Synthesis, structural characterization, reactivity and catalytic activity of mixed halo/triflate ArI(OTf)(X) species

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ABSTRACT

Both mixed λ^3-iodoarenes and λ^3-iodoarenes possessing -OTf ligands are coveted for their enhanced reactivities. Here we describe the synthesis, reactivity, and comprehensive characterisation of two new ArI(OTf)(X) species, a class of compound that were previously only invoked as reactive intermediates where X= Cl, F and their divergent reactivity with aryl substrates. A new catalytic system for electrophilic chlorination of deactivated arenes using Cl_2 as the chlorine source and ArI/HOTf as the catalyst is also described.

INTRODUCTION

Iodine(III) reagents are widely used in organic and inorganic chemistry as oxidants for a variety of applications.[1-3] A common motif is $ArIX_2$, where X can be a halide, an acetoxy group, cyano group or a neutral pyridyl ligand amongst others. The most widely used species from this family are $PhI(OAc)_2$, which is commercially available, and $PhICl_2$, which is not commercially available due to its instability to prolonged storage, but is easy to generate and store at low temperatures. $PhICl_2$ is used as a replacement for Cl_2 in chlorination applications, with the advantage of increased safety and ease with which an equivalent of Cl_2 may be delivered stoichiometrically. $PhIF_2$ is the corresponding reagent for electrophilic fluorinations. We recently showed that for aryl chlorinations the mode of action for $PhICl_2$ is decomposition to Cl_2 followed by electrophilic chlorination, thus the chlorination capacity is equal to that of Cl_2,[4] whereas $PhIF_2$ is not prone to decomposition into F_2. In both cases methods to either thermodynamically or kinetically increase the activity of these reagents is desirable and successful reports include the utilization of Lewis acids and bases, silver salts and the generation of asymmetric intermediates *in situ*.[5-12] $ArIX_2$ species where an X is OTf have been identified to have the highest oxidative potentials from a series of regular I(III) associated ligands making PhIX(OTf) species of particular interest.[13-15]

Recently our group successfully isolated and structurally verified an $ArI(OTf)_2$, NO_2-$PhI(OTf)_2$ (**I1**) by substituting the phenyl ring with a *p*-nitro substituent which successfully inhibited decomposition *via* electrophilic aromatic substitution (EAS) processes previously encountered on the phenyl moiety during attempts to access an $ArI(OTf)_2$ species (Scheme 1).[6] In light of this, we sought to further exploit the EAS resistance of *p*-nitro substituted λ^3-iodanes to target species that have been previously implicated but were unable to be isolated or even observed, specifically mixed ArIX(OTf) species where X = F or Cl, for applications

in electrophilic halogenations targeting an increase in reactivity over the parent $ArIX_2$ complexes.

I1
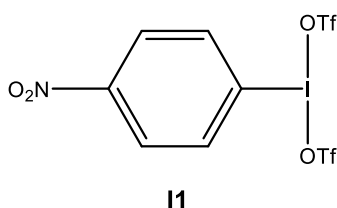
Scheme 1. Structure of recently isolated $ArI(OTf)_2$, **I1**.

The parent PhIF(OTf) was first reported by Stang and co-workers in 1997 from iodobenzene and xenon fluorotriflate at -78 °C in CH_2Cl_2.[16] In this report PhIF(OTf) was proposed to be generated *in situ* and shown to generate iodonium salts in reactions with alkynes; however PhIF(OTf) was not directly observed in the report by any technique (Scheme 2). The compound was depicted as a salt [Ph-I-F]$^+$[OTf]$^-$. They later reported a compound of the same family with the phenyl group being a *p*-diiodobenzene which displayed analogous reactivity, but again it was only proposed as an intermediate at low temperatures based on the reactant and products and could not be observed. During this period, the methanesulfonate (oMS) analogue in PhIF(oMS) was also reported,[17-19] and displayed analogous reactivity to PhIF(OTf). Again, this compound was not subject to characterization.
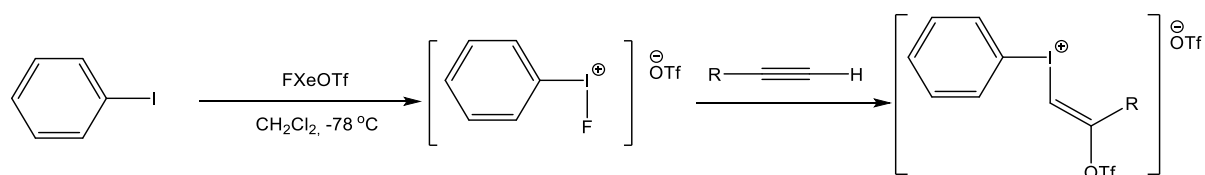
Scheme 2. First report of PhIF(OTf) and observed reactivity by Stang and co-workers.

Subsequent to these initial reports, PhIF(OTf) and PhIF(oMS) have been used in synthetic applications several times by Zefirov including reactions with norbornene,[19] cyclic & acyclic olefins[18, 20] and as a pathway to Weiss' reagents.[21-23] Stang's first report mentions that PhIF(OTf) formed a [Ph-I-Ph-I]$^+$[OTf]$^-$ on exposure to iodobenzene,[16] demonstrating that PhIF(OTf) decomposes *via* an EAS pathway to form this iodonium salt, explaining why

PhIF(oMS) and PhIF(OTf) were never characterized. We found that the reaction of $PhIF_2$ with two equivalents of TMS-OTf results in consumption of only half of the TMS-OTf, with formation of $[Ph-I-Ph-I]^+[OTf]^-$, indicating that PhIF(OTf) decomposes *via* EAS if not immediately trapped with another reagent.[6]

Attention towards PhIF(OTf) has diminished since 2002, the last time it appears in the literature. XeFOTf is also clearly not a convenient reagent that finds widespread use. However, if a more convenient synthesis was available and a derivative could be isolated or handled at ambient temperatures ArIF(OTf) could be a valuable species with both inorganic and organic applications. Following on from our recent isolation of **I1** where the $-NO_2$ group suppresses decomposition by EAS allowing for the previously unattainable $ArI(OTf)_2$ class of compounds to be isolated, here we exploit this system to isolate NO_2-PhIF(OTf) (**I3**), as well as the chlorine analogue **I5**, which displays markedly contrasting reactivity and has not previously been proposed as an attainable species.

