Reactions of PhIX2 I(III) Oxidants with Heavy Triphenyl Pnictines

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The reactions of [PhI(pyridine)2]2+, PhI(OAc)2 and PhI(OTf)(OAc) with Ph3As, Ph3Sb and Ph3Bi are described. The reactions of [PhI(pyridine)2]2+ with Ph3Sb and Ph3Bi affords dicationic Pn(V) complexes ligated by pyridine in one step. These were previously reported by Burford in multi step syntheses. Reactions with PhI(OAc)2, which were already known for Sb and Bi giving Pn(V) diacetates, was confirmed to give the same type of compound for As. Reactions with PhI(OAc)(OTf) were less clean, resulting in the isolation of iodonium cations [Ph-I-Ph]+ for As and Bi, while Ph3Sb gave an oxobridged di-antimony species characteristic of the decomposition of a high valent triflate bound species.

File list (2)

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Reactions of PhIX$_2$ I(III) oxidants with heavy triphenyl pnictines

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**ABSTRACT**

The reactions of [PhI(pyridine)$_2$]$^{2+}$, PhI(OAc)$_2$ and PhI(OTf)(OAc) with Ph$_3$As, Ph$_3$Sb and Ph$_3$Bi are described. The reactions of [PhI(pyridine)$_2$]$^{2+}$ with Ph$_3$Sb and Ph$_3$Bi affords dicationic Pn(V) complexes ligated by pyridine in one step. These were previously reported by Burford in multi-step syntheses. Reactions with PhI(OAc)$_2$, which were already known for Sb and Bi giving Pn(V) diacetates, was confirmed to give the same type of compound for As. Reactions with PhI(OAc)(OTf) were less clean, resulting in the isolation of iodonium cations [Ph-I-Ph]$^+$ for As and Bi, while Ph$_3$Sb gave an oxobridged di-antimony species characteristic of the decomposition of a high valent triflate bound species.
Introduction
The synthesis of polycationic species of the heavier late p-block elements has seen little investigation as compared to the lighter elements due to reactivity of the intermediates and target complexes as well as the requirement of a main-group halide starting material which can be difficult to handle.\(^1\) Much of the work utilises halide abstraction resulting in a triflate containing species which can used in further ligand exchange with other mono-, di- and tridentate ligands.\(^2\) Work by Burford et al. highlights this as using the above method they was able to isolate the bis-triflate bismuth(V) \(1\) followed by exchange with pyridine ligands to give the dicationic bismuth species \(2\) and monocationic species \(3\) (Scheme 1).\(^3\) The corresponding chemistry for antimony was also reported by the Burford group.\(^4\)

Scheme 1. Isolation of bismuth (V) complexes 2 and 3 using triphenylbismuth.

This strategy is a general route to ligand stabilized polycations in groups 15 and 16. As shown in Scheme 2, the commonly used route in the literature is the abstraction of a halide with a species
that introduces triflate or another good leaving group, with some examples requiring a specific halide for this reaction to proceed as well as the element in the correct oxidation state. Addition of ligands to late main group halides can result in spontaneous reduction reactions, with elimination of elemental halogen as a possible by-product leading to deleterious effects. The triflate adducts can be very sensitive to moisture and air making them relatively difficult to store and handle.

Scheme 2. The common method utilised for the isolation of cationic p-block species showing possible undesired outcomes.

With the issues of intermediate stability and the side reactions that can occur during the isolation of these molecules a more direct route would be ideal. Our group has been examining the chemistry of dicationic I(III) reagents [PhI(Pyr)₂]²⁺ (Pyr = Pyridine, 4-DMAP, 4-Cyanopyridine) with a major feature of their chemistry being of simultaneous oxidation of a metal along with delivery of the pyridine ligand, an example is the generation of Au(III) trications 5 from Au(I) precursor 4 (Scheme 3).
Scheme 3. Isolation of the cationic gold species was performed in 1 step using the iodine(III) oxidant.

