Synthesis of Fluorinated Aminium Cations Coupled with Carborane Anions For Use as Strong One-Electron Oxidant

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Complete List of Authors:	Davidson, Jillian; Texas A&M University, Department of Chemistry Gunther, S.; Texas A&M University, Department of Chemistry Leong, Derek; Texas A&M University, Department of Chemistry Ozerov, Oleg; Texas A&M University, Department of Chemistry; Texas A&M University

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Synthesis of Fluorinated Aminium Cations Coupled with Carborane Anions for Use as Strong One-Electron Oxidants

Jillian J. Davidson, S. Olivia Gunther, Derek W. Leong, and Oleg V. Ozerov*[a]

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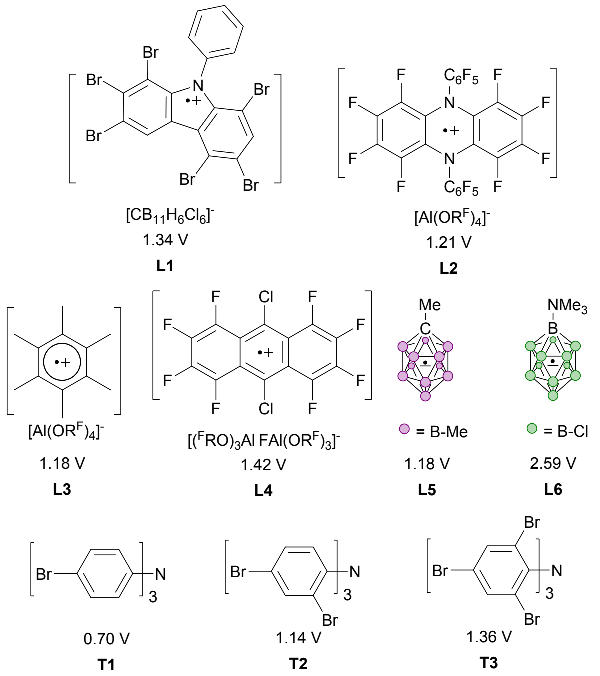
Synthesis of a series of hydrocarbon-soluble triarylamines bearing F, CF_3, and Br substituents showing quasi-reversible redox events in the 0.59 – 1.32 V range is reported. Chemical oxidation of the amines was carried out with $0.5PhI(OAc)_2/Me_3SiX/Na[RCB_{11}Cl_{11}]$ (X = Cl or OTf, R = H or Me), and a few aminium salts were isolated as pure solids.

Introduction

One-electron oxidants find broad use as reagents in initiation of catalysis and in the synthesis of desired compounds in a controlled fashion.[1] Oxidation by single-electron transfer is often a convenient way to access highly reactive cationic compounds.[2-5] Such reactive species can be isolated with an appropriately weakly coordinating anion[6] (WCA). The ideal cationic, one-electron oxidant-WCA pair would have to be reasonably soluble in low coordinating solvents. In addition, the resultant reduced form of the oxidant should be easily removed from the products of interest and be generally inert to the cations being generated.

The ferrocenium cation holds a special place among simple single-electron oxidants. However, the oxidizing power of ferrocenium is modest, and comparably well-defined single-electron oxidants of higher oxidizing power are relatively few and have their drawbacks. The triphenylmethyl cation, NO^+, and Ag^+ have been used as oxidants, however these reagents may get involved in ways beyond simple outer-sphere oxidation.[1] Reed's brominated N-phenyl carbazole cation[7] (**L1**) has been used to oxidize C_{60}, but it suffers from poor solubility. Krossing's perfluorinated aminium radical cation (**L2**)[8] is a more soluble alternative, but the synthesis is far from trivial. The C_6Me_6 radical cation (**L3**)[9,10] reported by the same group is promising, although it was not isolated in the solid state. On the other hand, the radical cation of commercially available perhalogenated anthracene (**L4**) was recently isolated and is an attractive option.[11] Michl's carborane radical $CB_{11}Me_{12}$ (**L5**)[12] and Klein's $Me_3NB_{12}Cl_{11}$ radical (**L6**)[13] are almost ideal in that they merge the oxidant cation and the WCA in one species, and the latter is arguably the strongest isolable oxidant with a well-defined redox pair, clocking in at 2.59 V vs $Fc^{+/0}$! **L6** was synthesized with the use of AsF_5, a highly toxic gas, and it may be too oxidizing for some solvents. We reasoned that easy-to-handle and easy-to-synthesize oxidants of intermediate oxidizing power may still be advantageous.