RESULTS AND DISCUSSION

ArIF(OTf)

We targeted **I3** through a pathway previously employed to access **I1**, but by treating of **I2** with 0.9 equivalents of TMS-OTf rather than 2.0 equivalents in $CDCl_3$. ^{19}F NMR analysis of this reaction showed the generation of TMS-F at -157.6 ppm, a new resonance at -190.7 ppm accompanied by a new triflate environment at -76.4 ppm and residual NO_2-$PhIF_2$ at -175.1 ppm. We attributed this new peak at -190.7 ppm to the iodine bound fluorine atom in **I3**. The peak at -76.4 ppm is indicative of a covalently bound triflate and presents between the OTf shift of **I1** at -75.3 ppm and the ionic triflate shift range of -78-79 ppm in $CDCl_3$.[24] Analysis of the ^1H NMR revealed the presence of two discrete aromatic environments attributed to NO_2-PhI(III) species, one being **I2**, and the other being attributed to **I3** (Scheme 2).

Treatment of a CH_2Cl_2 solution of this reaction with hexanes yielded colourless crystals suitable for X-ray crystallography when held at -35 °C overnight. Subsequent X-ray analysis confirmed product of the reaction to be **I3** (Figure 1).
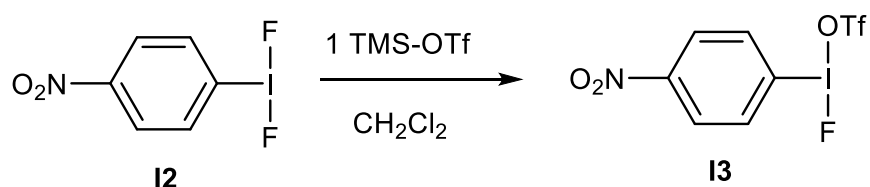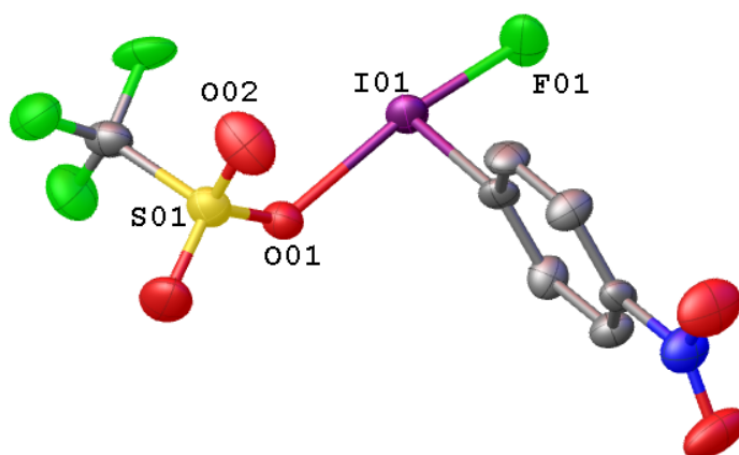

Scheme 3. Synthetic pathway for access to **I3**.

Figure 1. Solid state structure of **I3**. Ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): F(1)-I(1) 1.932(12), I(1)-O(1) 2.277(5), I(1)-S(1) 1.492(13), S(1)-O(2) 1.432(18).

Comparing **I3** and **I2**, the I-F bond distance is notably shorter in **I3** at 1.932 Å compared to 1.993 Å in **I2**. Inspection of the CCDC indicates that this is the shortest I(III)-F bond reported to date. The I-O bond is 2.277(5) Å, which is longer than the I-O bond in **I1** (2.145(4) Å). However, the interaction is still clearly covalent in nature given the substantial difference in the S-O bonds for the bound (1.492(13) Å) and unbound oxygens (1.432(18) Å), which is

also consisted with the ^{19}F NMR chemical shift. Our findings demonstrating that **I3** is covalently bound to the triflate is divergent to Stang's initial representation of PhIF(OTf) as a salt.[16]

We were interested if **I3** could potentially act as a source of electrophilic fluorine for aryl fluorination reactions.[25] We have previously shown that chloride abstraction from PhICl$_2$ using [Ag]$_2$[B$_{12}$Cl$_{12}$] *via* a proposed [PhICl]$^+$ intermediate facilitated chlorination of substrates with poor reactivity towards PhICl$_2$.[26]

As an initial test reaction, **I3** was treated with an electron rich aryl substrate, anisole, in CDCl$_3$. ^{1}H NMR spectroscopy of the reaction revealed a set of aromatic environments consistent with **IS1** and the ^{19}F NMR spectrum did not contain a peak indicative of the targeted product in 4-fluoroanisole at -124.8 ppm.[27] **IS1** was confirmed by mass spectrometry. The same reactivity was observed with less activated toluene, where ESI-MS confirmed the production of **IS2**. There was no indication of either fluorination or iodonium salt formation when **I3** was reacted with a deactivated species in bromobenzene. The previously mentioned upfield ^{19}F NMR shift from the difluoride possibly indicates a decrease in electrophilic character of the fluorine atom explaining the favourability for delivery of the [PhI]$^+$, consistent with Stang's previous observations.[16]
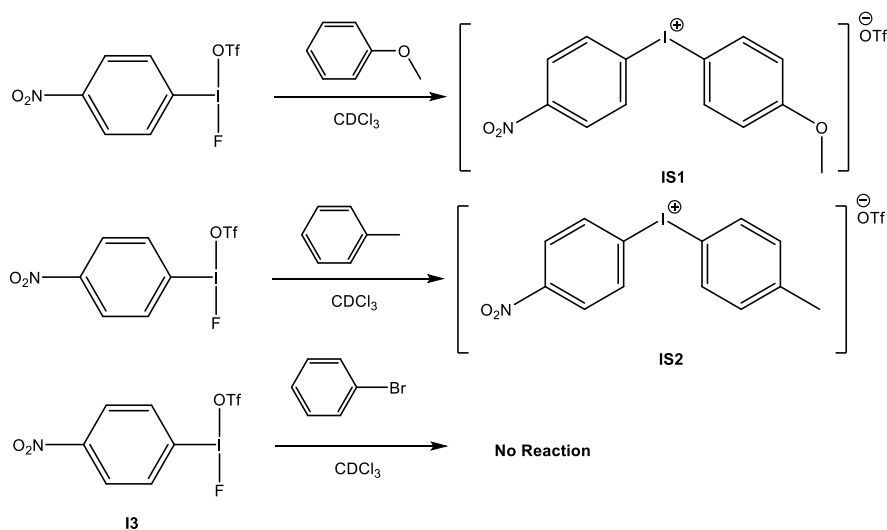

Scheme 4. Observed reactivity of **I3** with anisole, toluene and bromobenzene.

ArICl(OTf)

In 1997 Evans reported the mixed species PhICl(OAc) as observable by ^{1}H NMR spectroscopy.[28] Lupton in 2009 used this compound as a chlorinating agent, and more recently Nagib presented it to be an effective and selective agent for a variety of substrates, as well as being more reactive than PhICl$_2$.[9, 29] The mixed analogue PhICl(OTFA) has also demonstrated similarly enhanced chlorinating activity compared to PhICl$_2$.[30-31] We have shown that [Ag]$_2$B$_{12}$Cl$_{12}$ reacts with PhICl$_2$ to increase its reactivity *via* a proposed [PhICl]$^+$ intermediate, but this could not be observed in the absence of a substrate self-chlorination reactions occurred giving a mixture of chlorinated iodobenzene derivatives.[26] A triflate analogue, PhICl(OTf), where the [PhICl]$^+$ is stabilized by binding triflate is yet unknown.