These I(III) pyridyl compounds were first reported in 1994 by Weiss and later reinvestigated by Zhdankin.8-10 Ritter also used the oxidant to access pyridine stabilized Pd(IV) complexes, where the pyridine could be displaced with 18F labelled fluoride to generate PET labelling agents.11 Wengryniuk has recently shown the efficacy of these oxidants in oxidative ring formation reactions.12-14

In the main group we have explored the chemistry of these dicationic I(III) oxidants with aromatic group 16 rings, which largely resulted in electrophilic aromatic substitution type reactions on the ring or ring substituents.15,16 We also reported one reaction in group 15, the reaction of Ph3P with [PhI(4-DMAP)2]2+, which resulted in oxidation of phosphorus to P(V) and ligation of a 4-DMAP giving dicaticion complex 6 (Scheme 4),17 previously reported by Burford using the oxidation/halide abstraction method from the phosphine.18 No reaction is observed between PPh3 and Phl(OAc)2. For Phl(OAc)(OTf), oxidation occurs giving a proposed P(V) triflate ligated intermediate which rapidly decomposes to Ph3P=O and triflic anhydride.
Scheme 4. Oxidation and delivery of 4-DMAP ligand to triphenylphosphine giving dication 6.

We initially viewed these reactions as indicating that I(III) oxidants are incompatible with phosphine ligands, although have since found they are compatible when the phosphine is bound to a metal in some cases. In light of Burford’s work on heavier pnictogen(V) dication described above, we wondered if these I(III) dications could be an effective reagent for their generation, circumventing the steps involving halogenation/halide abstraction.

In this study we examined the ability of iodine(III) oxidants with anionic and neutral ligands as potential reagents to isolate dicationic complexes of arsenic, antimony and bismuth using AsPh$_3$, SbPh$_3$ and BiPh$_3$ as starting materials.

Results and Discussion

Arsenic

Triphenylarsine was stirred with 1 equivalent of [PhI(Pyr)$_2$][OTf]$_2$ in CD$_3$CN for 4 hours resulting in a colourless solution. Acetonitrile was employed as reactions in CDCl$_3$ or CD$_2$Cl$_2$ resulted in the immediate formation of complex mixtures. The $^1$H NMR spectrum of the in situ CD$_3$CN
reaction had peaks corresponding to PhI indicating that an oxidation has occurred, at least one other phenyl containing species and protonated pyridine as compared with an authentic sample. A colourless single crystal was grown from the solution left to stand at -30°C for 24 hours and the X-ray crystallography revealed the product to be bis-As(V) cation (7) with a completely depronotated acetonitrile fragment bridging the two As(V) centres. This compound has been reported in literature by a different route.\textsuperscript{20} We surmise in this case that acetonitrile coordinates to the oxidized arsenic centres, rendering the hydrogen atoms more acidic, resulting in deprotonation by pyridine and eventual rearrangement to the observed product. It should be noted here that the As analogue of 3 is not known and may not be stable as it is for Bi and Sb.

Scheme 5. Oxidation of Ph\(_3\)As using [PhI(Pyr)\(_2\)][OTf]\(_2\) giving 7.
The addition of 1 equivalent of PhI(OAc)(OTf) to triphenylarsine in CDCl₃ resulted in immediate change in ¹H NMR with all starting material consumed within minutes and the formation of a complex mixture. A vapor diffusion of the solution with n-hexane led to colourless crystals. X-ray crystallography of a single crystal revealed a diarylidionium triflate salt (8) via unit cell analysis (Scheme 6), this cation was also observed in the mass spectrum of the reaction mixture. No oxidized arsenic species could be identified in the mass spectrum. Compound 8 is known and most commonly synthesized by the reaction of iodoarenes with a suitable oxidant.

Scheme 6. Addition of PhI(OAc)(OTf) to Ph₃As results in isolation of 8.

Next, triphenylarsine was reacted with PhI(OAc)₂ in CDCl₃. The ¹H NMR spectrum of the colourless reaction mixture confirmed that reaction was driven to completion with no starting material after stirring for 24 hours. The spectrum had peaks corresponding to PhI and another species which indicates the possible formation of As(V) as the iodine became reduced. Colourless crystals were grown at -30°C. The crystals were of poor quality, but X-ray crystallography allowed for structural confirmation of the formation of triphenylarsine diacetate (9, Scheme 7). Compound 9 is a known compound and has been synthesized by other routes.

