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Diverse Reactions of $PhI(OTf)_2$ with Common 2-Electron Ligands: Complex Formation, Oxidation, and Oxidative Coupling

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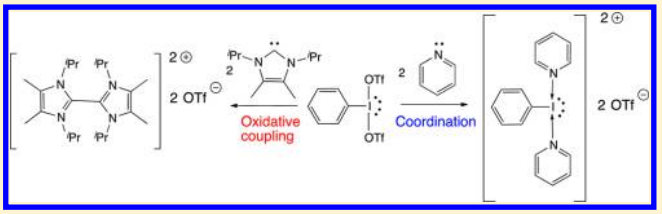
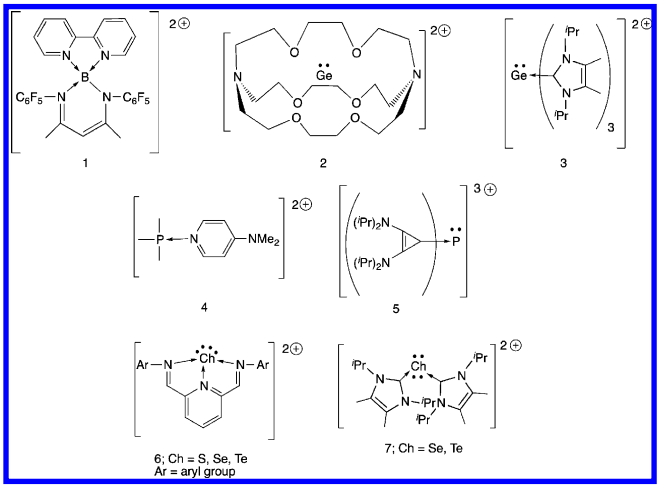
Supporting Information

ABSTRACT: The crystal structures of bis-pyridine stabilized iodine dications $[PhI(pyr)_2]^{2+}$ are reported as triflate salts, representing the first ligand supported iodine dications to be structurally characterized. The pyridine complexes are susceptible to ligand exchange in reaction with stronger N-based donors such as 4-dimethylaminopyridine. Attempts to extend this reactivity to N-heterocyclic carbene and phosphine ligands, as has been accomplished in the earlier p-block groups, resulted in redox chemistry, with oxidation of the ligands rather than coordination.

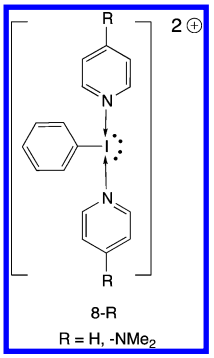


INTRODUCTION

The study of ligand stabilized polycationic p-block centers has emerged as a major area of study in synthetic chemistry.[1] In recent years there have been notable successes in the isolation of compounds containing B^{2+},[2] B^{3+},[3] Ge^{2+},[4−6] Sn^{2+},[7] P^{2+},[8] P^{3+},[9] S^{2+},[10,11] Se^{2+},[12,13] and Te^{2+}.[14−16] The accepted bonding model for these compounds is a coordinative interaction between the ligands and the main group element center, and the propensity for these compounds to engage in ligand exchange reactions has been harnessed to form compounds with unique bonding arrangements for a variety of elements (e.g., **1**−**7**).



The concept of using ligands to stabilize main group centered polycations has only very rarely been extended to the halogens. The primary reason for this is that potential starting materials are unavailable, especially so for the lighter elements. Iodine, however, has a variety of compounds which could be used as Lewis acidic starting materials for the formation of precursors to dications (e.g., I(III) halides and *pseudo*-halides). There is a single system comprising ligand stabilized iodine dications, with a $[PhI(pyr)_2]^{2+}$ architecture generated from the iodine(III) *pseudo*-halide $PhI(OTf)_2$ (**8-R**; R = -H, $-NMe_2$). This class of compound was first reported in 1994 and subsequently reinvestigated by Zhdankin in 2002, but has not been structurally verified, nor described in terms of electronic structure.[17,18] Nevertheless, these compounds have found some recent use in organic synthesis,[19−21] and the related derivative with R = CN was recently used to access high-valent palladium compounds.[22] Our interest in this class of compound, and the precursor $PhI(OTf)_2$, lies in using them as an entry point to study the coordination chemistry of polycationic iodine species.



