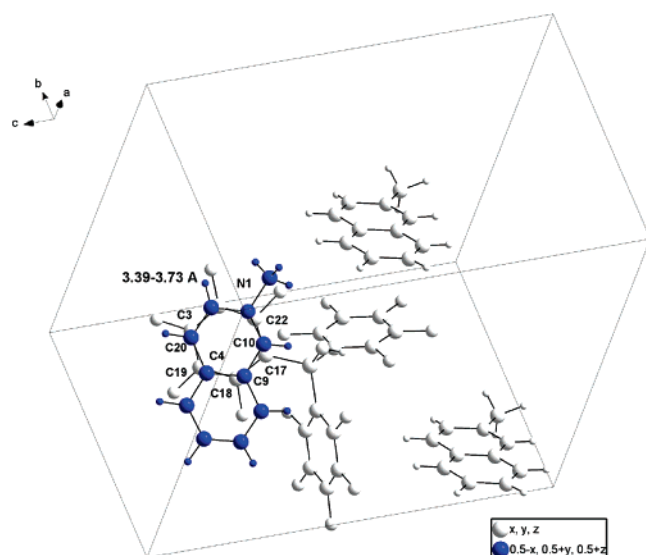
FIGURE 3. Crystal structure of compound **1**.

FIGURE 4. Packing diagram showing the contact ion pair in **1**.

$B(C_6F_5)_3^-$ was discovered, and an intramolecular mechanism was proposed. The X-ray crystal structure of **1** showed that the *N*-methylisoquinolinium cation and $HO-B(C_6F_5)_3^-$ exist as a contact ion pair. The anion interacts with the isoquinolinium cation through an aromatic C_6F_5 group.

Experimental Section

General experimental details are provided in the Supporting Information. Tris(pentafluorophenyl)borane, isoquinoline, quinoline, phenanthridine, dichlorophenylborane, and all the solvents were purchased from a commercial supplier. [13]C spectra were taken using a Varian Gemini 200 NMR spectrometer and a Unity Plus 400 NMR spectrometer. ^{19}F NMR spectra and ^{11}B NMR spectra were referenced externally to $CFCl_3$ and $BF_3 \cdot OEt_2$, respectively. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm internal diameter (ID) and a 0.25 mm film thickness DB-5 ((5%-phenyl)methylpolysiloxane, nonpolar) column, interfaced to an HP 2623A data processor. UV−vis spectra were recorded using a Shimadzu UV-2401(PC) spec-

trophotometer. Nanosecond laser-flash photolysis experiments were carried out using the third (355 nm) harmonic of a Q-switched Nd/YAG laser. *N*-Methylisoquinolinium methyltryphenylborate (**9**)[27] and $H_2O \cdot B(C_6F_5)_3$[48] were synthesized using literature procedures and identified by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR, and ESIMS. *N*-Methylisoquinolinium, *N*-methylquinolinium, and *N*-methylphenanthridium triflates were synthesized[49] and identified using ^{1}H NMR and ^{13}C NMR. High-resolution mass spectral analyses were performed by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign, IL. Elemental analyses were performed by Atlantic Microlab Inc. in Norcross, GA.

N-Methylisoquinolinium Hydroxytris(pentafluorophenyl)borate (1). An aqueous solution of *N*-methylisoquinolinium triflate (1.13 g, 3.85 mmol) was added to an aqueous solution of freshly prepared lithium hydroxytris(pentafluorophenyl)borate (2.063 g, 3.85 mmol) under argon at room temperature. A white solid precipitated immediately. The mixture was stirred for 2 h. The precipitate was filtered and washed with water. The solid was dissolved in CH_2Cl_2, and addition of hexane yielded white needle-shaped crystals (66%): mp 154−155 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.95 (s, 1H, OH), 4.47 (s, 3H, N−CH$_3$), 8.10−8.34 (m, 5H), 9.82 (s, 1H); ^{13}C NMR (400 MHz, acetone D$_6$) δ 47.9 (N−CH$_3$), 127.0, 128.3, 128.6, 131.1, 132.0, 136.6, 137.9, 151.7, anion 136.15, 137.0, 138.2, 140.0, 147.6, 150.0; ^{19}F NMR (400 MHz, CD_2Cl_2, $CFCl_3$) δ −134.4 (d, 2F, o−F, J_{F-F} = 19.2 Hz), −161.3 (t, 1F, p−F, J_{F-F} = 19.2 Hz), −165.0 (s, 2F, m−F); ^{11}B NMR (400 MHz, CD_2Cl_2, $BF_3 \cdot Et_2O$) δ − 4.1; ESIMS *m/z* M$^-$ (anion) 528.7, M$^+$ (cation) 144.0. Anal. Calcd for $C_{28}H_{11}BNF_{15}O$: C, 49.95; H, 1.64; N, 2.08. Found: C, 50.05; H, 1.62; N, 2.13.