Attempts to exchange the acetate groups in 9 for triflates as a better leaving group using TMS-OTf resulted in no reaction. In summary, reactions of these I(III) oxidants with triphenylarsine did not result in productive advances.
Scheme 7. Isolation of 9 utilizing PhI(OAc)$_2$ and attempted ligand exchange with TMS-OTf.

Antimony

The addition of [PhI(Pyr)$_2$][OTf]$_2$ to a CD$_3$CN solution of triphenylantimony did not give an immediate reaction as monitored by $^1$H NMR spectroscopy however upon overnight stirring the NMR showed the oxidant had been consumed, with PhI and a new species generated. A white powder was obtained by removing the volatiles in vacuo.

Scheme 8. Oxidation of Ph$_3$Sb using [PhI(Pyr)$_2$][OTf]$_2$ yielding 10.
Single crystals were grown from a CH$_2$Cl$_2$ solution of the isolated material via vapour diffusion of n-hexane. X-ray crystallographic studies revealed the target dicationic antimony(V) complex 10 (Scheme), previously reported by Burford via the multistep route outlined in Figure 1 using 4-DMAP ligands. The two pyridyl groups are coordinated axial to the central antimony with the three phenyl rings in the equatorial positions. One triflate anion with a Sb-O distance of 2.760 Å completes a distorted octahedral geometry. Overall the structure is very similar to that determined by Burford using 4-DMAP ligands.

![Figure 1](image_url)

**Figure 1.** Solid-state structure of 10. Chloroform and acetonitrile solvate and hydrogen atoms omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Selected bond distance (Å): Sb(1)-C(1) 2.100(4), Sb(1)-C(2) 2.124(4), Sb(1)-C(3) 2.111(4), Sb(1)-N(1) 2.272(4), Sb(1)-N(2) 2.264(4).
Scheme 9. The reaction of PhI(OAc)(OTf) with Ph₃Sb giving 11.

The 1:1 reaction of Ph₃Sb and PhI(OAc)(OTf) in CD₃CN resulted in a yellow solution after stirring for 2 hours. The ¹H NMR spectrum of the reaction mixture showed a clean reaction the peaks associated with PhI(OAc)(OTf) replaced with PhI indicating an oxidation had taken place, as well as other peaks associated with phenyl fragments. Addition of n-hexane resulted in precipitation of a white powder, for which the isolated material returned a similar proton NMR to the in situ reaction mixture, without the PhI. A CDCl₃ solution of the isolated material was held at -30°C overnight yielding colorless crystals. X-Ray diffraction by unit cell analysis and confirmed by partial refinement revealed the product to be an oxo-bridged Sb(V) species 11 with a single oxygen in the centre and each antimony capped with a triflate. This compound has been previously reported and structurally characterized using a different route in which triphenylantimony oxide is reacted with triflic acid in acetone.²⁴,²⁵ This result is reminiscent of the outcome with Ph₃P with the PhI(OAc)(OTf) oxidant, in which the proposed P(V)-OTf intermediates decompose into phosphine oxide species.¹⁷ In the case of the phosphine, anhydrides could be observed in the reaction mixture, however in this case neither triflic or acetic anhydride is observed in the in situ reaction mixture.

The reaction of Ph₃Sb with PhI(OAc)₂ has been previously reported to oxidize the antimony and give the expected diacetoxy Sb(V) complex.²⁶
Bismuth

Ph₃Bi was added to a CD₂Cl₂ solution of [PhI(4-DMAP)₂][OTf]₂. CD₂Cl₂ solvent was chosen to most easily match observations from Burford using the oxidation/halide abstraction route as their NMR studies for the expected compound were done in CD₂Cl₂.¹ ¹H NMR of the solution after 2 hours showed little conversion and the mixture was left to stir overnight. After 16 hours complete conversion of the oxidant to PhI was observed, as well as one set of signals identical to that observed by Burford in CD₂Cl₂ for 12 (Scheme 10). In a bulk synthesis in CH₂Cl₂ compound 12 could be isolated in a 66% yield, an improvement over Burford’s yield (41%), and now in one step.