In this study, we have confirmed the structural form of these iodine-centered dications and analyzed the electronic structure and bonding using density functional theory (DFT) calculations. Attempts at extending the chemistry to utilize phosphine and N-heterocyclic carbene ligands resulted in

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significantly different reactivity, with oxidation of the ligands rather than coordination being observed.

EXPERIMENTAL PROCEDURES

All manipulations were carried out in a Saffron Beta model glovebox under an N_2 atmosphere. All solvents were dried over CaH_2, vacuum distilled, and stored in the glovebox over 3 Å molecular sieves. All reagents were obtained from Alfa Aesar. Triphenylphosphine, $PhI(OAc)_2$, and 4-dimethylaminopyridine were dried under vacuum prior to transfer into the glovebox. TMS-OTf was used as received. Pyridine was dried over CaH_2, distilled, and stored in the glovebox over 3 Å molecular sieves prior to use. The N-heterocyclic carbene (NHC) $^{i}Pr_2IM(Me)_2$ was synthesized according to Kuhn's protocol.[23] Compounds **8-H** and **8-NMe$_2$** were synthesized according to the reported procedure;[17] however, our ^{1}H NMR data differed significantly from the original report, and is provided below. Single crystals of compounds **8-H** and **8-NMe$_2$** were grown from the CD_3CN solutions at −35 °C in the glovebox. Single crystals were *very rapidly* (<30 s) selected from samples of crystals transferred into paratone-n oil and immediately into a cold stream of N_2 gas on the diffractometer. The solution and refinement of **8-H** was nontrivial. The metrical parameters from the data collection suggested an orthorhombic or tetragonal crystal system, but no suitable space group for solution could be found (Table 1). A solution was possible in the triclinic space

Table 1. X-ray Refinement Details for 8-H and 8-NMe$_2$

	8-H	8-NMe$_2$
empirical formula	$C_{18}H_{15}F_6I_1N_2O_6S_2$	$C_{22}H_{25}F_6I_1N_4O_6S_2$
FW (g/mol)	660.34	746.48
crystal system	orthorhombic	orthorhombic
space group	*Pbcn*	*Pnma*
a (Å)	10.879(2)	21.866(4)
b (Å)	20.300(4)	9.752(2)
c (Å)	10.876(2)	13.102(3)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	2401.9(8)	2793(1)
Z	4	4
D_c (mg m^{-3})	1.826	1.775
radiation, λ (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
$R1[I > 2\sigma I]$	0.0300	0.0584
$wR2(F^2)$	0.0633	0.1387
GOF (S)	1.162	1.355

group $P\bar{1}$, which allowed for identification of the iodine atom and triflate anions. Use of the ADDSYM routine in the PLATON software suite[24] suggested $P2/c$ as an alternate space group, which allowed for location of the rings about the iodine center. At this stage many of the atoms gave nonpositive definite thermal parameters upon refinement. Rerunning the ADDSYM routine suggested an orthorhombic crystal system with a *Pbcn* space group. This allowed for suitable refinement of the thermal parameters, but the refinement values and residual electron density were unacceptably high. Finally, the TWINROTMAT routine in PLATON suggested the presence of a twin with the matrix 0 0 1 0 −1 0 1 0 0 and a BASF of approximately 0.25. Application of this twin law finally gave a satisfactory refinement.

Density functional theory (DFT) calculations were performed using the GAUSSIAN-09 program[25] at the ωB97XD/6-311++G(d,p) level of theory.[26−29] Geometries were optimized at this level, and second derivative calculations determined to ensure correct identification of stationary points and to determine harmonic vibrational frequencies for zero-point, thermal and entropic corrections to the electronic energy. Solvent contributions to the free energies were calculated employing the polarizable continuum model (PCM) approach.[30]

Updated ^{1}H NMR data for **8-H** and **8-NMe$_2$** (500 MHz, CD_3CN, δ ppm).

8-H: 8.62 (d, $^3J_{H-H}$ 4.5 Hz, 4H, *o*-py), 8.37 (bs, 2H, *o*-Ph), 8.05 (bs, 2H, *p*-py), 7.83 (bs, 4H, *m*-py), 7.67 (t, $^3J_{H-H}$ 7.0 Hz, 1H, *p*-Ph), 7.45 (t, $^3J_{H-H}$ 7.0 Hz, 2H, *m*-Ph).