N-Methylphenanthridium Hydroxytris(pentafluorophenyl)borate (2). The same procedure as that employed for the synthesis of **1** was used. *N*-Methylphenanthridium triflate was used in the ion exchange. In the synthesis, *N*-methylphenanthridone was obtained in substantial amounts. The salt **2** was purified using preparative thin-layer chromatography (TLC), and recrystallization using CH_3CN/CH_2Cl_2 yielded needle-shaped crystals (40%), mp 174−175 °C. Unlike quinolinium salts, this was only partially soluble in CH_2Cl_2: ^{1}H NMR (400 MHz, CD_3CN) δ 4.60 (s, 3H, N−CH$_3$), 8.00−8.18 (m, 3H), 8.37 (m, 2H), 8.40 (d, 1H), 8.9−9.0 (dd, 2H), 9.76 (s, 1H); ^{13}C NMR (400 MHz, CD_3CN) δ 46.8 (N−CH$_3$), 20.4, 123.8, 124.5, 125.4, 125.4, 126.7, 131.3, 131.5, 133.0, 133.3, 135.2, anion 135.8, 137.80, 138.5, 140.2, 147.6, 149.8, 156.0; ^{19}F NMR (400 MHz, CD_3CN, $CFCl_3$) δ −131.8 (d, 2F, o−F, J_{F-F} = 7.84 Hz), −159.2 (t, 1F, p−F, J_{F-F} = 7.84 Hz), −163.0 (s, 2F, m−F); ^{11}B NMR (400 MHz, CD_2Cl_2, $BF_3 \cdot Et_2O$) δ − 4.1.; ESIMS *m/z* M$^-$ (anion) 528.7, M$^+$ (cation) 194.0. Anal. Calcd for $C_{32}H_{13}$-$BNF_{15}O$: C, 53.11; H, 1.81; N, 1.93. Found: C, 53.22; H, 1.66; N, 2.02.

2-Methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydroisoquinoline (3). Upon irradiation at 350 nm in degassed CH_2Cl_2, THF, or CH_3CN, **1** yielded the product (**2**) that was partially purified by extracting with diethyl ether: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 1H, J_{H-H} = 7.2 Hz), 7.16 (m, 2H), 6.85 (d, 1H, J_{H-H} = 7.2), 6.45 (s, 1H), 6.20 (d, 1H, J_{H-H} = 7.6 Hz), 5.40 (d, 1H, J_{H-H} = 7.6), 2.83 (s, 3H, N−CH$_3$); ^{19}F NMR (400 MHz, $CDCl_3$) δ −141.0 (d, 2F, o−F, J_{F-F} = 16 Hz), (d, 2F, o−F), −153.47 (s, 1F, p−F), −160.7 (s, 2F, m−F); MS (*m/z*) 311 (11), 144 (100), 115 (14).

2-Methyl-1-(2,3,4,5,6-pentafluorophenyl)-1,2-dihydrophenanthridine (4). When irradiated in degassed CH_3CN at 350 nm, **2** gave the product **4** that was isolated using thin-layer chromatography: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 1H, J_{H-H} = 8 Hz), 7.81 (d, 1H, J_{H-H} = 7.6 Hz), 7.34 (t, 1H, J_{H-H} = 7.2), 7.21 (m, 2H), 7.05 (d, 1H, J_{H-H} = 7.6 Hz), 6.88 (t, 1H, J_{H-H} = 7.6, 8.4 Hz), 6.62 (d, 1H, J_{H-H} = 8 Hz), 6.25 (s,

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(49) Bockman, T. M.; Kochi, J. K. *J. Phys. Org. Chem.* **1997**, *10*, 542.