Figure 1. Previously reported oxidant-WCA pairs (**L**) and triarylamines (**T**) with their reported reduction potentials ($E_{1/2}$) vs Fc^+/Fc. Note that $E_{1/2}$ for **L3** was measured vs. SCE in the original publication, it has been converted to V vs. Fc^+/Fc.



Triarylaminium cations are a class of compounds that potentially offer these desired benefits. The reversible

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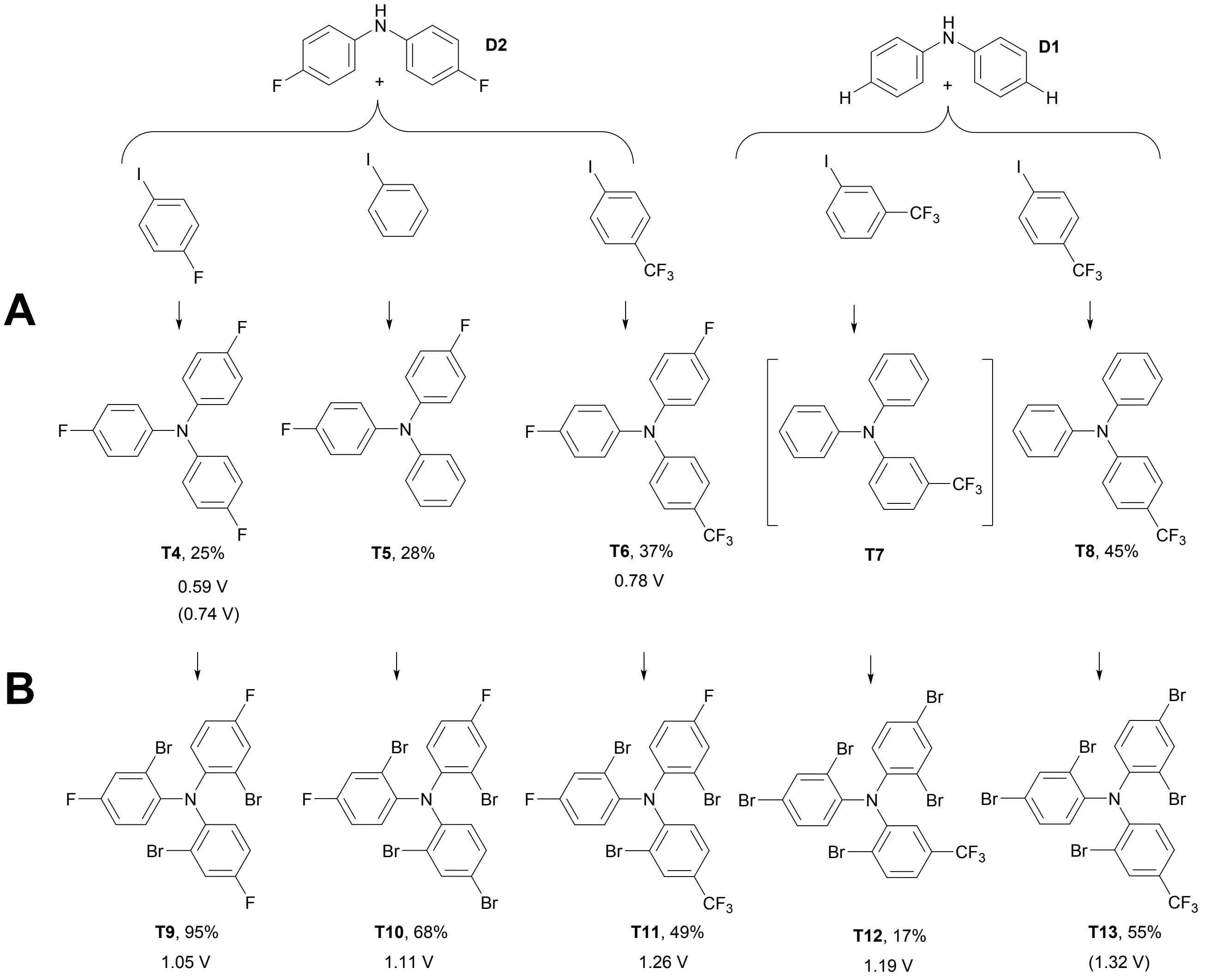
[a] Department of Chemistry, Texas A&M University, College Station TX 77842, USA
E-mail: ozerov@chem.tamu.edu.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x oxidation of triarylamines is well-established and frequently exploited.[14] Krossing et al. provided a cogent analysis of the advantages of aminium cations as single-electron oxidants.[8] Decoration of the triarylamine framework with electron-withdrawing groups can allow for a wide range of formal redox potentials, potentially matching or exceeding the oxidizing power of **L1**-**L5**.[14] Tris(*p*-bromophenyl)aminium (**T1**, Scheme 1) possesses a respectable potential of 0.70 V and is commercially available as an $SbCl_6^-$ salt. Decomposition pathways have been noted upon storage of this material.[15] However, the use of triarylaminium cations with potentials of >1 V and partnered with state-of-the-art WCAs is still not widespread. In this work, we endeavoured to develop reliable syntheses of triarylaminium WCA salts with higher formal potentials and advantageous solubility.