8-NMe$_2$: 7.95 (d, $^3J_{H-H}$ 7.5 Hz, 4H, *o*-DMAP), 7.78 (bs, 2H, *o*-Ph), 7.54 (t, $^3J_{H-H}$ 8.0 Hz, 1H, *p*-Ph), 7.35 (t, $^3J_{H-H}$ 8.0 Hz, 2H, *p*-Ph), 6.78 (d, $^3J_{H-H}$ 7.5 Hz, 4H, *m*-DMAP), 3.16 (s, 12 H, -NMe_2 DMAP).

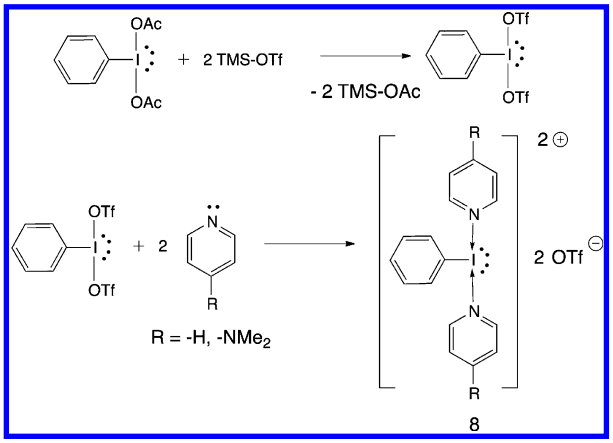
Generation of 9. A solution of $^{i}Pr_2IM(Me)_2$ (0.2 mmol; CD_3CN 1 mL) was added to solutions of $PhI(OTf)_2$ or $PhI(OAc)_2$ or **8-NMe$_2$** (0.1 mmol; CD_3CN 1 mL) giving colorless solutions. Aliquots were removed for ^{1}H and $^{13}C\{^1H\}$ NMR and mass spectral studies, confirming quantitative generation of **9** and PhI by comparison to Clyburne's data.[31]

Generation of 10. A solution of Ph_3P (0.05 g, 0.1908 mmol; CH_2Cl_2, 2 mL) was added to a slurry of **8-NMe$_2$** (0.143 g, 0.1908 mmol; CH_2Cl_2 3 mL) and stirred for 30 min, giving a colorless solution. *N*-hexane (15 mL) was added resulting in the deposition of an oil. The solution was stored at −35 °C overnight giving **10** as a colorless solid. Yield 0.088 g, 86%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm) 8.10−7.75 (overlapping multiplets, 17H) 7.20 (d, $^3J_{H-H}$ 6.5 Hz, 2H), 3.42 ppm (s, 6H) ; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.5 MHz, δ ppm) 58.

RESULTS AND DISCUSSION

Weiss' original methods were used to prepare compounds **8-NMe$_2$** and **8-H**, via $PhI(OTf)_2$, formed in situ from $PhI(OAc)_2$ and TMS-OTf (Scheme 1).

Scheme 1. Synthesis of Base Stabilized Iodine Polycations Following Weiss' Protocol



The syntheses proceeded smoothly in both CH_2Cl_2 and CD_3CN. The original synthetic report gave low-field proton NMR data for $PhI(OTf)_2$,[32] but a recent study collected higher resolution proton NMR data, which our findings matched.[33] In addition we collected ^{19}F NMR data, which sheds some light on the bonding. The ^{19}F chemical shift in CH_2Cl_2 was found to be −78.5 ppm. Fluorine chemical shifts of triflate groups have been used in several cases to establish the ionic/covalent nature of the triflate, by comparison with known model systems.[7,34,35] In this case the chemical shift of the triflate is much closer to that of "free" triflate (c.f. $[NOct_4][OTf]$, −79.0 ppm), than bound triflate (c.f. TMS-OTf −77.0 ppm, Me-OTf −75.0 ppm), indicating that $PhI(OTf)_2$ could be considered as a synthetic equivalent of $[PhI]^{2+}$ in solution. The stability of $PhI(OTf)_2$ has also not been reported. A sample of $PhI(OTf)_2$ in $CDCl_3$ (0.15 M), kept in the glovebox at room temperature under normal laboratory light, was monitored using ^{1}H NMR spectroscopy. No decomposition was apparent after 3 days;

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after 5 days some dark material precipitated from solution and other phenyl containing compounds could be observed in the ^{1}H NMR spectrum. A sample left undisturbed for 14 days resulted in the growth of a large number of needle-like crystals in addition to the dark material. Unit cell analysis of the crystals by X-ray diffraction and subsequent full data collection revealed the crystals to be the known salt [*para*−I-C_6H_4−I-C_6H_5][OTf], containing iodine in both the +1 and +3 formal oxidation states.[36]