Somewhat surprisingly, given the known lability of the I-Cl bond and the wide applicability of TMS-OTf in performing metathesis reactions on E-Cl compounds, the reaction of TMS-OTf with PhICl$_2$ in either CDCl$_3$ or CD$_3$CN resulted in no reaction.

When PhICl$_2$ was treated with stoichiometric HOTf in CDCl$_3$, an immediate colour change from yellow to colourless was observed. ^{1}H NMR analysis presented a mixture of 2-chloro and 4-chloro-iodobenzene with residual iodobenzene in a 1:0.7:0.1 ratio, similar to that observed when PhICl$_2$ was treated with [Ag]$_2$[B$_{12}$Cl$_{12}$].[26]
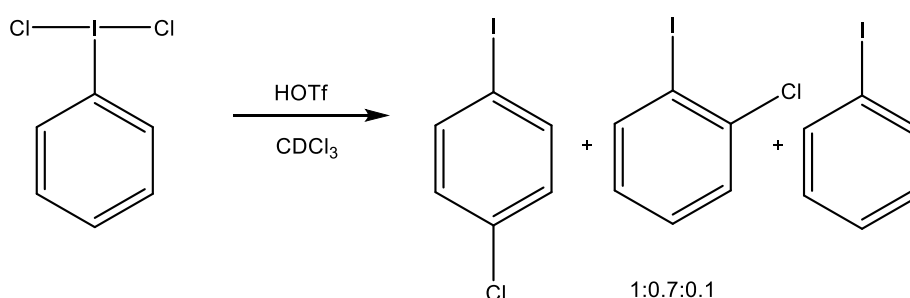
Scheme 5. Reactivity observed upon treatment of PhICl$_2$ with HOTf.

Similar conditions were applied to a CDCl$_3$ solution with toluene (which does not react with only PhICl$_2$ or Cl$_2$) as an added substrate to probe whether the HOTf/PhICl$_2$ system could be exploited to perform chlorinations on more activated aryl substrates than PhI without self-

chlorination. ^{1}H NMR analysis of the reaction between $PhICl_2$ and toluene in the presence of HOTf, 2-chlorotoluene,4-chlorotoluene and iodobenzene were observable in a respective 0.40:0.53:1 ratio (93% chlorination yield). Based on the normal mechanism for electrophilic chlorination, HOTf should be regenerated in the reaction and complete conversion was observed with a 10% catalytic loading of HOTf.
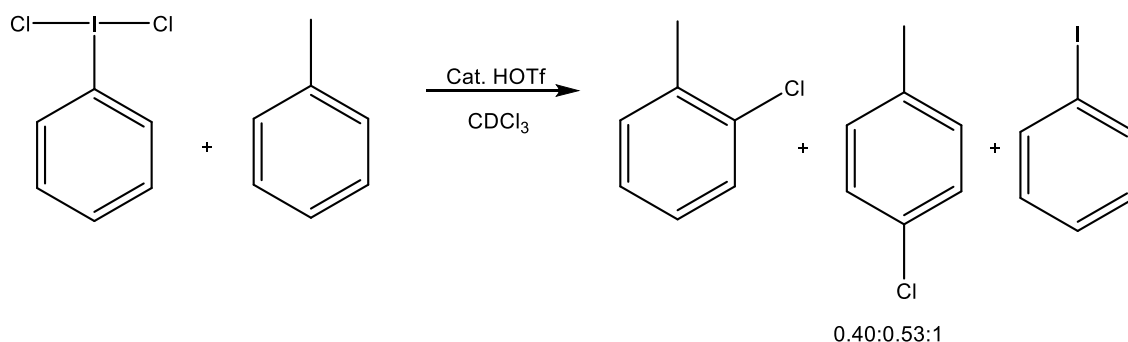
Scheme 6. Observed reactivity upon treatment of $PhICl_2$ with HOTf in the presence of toluene.

As Cl_2 does not react with toluene we propose that the active chlorinating species is PhICl(OTf), generated from protonolysis of an I-Cl bond by HOTf. An apparent limitation with this system is that attempted chlorination of any substrate less activated than iodobenzene will result in chlorination of iodobenzene rather than chlorination of the substrate.

Consequently, we again employed a p-nitro substituted λ^3-iodane derivative due to our recent success in inhibiting EAS reactions with electron poor I(III) species using this strategy and used the known **I4** as a starting material. In addition to its resistance to EAS processes, it is easily accessible on a high gram scale and has been reported to only display 12% decomposition in $CDCl_3$ after 24 hours, considerably slower than what we have observed with $PhICl_2$.[26, 32-33] When **I4** was treated with 10% loading of HOTf in $CDCl_3$ solution, ^{1}H NMR analysis revealed that there was no chlorination of NO_2-PhI. The **I4** was almost entirely consumed, presenting in 10% abundance, with the reaction stopping at this ratio and no species indicative of **I5** being observed.
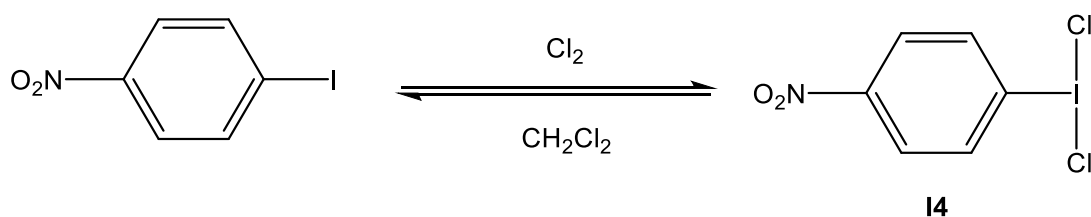
Scheme 7. Equilibrium of NO_2-PhI and **I4** with Cl_2.