Results and Discussion

Bromination of tris(*p*-bromophenylamine) (T1) We were first attracted to known compounds from the literature that were reported to be available via simple bromination of triphenylamine. Compounds **T1**, **T2**,[16] and **T3** (Figure 1) possess attractive formal potentials. Unfortunately, in our hands, bromination of the commercially available **T1** with Br_2 (with or without added $FeBr_3$ or $SbCl_5$) did not lead to selective formation of **T2** or **T3**.[17] Treatment of **T1** with NBS did not lead to any further bromination (see ESI).

Scheme 1. Synthesis of fluorinated triaryl amines. **A**. $Pd(OAc)_2$ (1 mol%), DPPF (0.2 mol %), $NaOCMe_2Et$. **B**. Excess Br_2, dichloromethane. **C**. 1 eq NBS in dichloromethane. $E_{1/2}$ values given are derived from cyclic voltammetry in CH_2Cl_2 with $Bu_4N[PF_6]$ as the electrolyte; values in parentheses were determined in fluorobenzene solvent.



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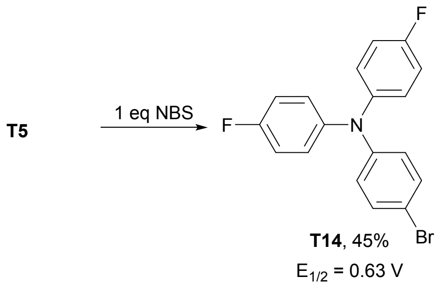
Synthesis of fluorinated triarylamines. We surmised that the presence of fluorine or trifluoromethyl substituents on a triarylamine framework would generate comparably electron-poor molecules relative to **T1**-**T3**, in addition to improving solubility and potentially providing a convenient ^{19}F NMR spectroscopic handle.[18] The literature on metal-catalyzed aromatic amination, and triarylamine synthesis in particular, is quite extensive.[19-23] We did not attempt to screen the available methods exhaustively, or to optimize every procedure, but instead employed a Buchwald-Hartwig amination method utilizing $Pd(OAc)_2$ with DPPF (1,1'-bis(diphenylphosphino)ferrocene) and sodium *tert*-pentoxide as a base. We set out to synthesize a range of fluorinated triaryl amines from diphenylamine (**D1**) and bis(*p*-fluorophenyl)amine (**D2**). Coupling **D1** or **D2** with iodobenzene or monosubstituted aryl iodides proceeded reasonably well (Figure 2, A) and **T4-T6** and **T8** could be isolated in 25-45% yield. **T7** was isolated at an oil and used without further purification in later steps.

Bromination of fluorinated triarylamines. In an effort to generate more electron poor triarylamines, we set out to further halogenate **T4-T8**. Bromination of **T4**-**T8** with excess Br_2 in dichloromethane proceeded smoothly with predictable selectivity, and isolated yields in the 17-95% range (Scheme 1). All available *para*-positions and one of the *ortho*-positions per ring in **T4**, **T5**, **T6**, and **T8** were brominated using this method to yield **T9**, **T10**, **T11**, and **T13**, respectively. The reaction of **T7**, containing a *m*-CF_3 group, afforded **T12**; one *ortho*-position in each ring was brominated in addition to the *para*-positions on the phenyl groups, but not on the CF_3-bearing ring. In addition (Scheme 2), reaction of **T5** with the 1 equiv. of N-bromosuccinimide (NBS) resulted in the selective bromination of the available *para*-position to yield compound **T14**. All of the triarylamines **T4**-**T14** could be readily recrystallized from concentrated alkane solutions.

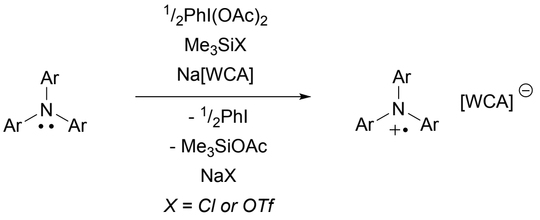
Scheme 2. Reaction of **T5** with N-bromosuccinimide (NBS).