Compounds **8-H** and **8-NMe$_2$** were synthesized from freshly prepared samples of PhI(OTf)$_2$ using Weiss' reported procedure and isolation. For both compounds the ^{1}H NMR data we obtained was in disagreement with the data in the original report in the same solvent (CD_3CN). The resonances in the literature for **8-H** in particular appear to be more consistent with protonated pyridine.[17] Indeed, we have found these compounds to be particularly sensitive to adventitious water, readily forming protonated pyridines if solvents and other solid reagents are not rigorously dried. Single crystals were grown from the NMR samples by holding the solutions overnight at −35 °C. Compound **8-H** is substantially less stable than **8-NMe$_2$**, decomposing within a few hours if held in solution at room temperature. The crystals of both compounds were also found to be highly moisture sensitive, rapidly degrading in paratone-n oil while being manipulated under the microscope. However, samples of sufficient quality could be mounted in both cases. X-ray diffraction studies conclusively identified the compounds as the dicationic pyridine-iodine complexes as OTf salts (Figures 1 and 2).

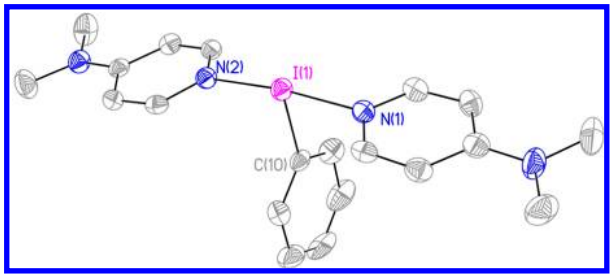


Figure 1. Solid-state structure of **8-NMe$_2$**. Hydrogen atoms and triflate counterions are omitted for clarity. Selected bond distances (Å) and angles (deg): I(1)−N(1) 2.185(8), I(1)−N(2) 2.217(8), I(1)−C(10) 2.104(10), N(1)−I(1)−N(2) 172.4(3), C(10)−I(1)−N(1) 85.7(3).

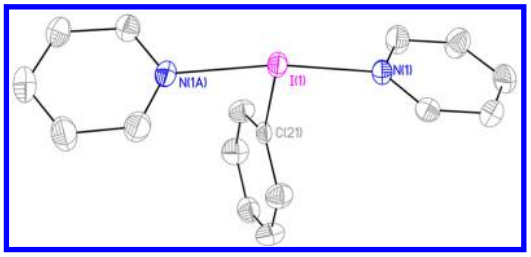
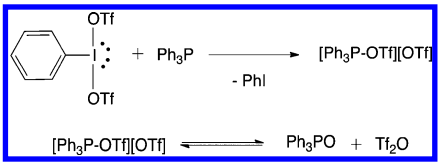


Figure 2. Solid-state structure of **8-H**. Hydrogen atoms and triflate counterions are omitted for clarity. Selected bond distances (Å) and angles (deg): I(1)−N(1) 2.220(3), I(1)−C(21) 2.089(4), N(1)−I(1)−N(1A) 167.6(2), C(21)−I(1)−N(1) 83.80(8).

We then investigated if this coordination chemistry could be extended to other ligand sets. In groups 15 and 16, both N-heterocyclic carbene and trisubstituted phosphine ligands have been found to be compatible with Lewis acids that also bind pyridines. Displacement of triflates by NHCs has been used in the clean syntheses of polycations **3**, **6**, and **7**,[4,13,14] and more recently displacement by phosphines from Ch(OTf)$_2$ synthons (Ch = Se, Te) has been successfully undertaken.[15] Triphenylphosphine (Ph_3P) was found not to react with PhI(OAc)$_2$, as monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction of PhI(OTf)$_2$ with 2 stoichiometric equivalents of triphenylphosphine (Ph_3P) in $CDCl_3$ gave a clear, colorless solution. A sample of the reaction mixture was examined by $^{31}P\{^1H\}$ NMR spectroscopy which revealed 2 resonances; one at 51 ppm and one at −6 ppm, in an approximate 1:1 ratio by integration. The signal at −6 ppm is consistent with free triphenylphosphine. The signal at 51 ppm is downfield of the expected resonance of Ph_3P acting as a ligand, and is consistent with an oxidation to P(V). The proton NMR spectrum of the same sample gave resonances consistent with PhI. Examination of the literature for potential oxidation products revealed that the [Ph_3P-OTf] cation has been reported to give an identical $^{31}P\{^1H\}$ NMR resonance to our observation.[37] The reaction was repeated using 1 equivalent of triphenylphosphine in $CDCl_3$ (Scheme 2), which showed complete conversion of