When probing whether the HOTf/NO_2-PhICl$_2$ system could chlorinate a highly deactivated substrate in benzotrifluoride, this ratio was once again observed *in situ* with a gradual reduction to a 5% abundance of **I4** after 10 hours. Although no electrophilic chlorinations were observed with this substrate (hence no consumption of chloride), the observation of this persistent ratio of **I4** and NO_2-PhI leads us to conclude that this system exists in equilibrium where the generation of chlorine gas is promoted by HCl as a chloride source with the electrophilic I-Cl chlorine. NO_2-PhI and **I4** have been previously reported to exist in equilibrium with Cl_2 (Scheme 7).[33]
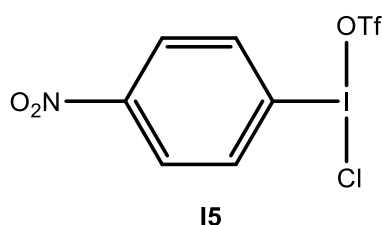
Scheme 8. Targeted ArICl(OTf) species, **I5.**

A reaction utilising benzene as the substrate was performed, where $CDCl_3$ solutions of NO_2-PhICl$_2$ and Cl_2 were separately treated with HOTf and subsequently analysed. ^{1}H NMR revealed a successful chlorination of benzene in the **I4** solution, however the Cl_2 solution displayed no evidence of benzene chlorination to demonstrate that the active species here is not Cl_2 or the combination of Cl_2 and HOTf (scheme 9) and therefore likely **I5**, which remained an unobservable intermediate.
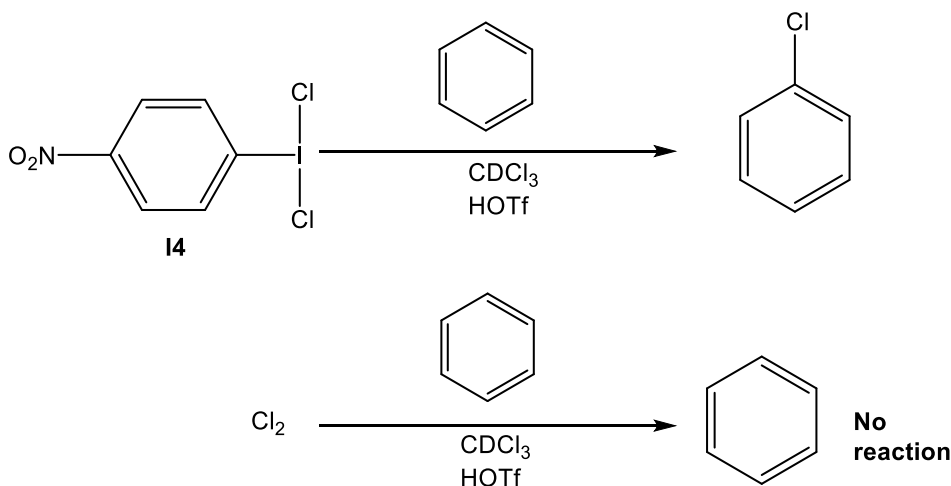
Scheme 9. Divergent chlorination activity levels observed between Cl_2 and **I4** in the presence of HOTf.

With no spectroscopic evidence of **I5** presenting, we sought to observe it at low temperature *via* combination with HOTf in $CDCl_3$. This however was unsuccessful, and once again an equilibrium heavily weighted towards the I(I) species was observed. Our hypothesis remained that the presence of HCl in the system was facilitating Cl_2 production from the proposed intermediate **I5** and generating iodine(I). To deliver a triflate ligand to **I4** while also removing chloride sources from solution AgOTf was selected as a halide abstraction agent. With this approach the abstracted chloride would be rendered inert as an AgCl precipitate. NO_2-$PhICl_2$ was treated with both 1 and 2 equivalents of AgOTf in $CDCl_3$ under N_2 in the glovebox. The reaction involving 2 equivalents of AgOTf was performed to see if it would provide an alternative pathway to **I1**. ^{1}H NMR revealed an identical product in both reactions, with a downfield shift from the starting **I4**, but different from **I1**. The parent iodine(I) compound was also present. Filtration and treatment of a $CDCl_3$ solution with n-hexane left overnight at -35 °C yielded pale yellow crystals suitable for X-ray crystallography which confirmed the product to be **I5** (Figure 2). Attempts to isolate **I5** for further reactivity investigations *via* AgOTf were hindered by low yields, with high abundance of I(I) being observed during *in situ* analysis. We surmised that AgCl and **I5** might be producing Cl_2 and the parent I(I), yields were higher when reaction time was limited and worked up rapidly. For

the purposes of isolating a pure product we sought a method that did not involve production of any source of chloride ions and found that a metathesis reaction between **I1** and **I4** in CH_2Cl_2 in a 1:1 ratio cleanly produced **I5**.
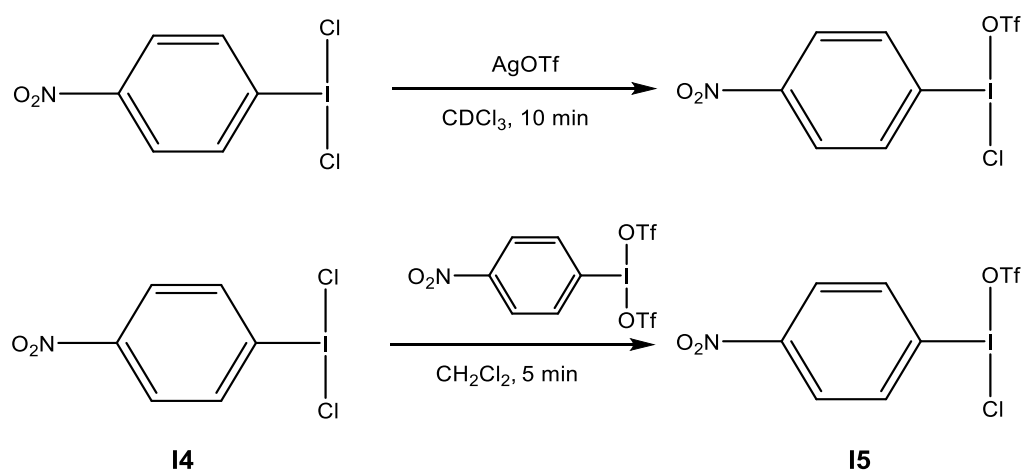
Scheme 9. Synthetic pathways for access to **I5**.
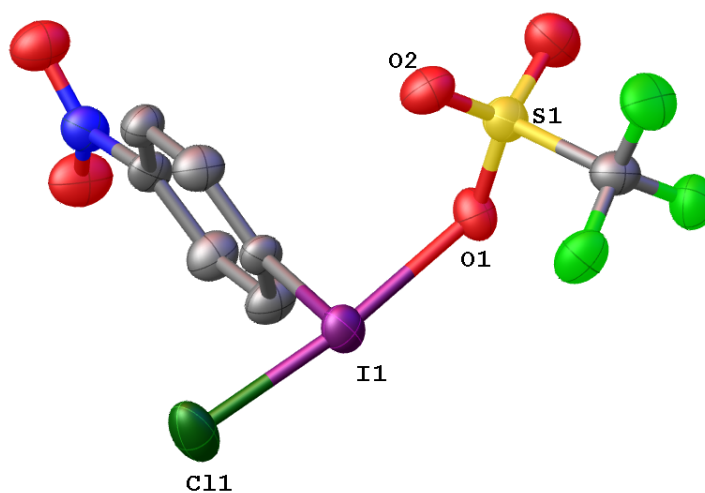
Figure 2. Solid state structure of **I5**. Ellipsoids are depicted at the 50% probability level. Hydrogen atoms are excluded for clarity. Selected bond distances (Å): Cl(1)-I(1) 2.362(2), I(1)-O(1) 2.333(5), O(1)-S(1) 1.490(5), S(1)-O(2) 1.432(6)