Scheme 10. The reaction of [PhI(4-DMAP)₂]²⁺ with Ph₃Bi giving 12.
The addition of 1 equivalent of PhI(OAc)(OTf) oxidant to triphenylbismuth (Ph₃Bi) in chloroform resulted in an immediate change in the \( ^1H \) NMR. Attempts to precipitate a solid resulted in a white powder, which was taken up in a small amount of chloroform and placed in the \(-30^\circ C\) freezer overnight.

\[
\begin{align*}
\text{PhBi} & + \text{PhI(OAc)(OTf)} \\
& \rightarrow \text{PhI(OAc)(OTf)}^+ + \text{Ph}^+ \\
& \text{13}
\end{align*}
\]

**Scheme 11.** Addition of PhI(OAc)(OTf) to Ph₃Bi results in isolation of 13.

Colourless crystals were obtained and X-ray diffraction studies showed via unit cell analysis\(^{27}\) the result was a diaryliodonium triflate salt 13 (Scheme 11) with \(^1H\) NMR of the crystals also matching literature reports.\(^{28}\) Compound 13 has been synthesised via numerous different methods one of which is known to involve a diarylstannane reagent.\(^{29, 30}\) The proposed mechanism for the formation of these diaryliodonium salts is thought to be by a ligand exchange reaction with a nucleophilic arylating reagent containing silicon, tin or mercury.

In some experiments the *in situ* mass spectrum of the reaction mixture showed a signal that could be attributed to diphenylbismuth acetate, indicating a possible aryl exchange process giving 13 but this could not be observed reliably.

The reaction of PhI(OAc)$_2$ with Ph$_3$Bi is known to give the triphenylbismuth(V) diacetate.\(^{31}\) As with Sb, an attempted synthesis of a bis-triflate complex via metathesis with TMS-OTf from triphenylbismuth(V) diacetate resulted in no reaction.
Conclusion

For bismuth and antimony, use of the [PhI(pyr)₂][OTf]₂ class of oxidants allows for the formation of dicationic Sb(V) and Bi(V) pyridyl complexes in one step from Ph₃Pn(III) starting compounds, demonstrating the potential efficacy of this I(III) reagent in isolating high oxidation state main group compounds. This method was not however able to be used to access the as yet unknown As analogue. PhI(OAc)₂ gave the expected Ph₃As(OAc)₂ product when reacted with Ph₃As, complementing the already reported chemistry for Sb and Bi. The more powerful PhI(OAc)(OTf) oxidant in reactions with Ph₃Pn gave varied and generally unproductive results.
**Experimental Section**

All manipulations were performed under a dry N$_2$ atmosphere in a glovebox. Bulk solvents were dried using an Innovative Technologies Solvent Press with dual alumina columns and stored over 3 Å molecular sieves in the glovebox. NMR solvents were dried for 2 days over CaH$_2$, distilled and then stored in the glovebox over 3 Å molecular sieves. PhI(OAc)$_2$, TMS-OTf, pyridine, 4-DMAP, Ph$_3$Sb and Ph$_3$As were obtained from Sigma-Aldrich and used as received. Ph$_3$Bi, [PhI(pyr)$_2$][OTf]$_2$, [PhI(4-DMAP)$_2$][OTf]$_2$ and PhI(OAc)(OTf) were synthesized according to literature procedures.$^3,8$

Synthesis of 7:

Ph$_3$As (100 mg, 0.326 mmol) was dissolved in a small amount of CD$_3$CN (3 ml) and added to a solution of [PhI(pyr)$_2$][OTf]$_2$ (215 mg, 0.326 mmol; 3 ml). The mixture was stirred for 4hr and examined by $^1$H NMR. The CD$_3$CN solution was left at -35°C overnight to afford large clear crystals. Yield 0.684 g 64% $^1$H NMR (400 MHz, CDCl$_3$): δ 7.70 (m, 12H), 7.54 (m, 18H); $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$): -78.41

Synthesis of 8:

Ph$_3$As (100 mg, 0.326 mmol) was dissolved in a small amount of CDCl$_3$ (3 ml) and added to a solution of freshly prepared PhI(OAc)(OTf) (0.326 mmol; 3 ml). The mixture was stirred for 1hr and examined by $^1$H NMR. Clear crystals were grown by a vapour diffusion of hexane/chloroform. Yield 0.468 g 79 % $^1$H NMR (400 MHz, CDCl$_3$): δ 7.82 (t, 4H), 7.73 (t, 4H), 7.64 (t, 1H); $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$): -78.06
Synthesis of 9:
Ph$_3$As (100 mg, 0.326 mmol) was dissolved in a small amount of CDCl$_3$ (3 ml) and added to a solution of PhI(OAc)$_2$ (105 mg, 0.326 mmol; 3 ml). The mixture was stirred for 24 hr and examined by $^1$H NMR. The CDCl$_3$ solution was left at -35°C overnight to afford large clear crystals. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05 (d, 8H), 7.51 (m, 12H), 1.72 (s, 6H).

Synthesis of 10:
Ph$_3$Sb (100 mg, 0.281 mmol) was dissolved in a small amount of MeCN (3 ml) and added to a solution of [PhI(Pyr)$_2$][OTf]$_2$ (186 mg, 0.281 mmol; 5 ml). The mixture was stirred for 1 hr and the volatiles were removed in vacuo leaving a white powder. Clear square crystals were grown by a vapour diffusion of hexane/CH$_2$Cl$_2$. Yield 0.272g 60% $^1$H NMR (400 MHz, CDCl$_3$): δ 8.91 (d, 4H, J = 4 Hz) 8.63 (d, 2H, J = 4 Hz), 8.03 (d, 4H, J = 4 Hz), 7.59 (t, 3H, J = 4 Hz) 7.54 (d, 6H, J = 4 Hz), 7.45 (t, 6H, J = 4 Hz); $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$): -78.2. Mp: 144-148°C.

Synthesis of 11:
12PhSb (100 mg, 0.281 mmol) was dissolved in a small amount of CD$_3$CN (3 ml) and added to a solution of PhI(OAc)(OTf) in CDCl$_3$ (114 mg, 0.281 mmol; 3 ml). The mixture was stirred for 1 hr and examined by $^1$H NMR. The CDCl$_3$ solution was left at -35°C overnight to afford large clear crystals. Yield 0.152g 53% $^1$H NMR (400 MHz, CDCl$_3$): δ 8.02 (d, 5H), 7.76 (m, 18H); $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$): -77.45

Synthesis of 12:
hBi100 mg, 0.227 mmol) was dissolved in a small amount of dichloromethane (3 ml) and added to a solution of \([\text{PhI(DMAP)}_2][\text{OTf}]_2\) (169 mg, 0.227 mmol; 3 ml). The mixture was stirred for overnight and filtered to remove unreacted oxidant. EtO₂ (5 ml) was added to the solution resulting in precipitation of a white solid. The solution was decanted and the solid dried \textit{in vacuo}. Yield 0.148g 66%. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.9 (br, 4H), 7.77 (d, 8H), 7.59 (br, 7H), 6.64 (br, 2H), 3.13 (s, 12H); ¹⁹F{¹H} NMR (376 MHz, CDCl₃): -74.8

Synthesis of 13:

Ph₃Bi (100 mg, 0.227 mmol) was dissolved in a small amount of dichloromethane (3 ml) and added to a solution of PhI(OAc)(OTf) (114 mg, 0.227 mmol; 3 ml). The mixture was stirred for 1 hour and stored overnight at -35°C. Large clear crystals were isolated from the solution followed by removal of the solution \textit{in vacuo}. Yield 0.034g 35% ¹H NMR (400 MHz, DMSO): δ 8.25 (m, 6H), 7.67 (d, 6H), 7.41 (m, 6H); ¹⁹F NMR (376 MHz, DMSO): -77.74
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Supporting Information For:

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Compound 7-\textsuperscript{1}H NMR

Compound 7-\textsuperscript{19}F NMR
Compound 9- $^1$H NMR

Compound 10- $^1$H NMR
Compound 10-^{19}F NMR

Compound 10-^{13}C NMR
Compound 11-¹H NMR

Compound 11-¹⁹F NMR
Compound 13- $^1$H NMR

Compound 13- $^{19}$F NMR