Scheme 2. Oxidation of Ph_3P Using PhI(OTf)$_2$



PhI(OTf)$_2$ to PhI, and only the signal at 51 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Addition of *n*-hexane to the solution resulted in the deposition of a colorless oil, which turned into a crystalline material upon standing at −35 °C overnight. Rather than the expected phosphonium salt, single crystal X-ray diffraction studies revealed the crystals to be the known, but not structurally characterized salt [Ph_3PO-SiMe$_3$][OTf]. This compound has approximately the same reported chemical shift as [Ph_3P-OTf], at 51 ppm.[38] A control experiment found that addition of Ph_3P to a CH_2Cl_2 solution of TMS-OTf resulted only in a slight broadening of the single resonance at −6 ppm in the $^{31}P\{^1H\}$ NMR spectrum, and no evidence of a peak at 51 ppm, allowing the conclusion that PhI(OTf)$_2$ is integral to the process. The production of this compound in the reaction can be rationalized in terms of reported behavior of [Ph_3P-OTf][OTf] and related compounds, where an equilibrium between [Ph_3P-OTf][OTf] and Ph_3PO + triflic anhydride has been described.[39]

We next turned to NHC ligands. The NHC ligand chosen was ^{i}Pr$_2$NHC(Me)$_2$, selected for its known ability to stabilize highly charged and/or low valent main group centers.[4,13,14] Dichloromethane is not compatible with NHC chemistry, so the transformations were carried out in CD_3CN. Reaction of two stoichiometric equivalents of NHC with PhI(OTf)$_2$ resulted in the immediate production of a dark orange solution. The ^{1}H NMR spectrum of the mixture was clean, revealing only signals arising from the iodine −Ph group and the NHC. The NHC signals were shifted from the free NHC in CD_3CN, in particular the methine proton of the isopropyl groups was shifted to 4.51 ppm, from 4.25 ppm in the free carbene. However, the −Ph had identical resonances as a sample of PhI dissolved in CD_3CN, indicating reduction of the iodine center, rather than formation of the target complex. The NHC containing product was isolated as a sticky resin by addition of

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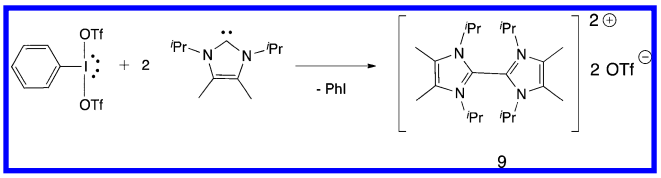
Et_2O to the solution. Single crystals could not be obtained, but an examination of the literature for possible oxidation products revealed that the coupled $[NHC\text{-}NHC]^{2+}$ dication has been reported by Clyburne from oxidation of the same NHC by the ferrocenium cation.[31] Our ^1H and $^{13}C\{^1H\}$ NMR data was virtually identical to that in Clyburne's report (Clyburne's NMR data was obtained in THF-d_8, ours in CD_3CN), allowing for assignment of **9** as the NHC containing product in the reaction (Scheme 3). An experiment reacting $PhI(OAc)_2$ with 2 equiv of the NHC resulted in an identical oxidative coupling reaction.