1H), 2.88 (s, 3H, N−CH$_3$); ^{19}F NMR (400 MHz, CD$_2$Cl$_2$, CFCl$_3$) δ −141.2 (d, 2F, o−F, J_{F-F} = 15.6 Hz), −155.1 (t, 1F, p−F, J_{F-F} = 23.6 Hz), −161.4 (t, 2F, m−F, J_{F-F} = 23.6, 15.6 Hz); MS (*m/z*) 361 (18.4), 194 (100), 152 (14); HRMS calcd for C$_{20}$H$_{12}$NF$_5$ 361.0899, found 361.0889.

N-Methylisoquinolinium Tetrakis(pentafluorophenyl)borate (5). The lithium tetrakis(pentafluorophenyl)borate ether complex (LiB(C$_6$F$_5$)$_4$·Et$_2$O) was synthesized according to a literature procedure.[50] Lithium tetrakis(pentafluorophenyl)borate ether complex (0.8 g, 1.07 mmol) was dissolved in 150 mL of distilled and degassed water. *N*-Methylisoquinolinium triflate (0.28 g, 0.94 mmol) was dissolved in 20 mL of degassed water and transferred to the solution of LiB(C$_6$F$_5$)$_4$·Et$_2$O under argon. A white solid precipitated immediately. The mixture was stirred for another 2 h at room temperature. The solid was washed with water and dried under vacuum. Recrystallization with CH$_2$Cl$_2$/hexane yielded needle-shaped white crystals (85.2% yield): mp 226−227 °C; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 4.48 (s, N−CH$_3$), 8.11 (t, 1H), 8.18−8.37 (m, 5H), 9.18 (s, 1H); ^{13}C NMR (300 MHz, CD$_3$CN) δ 44.3 (N−CH$_3$), 126.1, 127.3, 127.6, 129.9, 131.5, 137.1, 137.3; ^{19}F NMR (400 MHz, CD$_2$Cl$_2$, CFCl$_3$) δ −133.4 (d, 2F, o−F, J_{F-F} = 26 Hz), −163.3 (t, 1F, p−F, J_{F-F} = 26, 19.6 Hz), −167.5 (s, 2F, m−F); ^{11}B NMR (400 MHz, CD$_2$Cl$_2$, BF$_3$·Et$_2$O) δ −16.8; ESIMS *m/z* M$^-$ (anion) 678.8, M$^+$ (cation) 144.1. Anal. Calcd for C$_{34}$H$_{10}$NBF$_{20}$: C, 49.60; H, 1.22; N, 1.70. Found: C, 49.47; H, 1.18; N, 1.79.

N-Methylisoquinolinium Phenyltris(pentafluorophenyl)borate (6). Lithium phenyltris(pentafluorophenyl)borate (LiC$_6$H$_5$−B(C$_6$F$_5$)$_3$) was synthesized according to the following procedure. C$_6$F$_5$I (3.6 mL, 26 mmol) was placed in 200 mL of dry and degassed hexane and cooled to −78 °C. *n*-BuLi (11 mL of 2.5 M solution in hexane, 27.5 mmol) was added, and the mixture was stirred for 2 h at −78 °C. Dichlorophenylborane (12.6 mL, 8 mmol) was added to the mixture, stirred at −78 °C for 2 h, allowed to warm to room temperature, and stirred overnight. The hexane was removed under vacuum, and the resulting solid dissolved in dry, degassed CH$_2$Cl$_2$. *N*-Methylisoquinolinium triflate (2.35 g, 8 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$ and transferred to the flask containing LiC$_6$H$_5$−B(C$_6$F$_5$)$_3$. The mixture was stirred overnight at room temperature. The solution was washed with water, and the evaporation of CH$_2$Cl$_2$ yielded a white solid. The white solid was dissolved in hot CH$_2$Cl$_2$ and on cooling yielded diamond-shaped white crystals (66%): mp 195 °C; ^{1}H NMR (400 MHz, CD$_3$CN) δ 4.49 (s, 3H, N−CH$_3$), 7.0 (t, 1H), 7.16 (t, 2H), 7.4 (d, 2H), 8.10 (t, 1H), 8.31 (m, 2H), 8.42 (m, 3H), 9.52 (s, 1H); ^{13}C NMR (400 MHz, CD$_3$CN) δ 49.5 (N−CH$_3$), 124.5, 126.89, 127.2, 128.3, 128.6, 130.98, 132.6, 133.8, 136.3, 138.2, 138.3,