I5 has good stability when generated in this manner. It presents as an easy to handle solid, storable for extended periods at reduced temperature under inert conditions and we have found it persists in dry $CDCl_3$ at room temperature for longer than $PhICl_2$ itself. The [19]F

NMR shift of **I5** is -76.9 ppm which is 0.5 ppm upfield than the triflate in **I3** representative of an increased ionic character for the triflate in **I5**, consistent with the increased *trans* influence of chlorine as compared to fluoride although still clearly associated in solution. Comparison of the I-O bond distances in the solid-state structures supports this trend with the I-O bond being longer in **I5** at 2.333(5) Å compared to 2.277(5) Å in the fluoride analogue. That the reaction with 2 equivalents of AgOTf stopped at a single chloride abstraction is due to the weak *trans* influence of the newly introduced triflate resulting in a stronger I-Cl bond which is observed here with a I-Cl bond length reduction from 2.48 Å to 2.362(2) Å when compared to **I4** (CCDC 207069).[34]

We note the significance of this isolation of **I5** with comprehensive characterization, where the previously reported species PhICl(OAc) and PhICl(OTFA) were only generated *in situ* and observed *via* ^{1}H NMR.[9, 11, 28-31] Despite **I5** being the only isolated species of these three examples, we also believe it is also the most reactive due to the nature of λ^3-iodane triflates.[13] Further examination of the CCDC indicates that this structure is also the first axially asymmetric λ^3-chloroiodane to be crystallographically with genuine [PhICl]$^+$ character. That being, it is not either cyclic or bridged in nature such as Togni's range of reagents,[35] or presents as ionic in nature for the chloride such as the [PhICF$_3$][Cl] iodonium salt (scheme 10).[36] Cyclic λ^3-chloroiodanes do not present with enhanced chlorinating activity comparative to the asymmetric species analogous to **I5,** are typically described as mild,[37] and their general application is to access Togni's range of trifluoromethylation reagents rather than for chlorination.[38]
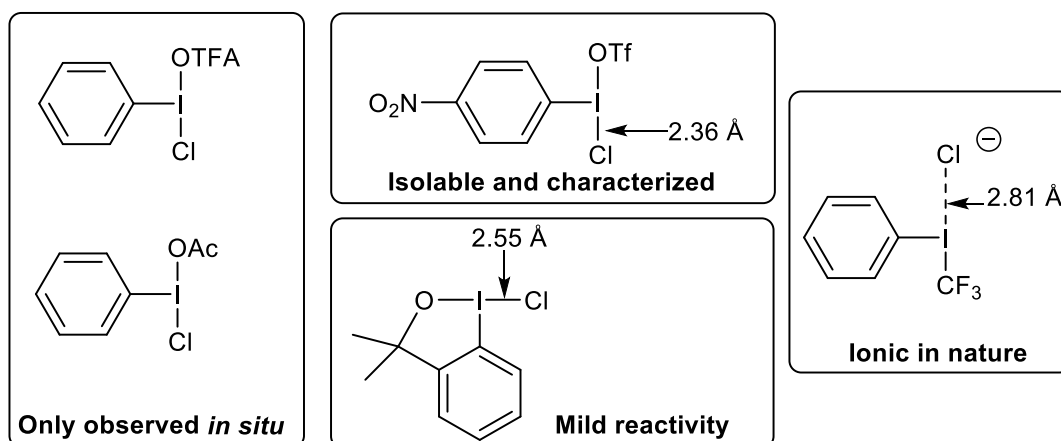
Scheme 10. Previously reported λ^3-chloroiodanes compared to **I5**.

CATALYSIS

With the hypothesis that **I5** is an active chlorinating reagent and a more powerful chlorinating agent than Cl_2 itself, its activity was screened *via* direct reaction against a range of deactivated aryl substrates as well as by catalytic activation of **I4**. It is common practice to observe and report the yields of EAS reactions by analysis of reactions mixtures with GC-MS or NMR analysis;[39-42] here *in situ* NMR yields are reported using NO_2-PhI as the internal standard to obtain results representative of system reactivity and regioisomer distribution. Having already identified HOTf as a catalytic activator of **I4**, activity was screened against substrates with a 10% HOTf loading. **I5** presented as a substantially more powerful chlorinator than catalytically activated **I4**; displaying higher yields of chlorination with shorter reaction times which can be compared in Schemes 11 and 12. We believe that the catalytically activated method is slower due to **I5** as the active species only presenting transiently under these conditions whereas isolated **I5** remains present until consumed to have a substantially higher amount of collisional abundance with the substrates. As the liberated Cl_2 in the HOTf activated **I4** system is consumed, the rate of **I4** regeneration and abundance of transient **I5** presentation would reduce to result in reduced chlorinating activity as the reaction proceeds, consistent with our observations where most of the chlorination was observed to occur rapidly over the first 15 minutes of reaction and sluggishly in the following

hours. Heating this system to 45 °C in sealed 1.5 mL tubes mildly improved yields, higher temperatures provided no substantial increase.