Scheme 3. Oxidative Coupling of $^iPr_2NHC(Me)_2$ Using $PhI(OTf)_2$

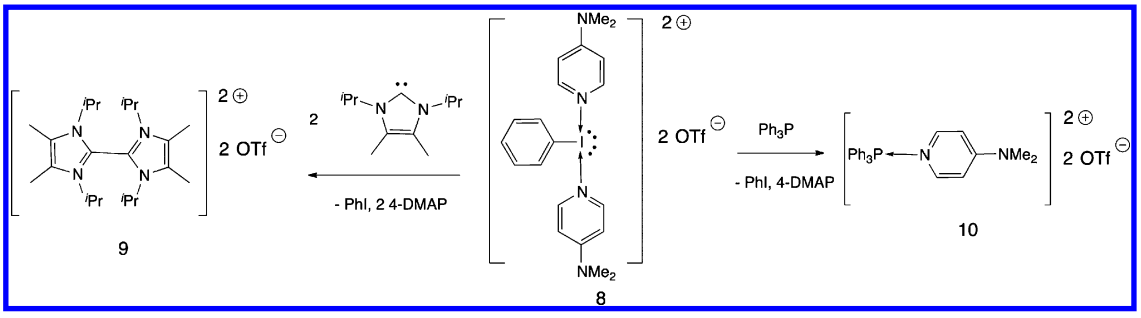


Ligand exchange reactions have been used to generate p-block coordination complexes that are otherwise inaccessible from simple electrophilic starting materials.[15] This is particularly the case in group 16, where use of binary or tetrahalides with R_3P or NHC ligands results in reduction of the group 16 centers and oxidation of the ligands.[40,41] We surmised that reaction of R_3P and NHC with the dicationic pyridine coordination complexes might furnish the corresponding complexes with new ligands. To confirm that the class of complexes is susceptible to ligand exchange reactions, **8-H** was reacted with two stoichiometric equivalents of 4-DMAP in CD_3CN, which resulted in a color change from colorless to yellow. An NMR spectrum of the sample revealed a mixture of broad peaks in the aryl region. Addition of Et_2O to the solution resulted in the formation of a light yellow precipitate. The precipitate was washed with Et_2O and dried in vacuo. A sample of the solid redissolved in CD_3CN revealed resonances in the ^1H NMR spectrum consistent with compound **8-NMe$_2$**, and no pyridine or pyridine-containing complexes was evident. The ligand exchange product **8-NMe$_2$** was isolated in 70% yield. To our knowledge, this is the first demonstration of ligand exchange reactions at a Lewis acidic iodine center using neutral two-electron donors.

Ligand exchange reactions were then attempted on compound **8-NMe$_2$** using Ph_3P and the NHC (Scheme 4). Reaction of **8-NMe$_2$** with $^iPr_2NHC(Me)_2$ resulted in an identical oxidative coupling of the NHC ligand with free 4-DMAP as an additional product as monitored by ^1H NMR spectroscopy. The use of Ph_3P in attempted ligand exchange reactions gave a different result than the reaction of Ph_3P with $PhI(OTf)_2$. As the reaction of Ph_3P with $PhI(OTf)_2$/TMS-OAc required only 1 equiv of Ph_3P to bring the reaction to completion, and with the observation that the reaction of the NHC with $PhI(OTf)_2$ or **8-NMe$_2$** gave the same result, one stoichiometric equivalent of Ph_3P was added to a CD_3CN solution of **8-NMe$_2$**. Over the course of 5 min the solution turned from yellow to colorless. An aliquot was removed for ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum showed a single peak at 59 ppm, slightly downfield from the 51 ppm observed for $[Ph_3PO\text{-}SiMe_3]^+$ in the reaction with $PhI(OTf)_2$/TMS-OAc. The ^1H NMR spectrum showed two 4-DMAP containing compounds. Iodobenzene could also be identified, indicating that the iodine had been reduced and the target complex was not formed. A small amount of Ph_3P was added to the NMR sample, and this simply resulted in the appearance of a signal for free Ph_3P appearing in the $^{31}P\{^1H\}$ NMR spectrum, confirming that only 1 equiv of Ph_3P was required. The reaction was repeated on a larger scale using CH_3CN as the solvent. Upon discharge of the yellow color, Et_2O was added which resulted in the formation of an oil, which solidified into a colorless powder upon standing at −35 °C for 1 h. The solution was decanted, the solids washed with Et_2O and were then dried in vacuo. A sample was redissolved in CD_3CN, the $^{31}P\{^1H\}$ NMR spectrum gave the same singlet at 59 ppm. The ^1H NMR spectrum was consistent with a compound containing Ph_3P and 4-DMAP in a 1:1 ratio by integration. Single crystals suitable for X-ray analysis have not yet been obtained; however, based on reports of related compounds by Burford,[8] we *tentatively* assign the complex as salt **10** (Scheme 4). Within the scope of this report, the important point to note is that a redox process rather than a ligand exchange reaction occurred.