anion (fluorinated ring) 138.0, 138.4, 140.50, 148.1, 150.0, 151.0; ^{19}F NMR (400 MHz, CD$_2$Cl$_2$, CFCl$_3$) δ −125.9 (d, 2F, o−F, J_{F-F} = 9.2 Hz), −160.1 (t, 1F, p−F, J_{F-F} = 9.2, 7.6 Hz), −164.9 (t, 2F, m−F, J_{F-F} = 9.2, 7.6 Hz); ^{11}B NMR (400 MHz, CD$_2$Cl$_2$, BF$_3$·Et$_2$O) δ − 4.1; ESIMS *m/z* M$^-$ (anion) 588.9, M$^+$ (cation) 144.0. Anal. Calcd for C$_{34}$H$_{15}$BNF$_{15}$: C, 55.68; H, 1.91; N, 2.06. Found: C, 55.65; H, 1.91; N, 2.04.

Tetramethylammonium Hydroxytris(pentafluorophenyl)borate (7). An aqueous solution of tetramethylammonium chloride (0.102 g, 0.943 mmol) was added to an aqueous solution of lithium hydroxytris(pentafluorophenyl)borate (0.505 g, 0.943 mmol) under argon at room temperature. A white solid precipitated immediately. The mixture was stirred for 2 h. The precipitate was filtered and washed with water. The solid was dissolved in CH$_2$Cl$_2$, and the addition of hexane yielded white needle-shaped crystals (87%): mp (decomposed at 132 °C); ^{1}H NMR (400 MHz, CD$_3$CN) δ 2.14 (s, 12H, N−CH$_3$); ^{13}C NMR (400 MHz, CD$_3$CN) δ 56.2 (N−CH$_3$), 135.2, 156.5, 136.9, 139.2, 146.3, 149.2; ^{19}F NMR (400 MHz, CD$_3$CN, CFCl$_3$) δ −134.5 (d, 2F, o−F, J_{F-F} = 31.2 Hz), −161.3 (t, 1F, p−F, J_{F-F} = 23.6 Hz), −165.1 (t, 2F, m−F, J_{F-F} = 23.6 Hz); ^{11}B NMR (400 MHz, CD$_2$Cl$_2$, BF$_3$·Et$_2$O) δ − 2.1; ESIMS *m/z* M$^-$ (anion) 528.85, M$^+$ (cation) 74.0. Anal. Calcd for C$_{22}$H$_{13}$BNF$_{15}$O: C, 43.80, H, 2.17, N, 2.32. Found: C, 43.80, H, 2.11, N, 2.32.

Tetramethylammonium Phenyltris(pentafluorophenyl)borate (8). The same procedure that was used for **6** was employed, except tetramethylammonium bromide was used in ion exchange (72% yield): mp 291−292 °C; ^{1}H NMR (400 MHz, CD$_3$CN) δ 3.16 (s, 12H, N−CH$_3$), 7.02 (t, 1H, J_{H-H} = 7.2 Hz), 7.10 (t, 2H, J_{H-H} = 7.2 Hz), 7.36 (d, 2H, J_{H-H} = 6.0 Hz); ^{13}C NMR (400 MHz, CD$_3$CN) δ 56.1 (N−CH$_3$), 124.3, 126.7, 133.6, anion (fluorinated ring) 136.2, 137.5, 138.5, 139.9, 147.6, 149.932; ^{19}F NMR (400 MHz, CD$_2$Cl$_2$, CFCl$_3$) δ −125.8 (d, 2F, o−F, J_{F-F} = 23.6 Hz), −159.9 (t, 1F, p−F, J_{F-F} = 23.4, 23.6 Hz), −163.2 (t, 2F, m−F, J_{F-F} = 23.2, 23.6 Hz); ^{11}B NMR (400 MHz, CD$_2$Cl$_2$, BF$_3$·Et$_2$O) δ − 7.6; ESIMS *m/z* M$^-$ (anion) 588.9, M$^+$ (cation) 74.0. Anal. Calcd for C$_{34}$H$_{15}$BNF$_{15}$: C, 55.68; H, 1.91; N, 2.06. Found: C, 55.65; H, 1.91; N, 2.04.

Supporting Information Available: General methods, ^{1}H and ^{13}C NMR spectra of **1**, **2**, and **4−8**, crystallographic data for **1**, the transient absorption spectra of **1**, **5**, and **9**, and kinetics at 360 nm of **1**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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