It is notable that *in situ* monitoring of reactions with **I5** revealed that HOTf was able to co-exist with **I5** in solution without the previously observed reduction into the parent I(I). This demonstrates that HOTf does not displace the chloride from **I5** and supports our previous hypothesis that HCl behaves as a chloride source to facilitate Cl$_2$ production. Though HOTf activated **I4** was sluggish compared to **I5** for chlorinating activity, it was found that their activity at room temperature ceased at similar substrate deactivation levels, with attempts to chlorinate nitrobenzene and benzotrifluoride being unsuccessful for both.
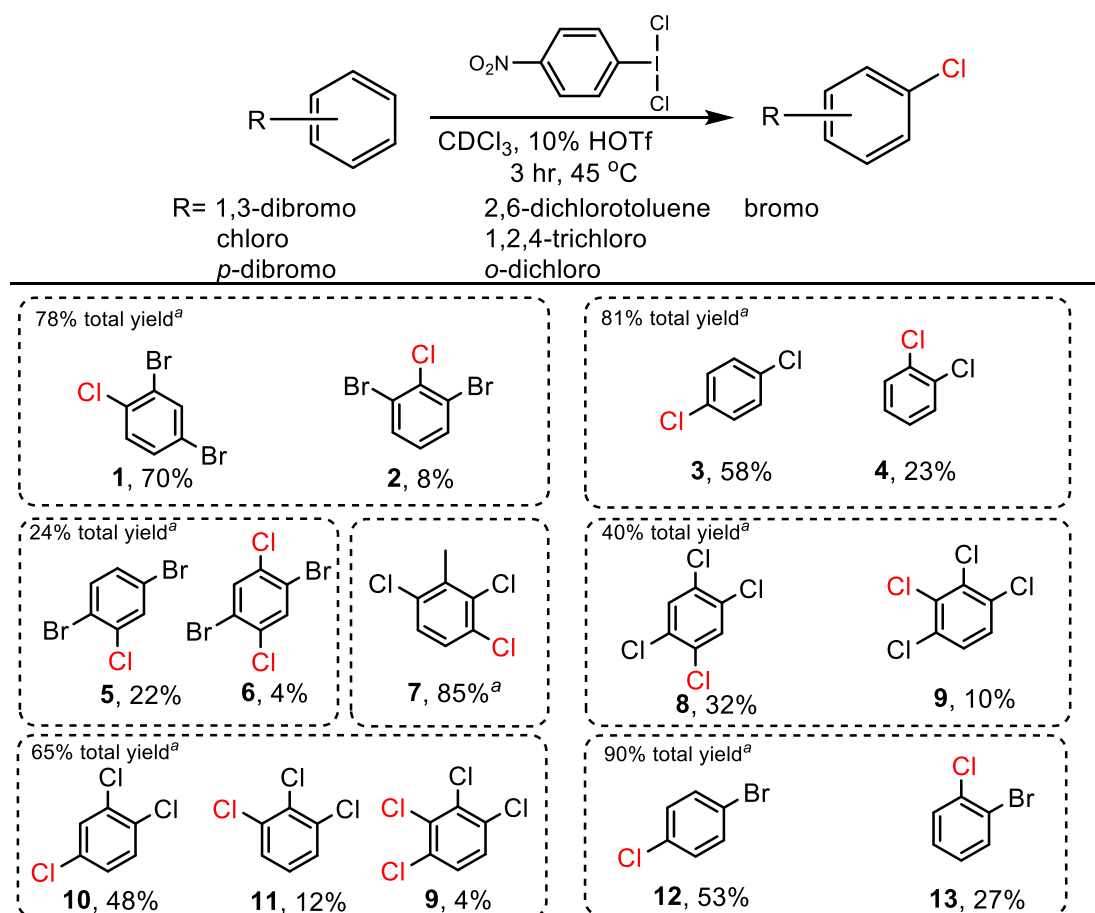
Scheme 11. Substrate screening for **I4** activated with catalytic HOTf. *[a]*Yield determined by ^{1}H NMR using NO$_2$-PhI as internal standard.
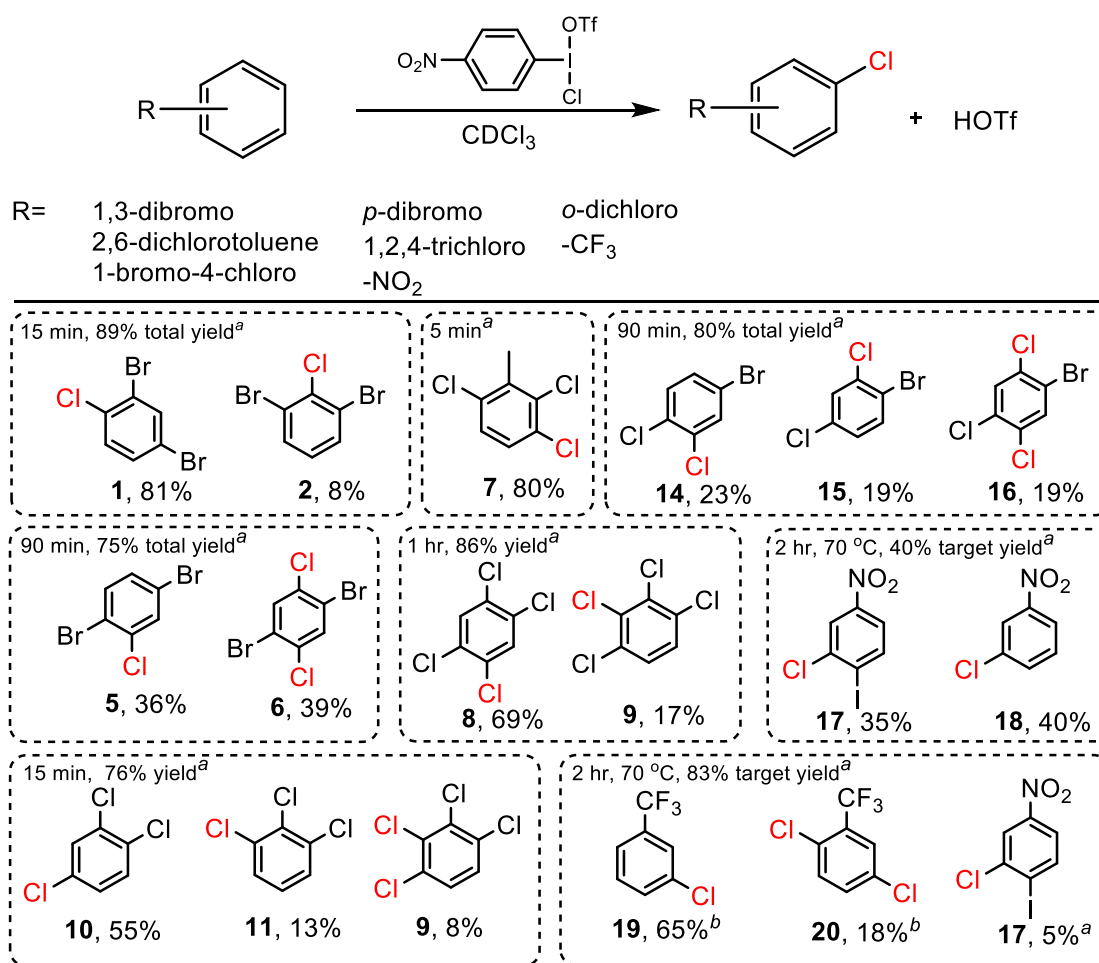
Scheme 12. Substrate screening for **I5**. [a]Yield determined by ^{1}H NMR using NO$_2$-PhI as internal standard. [b]Yield determined by 19F NMR using OTf as internal standard.

Chlorinations of highly deactivated substrates nitrobenzene and benzotrifluoride were obtainable in modest yields when a solution of **I5** and the corresponding aryl substrate were heated to 70 °C for 2 hours. Unfortunately, these reactions were subject to the competitive chlorination of NO$_2$-PhI due to its ring activation levels being at similar levels to the target substrates. This level of chlorinating ability was unprecedented when we were initially targeting **I5**.