Bonding and Theoretical Studies. Compounds **8-H** and **8-NMe$_2$** are the first ligand stabilized iodine-centered polycations to be structurally characterized. An examination of the solid-state structures reveals the expected T-shaped geometry about the iodine(III) center based on an AX_3E_2 electron pair geometry, with the pyridine ligands orientated *trans* with respect to each other. The I−N bond distances are 2.19−2.22 Å which can be compared to the slightly longer 2.26 Å I−N bond in the linear bispyridine iodine(I) cation.[42] The I−N bonds in **8-H** are slightly longer than **8-NMe$_2$**. The I−C bond distances are 2.10(1) and 2.089(4) Å for **8-H** and **8-NMe$_2$**, respectively. The N−I−N bond angles were found to be 167.6(2)° for **8-H** and 172.4(3)° for **8-NMe$_2$**. DFT optimization of **8-H** yielded a geometry with an I−C bond length of 2.115 and I−N bond lengths of 2.270 Å, slightly

Scheme 4. Reactions of $^iPr_2NHC(Me)_2$ and Ph_3P with 8-NMe$_2$



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longer than those found in the crystal structures. The N−I−N bond angle was calculated to be 176.6°. The Mulliken atomic charge on the iodine atom in **8-H** was calculated to be +1.14, highly positive for a halogen atom, and reflective of the "dative" nature of the N−I bonds.

In MO terms, the geometry about the iodine(III) centers in **8-H** and **8-NMe$_2$** can be understood in terms of donation of a pyridine lone pair into the p-based Lewis acidic lowest unoccupied molecular orbital (LUMO) of the esoteric $[PhI]^{2+}$ fragment, orientated orthogonal to the I−C bond axis. The LUMO for the resulting $[PhI\text{-}Py]^{2+}$ fragment is also a σ symmetric orbital, orientated along the I−N bond axis, allowing for formation of the second N−I bond. The highest occupied frontier orbitals in **8-H** are all ligand based π-type orbitals (Figure 3). The p-orbital based lone pair on the iodine

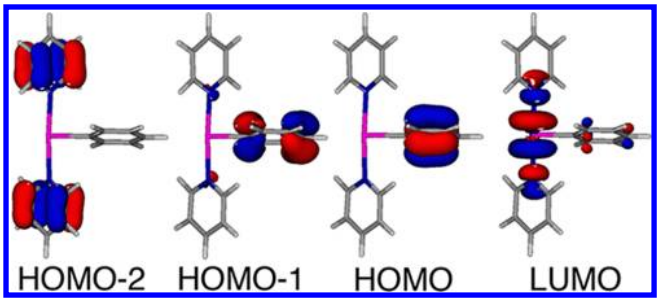

Figure 3. Frontier molecular orbitals of **8-H**.

atom is buried, with its largest contribution in the HOMO-7. This can be compared to the p-type lone pair orbitals in PhI, found in the highest occupied molecular orbital (HOMO) and HOMO−1.[43] The LUMO of **8-H** is a σ symmetric antibonding orbital associated with the I−N bonds, which is consistent with a 2-electron reduction of the compound rupturing these bonds giving PhI, and with their ability to engage in ligand exchange reactions. The I−N bond dissociation energy (ΔH_0) for **8-H** was calculated to be 244 kJ/mol in the gas phase, as compared to 154−164 kJ/mol for the bis-pyridine iodine(I) cation.[44]

The electronic structures of the $PhI(OTf)_2$ and $PhI(OAc)_2$ precursors were also investigated. The $^{19}F\{^1H\}$ NMR chemical shift of $PhI(OTf)_2$ suggested that the triflates were only weakly bound to the iodine center, with a chemical shift closer to that of ionic OTf^- than known bound systems. This weakly bound system is not reproduced by DFT calculations. The optimized geometry of $PhI(OTf)_2$ (Figure 4) gives a structure consistent with relatively strongly bound triflate substituents, with large asymmetry in the S−O bond distance. The S−O bond distance for the oxygen bound to I is 1.563 Å, while the S−O distances for the unbound oxygens are much shorter at 1.434 Å. The I−O bond distance is calculated to be 2.154 Å, which is essentially identical to the bond distance calculated (2.178 Å), and observed (2.172 Å) in PhI(OAc).[45] A possible explanation for the anomalous NMR chemical shift of the fluorine atoms lies in the minimum energy conformation for the triflates with respect to the phenyl ring. They are found orientated with the $-CF_3$ groups positioned above and below the plane of the ring, 3.201 Å from the centroid. In this region, the NMR shifts are likely to be shielded by phenyl ring current, accounting for the upfield shift of the $-CF_3$ groups versus that expected for a strongly bound triflate.