Cyclic voltammetry studies. Cyclic voltammetry was used to determine the $E_{\frac{1}{2}}$ values of the amines analyzed within this work. The cyclic voltammetry experiments were conducted in dichloromethane with 0.1–0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte at a scan rate of 100 mV/s. The concentrations of the analyte solutions were approximately 0.001 M. The observed potentials were referenced to a Fc^+/Fc redox couple (as an internal standard) as recommended by IUPAC.[1,24] The corresponding $E_{\frac{1}{2}}$ values are noted in Schemes 1 and 2. In each case, a quasi-reversible one-electron redox event was observed. The potentials cover a range of ca. 0.7 V, from 0.59 V to 1.32 V. The influence of the substituents on the increasing difficulty of oxidation is *p*-CF_3 > *m*-CF_3 > *p*-Br > *p*-F, consistent with the literature σ and σ^- values.[25] Introduction of *ortho*-Br substituents increases the formal potential.

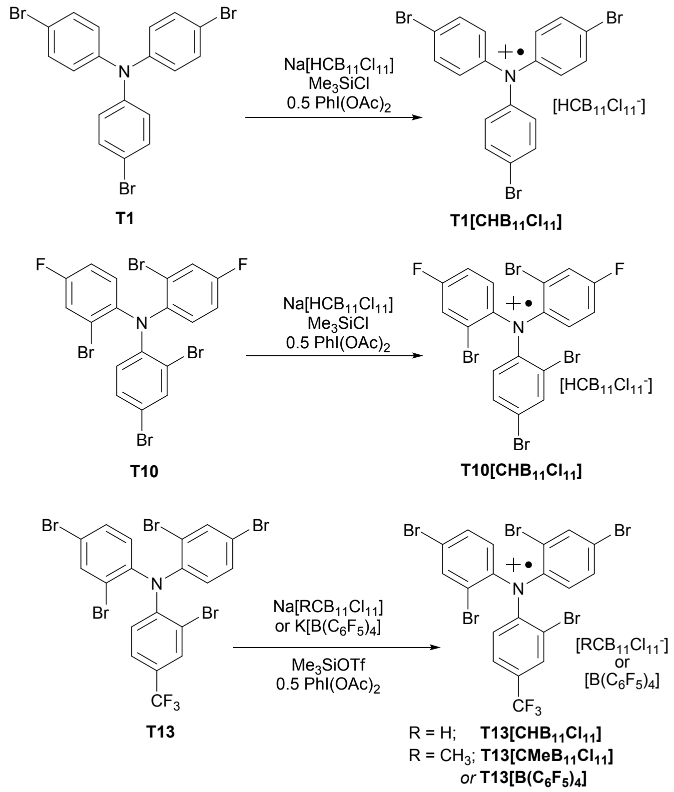
Synthesis of aminium salts. With attractive amine precursors in hand, we devised a convenient oxidation protocol that would a) be suitable for the high formal potentials of fluorinated triarylamines; b) utilize simple WCA precursors such as alkali metal salts; c) avoid the use of especially hazardous substances; and d) lead to product isolation as a WCA salt in a one "pot" synthesis. Our designs were guided by the previous use of acids to augment the strength of simple oxidants in chemistry related to carboranes. Michl *et al*. used treatment of PbO_2 with trifluoroacetic anhydride in order to oxidize $[MeCB_{11}Me_{11}]^-$,[12] while Reed et al. employed Ag^+ salts of halogenated carboranes not as formal oxidants themselves but as enhancers of the thermodynamic oxidative ability of Br_2 and Cl_2 via "capture" of the bromide/chloride reduction products as AgBr or AgCl.[7,16] A similar approach was used by the Krossing group for **L2** and **L3** with fluorinated alkoxyaluminate anions.[8,9] We were further inspired by the use of iodine(III) reagents as oxidants in organic chemistry.[26] The formal oxidative ability of bis(acetoxy)iodobenzene has been similarly enhanced by addition of Lewis acids such as $BF_3(OEt_2)$[27] and Me_3SiOTf[26b,28].

Scheme 3. Proposed synthetic method to access WCA salts of triarylaminium radical cations.



We envisaged that treatment of $PhI(OAc)_2$ with either Me_3SiCl or Me_3SiOTf, combined with Na[WCA], would result in significant enhancement of the oxidative ability of the I(III) center and lead to facile isolation of the oxidized triarylaminium as a WCA salt (Scheme 3). The expected by-products are inorganic salts (NaCl or NaOTf) and low molecular weight substances of low polarity (PhI and Me_3SiOAc) that should be all easily separable from the aminium salt. We have used this method recently to synthesize WCA salts of ferrocenium.[29] One can view the $0.5Ph(IOAc)_2/Me_3SiX/Na[WCA]$ (X = Cl or OTf) combination as an equivalent of a "deelectronator", as coined by Krossing et al.,[9] analogously to the $0.5Cl_2/Ag[WCA]$ or the $0.5Br_2/Ag[WCA]$ pair.