We also investigated the activation of **I4** with AgOTf at a 10% loading. We hypothesised that catalytic AgOTf activation would be successful due to our previous experience with Ag salt activation and assume that the fate of the proton removed in EAS processes would be HOTf to self-perpetuate **I4** activation. In this case the yields were lower than when activated with

HOTf. Utilisation of AgOTf as the catalytic activator of **I4** holds potential advantages over HOTf because it is more accessible due to the general ubiquity of silver salts in the laboratory, and it circumvents the handling of the highly corrosive acid in environments or situations were HOTf might be undesirable.

Given the results reported above, it is feasible that this I(I)/I(III)/HOTf system could be used catalytically with Cl_2 as the chlorine source. While use of Cl_2 requires careful thought about its handling in the laboratory, it is the most atom efficient electrophilic chlorine source and widely used in industrial applications.

In lieu of using compressed Cl_2 gas, Cl_2 was generated using trichloroisocyanuric acid (TCICA) by dropwise addition of concentrated aq. HCl.[43] However all transformations reported below would be feasible by direct bubbling of compressed Cl_2 into the solutions. Chlorobenzene was selected as a deactivated substrate for investigation. Cl_2 was bubbled into a solution of NO_2-PhI, HOTf and a substantial excess of chlorobenzene. The complete consumption of the chlorobenzene substrate and the subsequently produced *o*-dichlorobenzene was observed to yield a mixture of the expected di- and tri-chlorobenzenes with a 4-hour reaction time. Examination of integration ratios in ^{1}H NMR revealed the chlorinated product to have been produced with a NO_2-PhI loading below 1% for each observed chlorination under modestly dry conditions (Scheme 13).
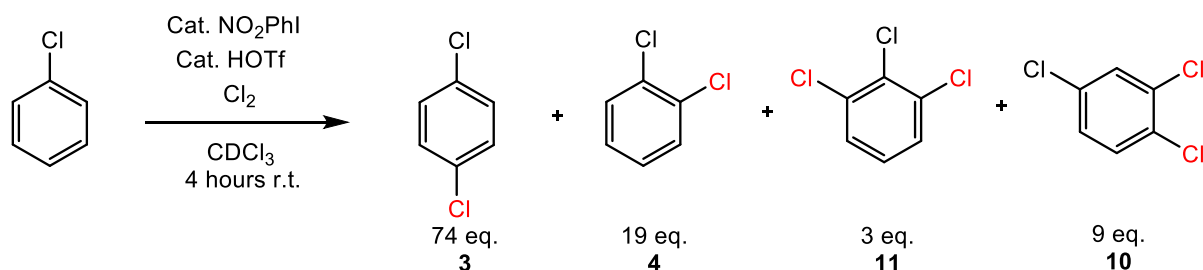
Scheme 13. Conditions and products for the catalytic activation of Cl_2 for electrophilic chlorination. Equivalency determined *via* ^{1}H NMR using NO_2-PhI as an internal standard.

Performing these reactions in CDCl$_3$ allowed for monitoring them *in situ* to determine the conditions required for chlorination to proceed. Chlorination ceased under three circumstances; when either the Cl$_2$ or substrate was consumed and when the HOTf was quenched by water (indicated by the lone presence of a ^{19}F NMR peak in the ionic region at -79.4 ppm, indicative of [H$_3$O][OTf]). In each of these cases, chlorination resumed when each respective deficiency was addressed by the delivery of one of Cl$_2$, substrate or HOTf to meet the condition requirements.

Expanding on this finding, this system was screened against a selection of substrates that were previously investigated against the **I4**/HOTf system at gram scale to validate its reactivity and scalability. Reaction time and products are largely determined by rate of Cl$_2$ delivery. With Cl$_2$ delivery being higher than we typically used (see supplementary information) the catalytic chlorination of *o*-dichlorobenzene was completed over the course of 2 hours with the highest yields despite it being the most deactivated substrate signifying that catalytic turnover can be pushed even further if desired (Scheme 14).
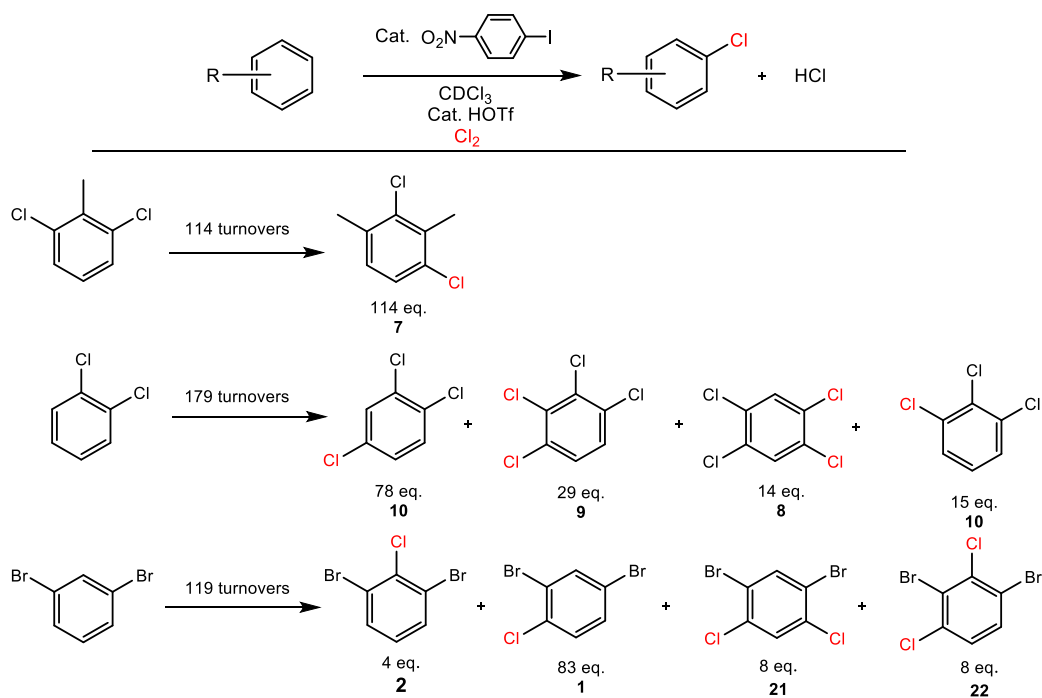
Scheme 14. Range of products observed from the catalytic activation of Cl$_2$ with NO$_2$-PhI and HOTf. Turnovers determined *via* ^{1}H NMR using NO$_2$-PhI as an internal standard.