The Mulliken charge on the iodine atom for $PhI(OTf)_2$ is 1.10, while for $PhI(OAc)_2$ it is 1.03, indicating that the iodine

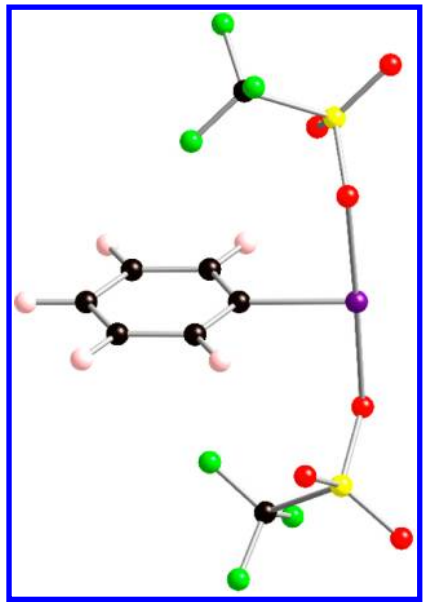

Figure 4. Optimized geometry of $PhI(OTf)_2$.

atom in $PhI(OTf)_2$ is likely to be slightly more electrophilic. This is also consistent with the dissociation energies (ΔH_0) calculated for the removal of a single OTf^- (509 kJ/mol) or OAc^- (590 kJ/mol), which indicates that while the OTf is rather strongly bound, the binding is weaker than that of the OAc fragment.

Thermochemical Studies of Coordination vs Oxidation. For the reactions between $PhI(OTf)_2$, $PhI(OAc)_2$, **8-H** and the NHC, thermochemical calculations were carried out to gain an understanding of how favorable the oxidation reactions are compared to the unobserved simple coordination reactions. In the gas phase, all reactions were found to be strongly endothermic, including those reactions observed experimentally. The role of solvent on these reactions was modeled using the continuum PCM approach. All of the reactions involving the NHC were found to be exothermic in CH_3CN; the values discussed are those calculated using CH_3CN as this was the solvent in which the experiments were conducted. The free energy (ΔG_{298}) for the simple coordination reaction of the NHC with $PhI(OTf)_2$ was calculated to be −276 kJ/mol. This compares to −587 kJ/mol for the observed oxidative coupling reaction. If the starting material is $PhI(OAc)_2$, ΔG_{298} for the oxidative coupling was calculated to be −378 kJ/mol, and finally if $[PhI(pyr)][OTf]_2$ is used as the oxidant, ΔG_{298} was calculated to be −481 kJ/mol. Therefore, in this system we can order the oxidative capacity of the iodine(III) compounds $PhI(OTf)_2$ > $[PhI(pyr)_2]^{2+}$ > $PhI(OAc)_2$. This is also consistent with the observation of Ph_3P reacting with $PhI(OTf)_2$ and the dications, but not $PhI(OAc)_2$.

■ CONCLUSIONS

The first structural verification of ligand stabilized dicationic iodine compounds, using pyridine ligands, has been carried out. With respect to triphenylphosphine, the $PhI(OTf)_2$ precursor was found to be a stronger oxidizing agent than $PhI(OAc)_2$. $PhI(OAc)_2$ has found use as an oxidizing agent in many important systems; the observation that $PhI(OTf)_2$ is a more reactive agent, coupled with the ease of its generation from commercially available $PhI(OAc)_2$, should mean that it finds increasing use in this respect. For NHCs, iodine(III) may

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represent a limit to the oxidative capacity of NHCs, which may have implications for the use of NHCs as spectator ligands, in for example, high oxidation state transition metal chemistry. The iodine dications, which can be isolated away from the TMS-OAc byproduct, were also found to be strong oxidizing agents in their own right. The work of Sanford, Yates, and Ritter has shown that iodine(III) reagents with an $PhIR_2$ framework are excellent oxidants for the clean generation of high-oxidation state transition metal compounds,[22,46−48] and we are currently investigating the redox chemistry of these dicationic species toward late transition metals.

■ ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates and comprehensive energies for calculated geometries/reactions. X-ray data for compounds **8-H**, **8-NMe$_2$**, and $[Ph_3P{-}O{-}SiMe_3][OTf]$ in .cif format. CCDC reference numbers 908359−908361. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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