Scheme 5. Synthesis of aminium[WCA] salts



Gratifyingly, treatment of **T1** or **T10** with one equivalent of $Na[CHB_{11}Cl_{11}]$, one equivalent of Me_3SiCl, and half an equivalent of $PhI(OAc)_2$ (Scheme 3) resulted in the isolation of analytically pure **T1[CHB$_{11}$Cl$_{11}$]** and **T10[CHB$_{11}$Cl$_{11}$]** respectively upon workup. Oxidation of **T13** did not proceed with the use of Me_3SiCl, but was successful with Me_3SiOTf, indicating that the latter engenders a stronger effective oxidative potential for the I(III) "deelectronator". The identity of **T13[CHB$_{11}$Cl$_{11}$]** was also supported by elemental analysis data. Furthermore, treatment of **T13[CHB$_{11}$Cl$_{11}$]** with ferrocene resulted in the observation of one equivalent of neutral amine **T13** and formation of $Fc[CHB_{11}Cl_{11}]$. Furthermore, when a CD_2Cl_2 solution of **T13[CHB$_{11}$Cl$_{11}$]** was treated with **T10**, apparent partial reduction of the former took place (the potentials of **T10** and **T13** are close), but the addition of **T4** resulted in the regeneration of neutral **T10** and **T13** (see Figure S32 and the associated experimental description in the ESI). The **T13**$^+$ cation was also isolated as a $[MeCB_{11}Cl_{11}]$ salt and as a $[B(C_6F_5)_4]$ salt. However, utilizing $Na[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ instead of $Na[HCB_{11}Cl_{11}]$ or $K[B(C_6F_5)_4]$ led to a complex mixture of products with evidence of anion degradation. This is consistent with the previously noted incompatibility of $[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]^-$ with silylium-like species.[30]

Conclusions

In summary, a series of fluorinated triarylaminium radical cations were formed and isolated as $[Ar_3N][RCB_{11}Cl_{11}]$ salts (R = H, CH_3). Their preparation was accomplished via oxidation of a neutral triarylamine by a "deelectronator" combination of Me_3SiX (X = OTf, Cl), $Na[CRB_{11}Cl_{11}]$ (R = H, CH_3), and half an equivalent of $PhI(OAc)_2$. The aminium salt with the highest studied potential of 1.32 V vs the Fc^+/Fc couple was successfully isolated as an analytically pure solid.

Experimental Section

General Considerations. Unless otherwise specified all manipulations were performed under an atmosphere of Ar using a standard Schlenk line or a glovebox. Toluene, diethyl ether, hexanes, tetrahydrofuran, dichloromethane, Me_3SiCl, Me_3SiOTf, C_6D_6, 2,6-lutidine, CD_3CN, and CD_2Cl_2 were all dried over CaH_2, distilled or vacuum transferred, and then stored over molecular sieves in an Ar filled glove box. $CHB_{11}H_{11}$ was purchased from Katchem. All other chemicals used were received from commercial venders. NMR spectra were recorded on a Varian Inova 500 (^1H, ^{13}C, ^{31}P, ^{19}F), or a Varian 500 (^1H, ^{13}C, ^{31}P, ^{19}F) spectrometer. ^{31}P and ^{19}F NMR spectra were referenced externally using H_3PO_4 (85%, 0 ppm) and CF_3COOH (-78.5 ppm) respectively. Electrochemical studies were carried out using a CH Instruments Model 700 D Series Electrochemical Analyzer and Workstation in conjunction with a three-electrode cell. The working electrode was a CHI 104 glassy-carbon disk with a 3.0 mm diameter and the auxiliary electrode was composed of platinum wire. The third electrode, the reference electrode, was a $Ag/AgNO_3$ electrode. This was separated from solution by a fine porosity frit. CVs were conducted in dichloromethane with 0.3 M $[Bu_4N][PF_6]$ as the supporting electrolyte at scan rate of 100 mV/s. The concentrations of the analyte solutions were approximately 0.001 M. CVs were referenced to the Fc^+/Fc redox couple. Elemental analyses were performed by CALI Laboratories, Parsippany, NJ.

Author Contributions

J.J.D., S.O.G., and D.W.L. performed the synthetic and characterization experimental work and prepared a draft of the manuscript. O.V.O. directed the research and edited the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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