These initial results demonstrate that a simple aryl iodide, NO$_2$-PhI behaves as a highly potent catalyst for electrophilic chlorination using Cl$_2$ gas following a I(I)/I(III) redox cycle when used in conjunction with HOTf to transiently generate **I5** as the active species. This catalytic system is adventitious because it is inexpensive, recyclable, metal free, does not require heating, provides short reaction times, and is performed in common chlorinated solvents.
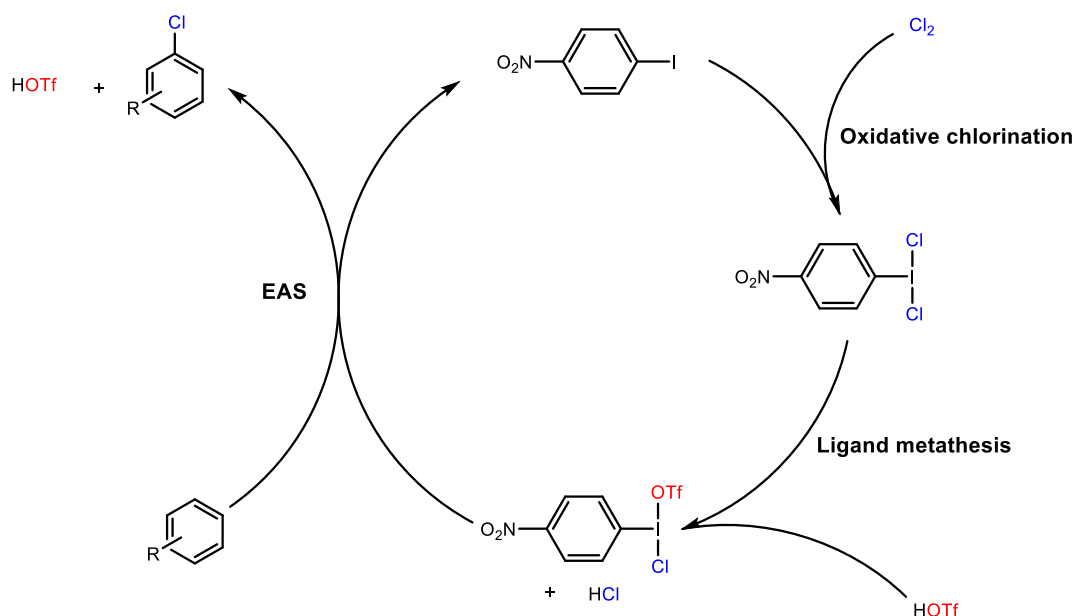
Scheme 15. Catalytic cycle for λ^3-iodoarene mediated activation of Cl$_2$ towards electrophilic chlorination.

COMPARISON OF CHLORINATING SYSTEMS

With the results for our systems in hand, we compared them against some recently reported and notable methods for electrophilic chlorination of deactivated substrates. Jiao and co-workers have recently reported the combination of HOTf and TCICA in hexafluoro isopropanol (HFIP) at 60 °C.[40] Comparing these systems, the chlorinating ability is similar to

ours, with similar levels of HOTf being used to catalyse both systems. We do however note that our systems are performed in chloroform, whereas HFIP is conditional for their system.[40] TCICA has also been activated by other means. This includes using 98% H_2SO_4 as the reaction media at elevated temperatures, this system was able to chlorinate highly deactivated substrates in nitrobenzene and *m*-dinitrobenzene in respectable yields,[44] though H_2SO_4 is potentially disadvantageous as a reaction media due to its corrosivity.

Lamar and co-workers have also activated TCICA with organic dyes, favourable for its acid free nature.[42] This system is reported to be regioselective and able to chlorinate highly deactivated species; inspection of the substrates tested in this report reveals those substrates with deactivating groups such as $-NO_2$ are also accompanied by strongly activating substituents such as alkyl, alkoxy, NH_2 and -OH. We consider this system to be weaker for chlorination than ours. Concerning regioselectivity, it is apparent that the selected substrates typically have substituent arrangements that coincidentally direct to the same position to produce reactivity selective to a singular site.[42]

Olah and co-workers have reported the activation of *N*-chlorosuccinimide using BF_3-H_2O as the reaction media. This system is highly reactive with the chlorination of nitrobenzene completing over 24 hours at 100 °C, but does require BF_3-H_2O as the reaction solvent.[45]

Xu and Dai recently reported the utilization of a highly deactivated λ^3-iodoarene for electrophilic chlorination using a *p*-CF_3-$PhICl_2$ for the chlorination of imidazo-fused heterocycles.[46] Their report mentions the increased reactivity of $ArICl_2$ species possessing highly electron withdrawing substituents in the *para* position, however does not mention the chlorination of deactivated substrates. Besides those mentioned, other chlorinating methods include the employment of alternative electrophilic chlorinating reagents like SO_2Cl_2, employment of Lewis acids such as $AlCl_3$ to activate Cl_2,[47] and the utilization of zeolite surfaces which can activate both Cl_2 and SO_2Cl_2.[48-49]

THEORETICAL CALCULATIONS

The propensity for **I3** to deliver [ArI]$^+$ to aromatic nucleophiles, *versus* the preference for chlorine delivery by **I5** was examined by theoretical methods. Calculations were carried out on NO$_2$-PhIX(OTf) using wPBE/def2TZVP which we have previously shown is a good method for the modelling of bound triflate.[50] For **I5** the NPA charge on the iodine is +1.22 and the charge on chloride is -0.38154. For **I3** the iodine carries a more positive NPA charge of +1.44 and the fluoride is -0.62546. In terms of molecular orbitals, for **I5** the LUMO has a major component with σ* symmetry aligned on the O-I-Cl bond axis. In **I3** the LUMO is predominantly a π* orbital localized on the phenyl ring and the σ* orbital associated with the O-I-F bond axis is found in the LUMO +1. This orbital is 1.17 eV higher in energy than the corresponding orbital on **I5**. Taken together the charge and MO data suggest why **I3** is a better source of iodonium and **I5** is a source of electrophilic chlorine. Comparing to **I4**, here the NPA charge on iodine is +1.07 and on the two chlorines it is –0.49. The σ* symmetry aligned on the Cl-I-Cl bond axis is found in the LUMO + 1 and 1.19 eV higher in energy than the corresponding orbital on **I5**, explaining why it is a more reactive source of electrophilic chlorine than **I4**.

CONCLUSIONS

In summary we have described the successful synthesis of two mixed ArI(OTf)(X) species in **I3** and **I5**. These species have demonstrated a resistance towards decomposition by the inhibition of the historically experienced self-decomposing EAS processes with their own phenyl moiety's. **I3** and **I5** present with alternative reactivities towards aryl substrates with **I3** behaving as a source of [PhI]$^+$ and **I5** providing Cl$^+$ towards target substrates in electrophilic substitution processes. **I5** presents with unprecedented levels of chlorinating ability, and we have implicated it as the active species in the newly developed I(I)/I(III) redox cycle

mediated catalytic activation of Cl$_2$ towards aryl substrates which displays high levels of reactivity.

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