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Article

Stabilized Arsenic(I) Iodide: A Ready Source of Arsenic Iodide Fragments and a Useful Reagent for the Generation of Clusters

Bobby D. Ellis and Charles L. B. Macdonald*

Department of Chemistry and Biochemistry, University of Windsor,
Windsor, Ontario, Canada N9B 3P4

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The new stable low oxidation state arsenic(I) iodide reagent [(dppe)As][I] (dppe = 1,2-bis(diphenylphosphino)-ethane) exhibits chemistry that is considerably different from its As^{III} analogues. While [(dppe)As][I] is not crystalline, the crystal structure of the derivative salt [(dppe)As][(dppe)As_2I_7] is reported and is compared to that of [(dppe)-As]$_2$[$SnCl_6$]·2CH_2Cl_2. The air oxidation of [(dppe)As][I] produces crystals of the salt [$Ph_2P(O)CH_2CH_2P(OH)Ph_2$]$_2$-[$As_6I_8$]·2$CH_2Cl_2$ and suggests that, in contrast to previous studies, the reaction of the univalent arsenic iodide salt with certain oxidants results in the oxidation of the dppe ligand and the release of "As^I-I" fragments that oligomerize to form As^I clusters. Such reactivity is confirmed by the reaction of 6[(dppe)As][I] with 12Me_3NO and 2[PPh_4][I] to produce [PPh_4]$_2$[As_6I_8] and 6dppeO_2. The reactivity is rationalized using density functional theory calculations.

Introduction

The chemistry of group 15 elements (pnictogens, Pn) in low-coordinate or multiple-bonded environments has been an active area of research over the last 30 years. The results of such investigations have provided for numerous insights into the rules governing the chemistry of the main group elements in general.[1,2] Research in this area has primarily concentrated on compounds containing pnictogen atoms in either of their typical oxidation states (+3 or +5), while the chemistry of compounds containing pnictogens in lower oxidation states has been largely ignored.

While the majority of the research into the chemistry of compounds containing group 15 elements in the +1 oxidation state has focused on P^I, there has been limited development of As^I chemistry. The first As^I cation was reported by Gamper and Schmidbaur in 1993, which was prepared by the reduction of $AsCl_3$ with $SnCl_2$ in the presence of a chelating diphosphine;[3] this approach is analogous to the method used by Schmidpeter et al. to isolate their first P^I cation.[4] Similarly, Dillon and co-workers have recently used $SnCl_2$ to reduce $AsCl_3$ in solutions containing various chelating phosphines to produce salts that were identified by their ^{31}P NMR shifts and, for two compounds, by X-ray crystallography.[5] An analogous approach to the synthesis of As^I cations is the reduction of $AsCl_3$ by an additional equivalent of phosphine, typically $P(NMe_2)_3$,[6,7] which generates the arsenic analogues of the acyclic P^I cation isolated by Schmidpeter and Lochschmidt.[8] A related, but perhaps surprising, approach to As^I-containing molecules involves the reaction of $AsCl_3$ with lithium salts, either $LiC(PPh_2)_2(SiMe_3)$ or $LiN(PPh_2)_2$, which act as both metathesis and reducing agents to produce cyclic As^I compounds.[9−11]

We have recently reported an improved synthesis of As^I cations from AsI_3, which disproportionates in the presence of a chelating diphosphine to give As^I-I fragments that are trapped by the ligand and I_2.[12] This simple approach obviates the external reducing agent and produces arsenic(I) iodide in high yield. We have undertaken an investigation of the

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* Author to whom correspondence should be addressed. Phone: (519)-253-3000, ext 3991. Fax: (519)973-7098. E-mail: cmacd@uwindsor.ca.

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low oxidation state chemistry of the p-block elements and herein we report some results concerning our new source for As^{I} and we demonstrate that our precursor is an effective reagent for the controlled production of As^{I}-I fragments.

Experimental Section

General Methods. All work was carried out using standard inert atmosphere techniques. Arsenic(III) iodide and 1,2-bis(diphenylphosphino)ethane (dppe) were purchased from Strem, Me_3NO was obtained from Aldrich, and $[PPh_4P][I]$ was procured from Fluka; all reagents were used without further purification. The preparations of [(dppe)As][I] (**1**) and $[(dppe)As]_2[SnCl_6]\cdot 2CH_2Cl_2$ (**3**$\cdot 2CH_2Cl_2$) are described in preliminary communications.[12,13] Solvents were dried on a series of Grubbs' type columns and were degassed prior to use.[14] NMR spectra were recorded at room temperature in CD_2Cl_2 solutions on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards ($SiMe_4$ for ^1H and ^{13}C, 85% aqueous H_3PO_4 for ^{31}P). Coupling constant magnitudes $|J|$ are given in Hertz. FT-IR spectra were recorded as Nujol mulls on KBr plates using a Bruker Vector 22 spectrometer and are presented as wavenumber (cm^{-1}) maxima. Melting points were obtained using an Electrothermal melting point apparatus on samples sealed in glass capillaries under dry nitrogen. Elemental analysis experiments were performed in-house in the Centre for Catalysis and Materials Research, Department of Chemistry and Biochemistry, University of Windsor. Please note that the yields reported are after the salt had been washed several times; unfortunately, some of the byproducts have similar solubility characteristics as the products and efforts to obtain satisfactory elemental analyses have been unsuccessful. It must also be noted that the reactions appear to be quantitative according to all spectroscopic data recorded.

Caution: Arsenic compounds are toxic and should be handled with care.

Preparation of $[(dppe)As][(dppe)As_2I_7]$ (2). AsI_3 (0.527 g; 1.157 mmol) and dppe (0.307 g; 0.771 mmol) were stirred in CH_2Cl_2 (20 mL) for 2 h to afford an orange solution with yellow precipitate. The precipitate was removed by filtration to produce an orange solution. The slow vacuum removal of volatile compounds from the filtrate yielded 0.452 g of a yellow crystalline solid in 61% yield. mp 116−118 °C (dec). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 60.4 (s), −13.6 (s, br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 133.5 (s), 133.4 (s), 133.3 (s), 131.5 (s), 130.4 (s), 130.3(s), 130.2 (s), 128.0 (s, br), 27.5 (s, br). ^1H NMR (CD_2Cl_2) δ: 7.59 (m, 20H), 2.97 (s, br, 4H). IR (cm^{-1}): 1584.1 (w), 1568.9 (w), 1434.8 (m), 1094.9 (w), 737.0 (w), 686.2 (m), 529.2 (w), 513.4 (w).

Preparation of $[PPh_4]_2[As_2I_8]$ (5). [(dppe)As][I] (0.270 g; 0.450 mmol) was stirred in CH_2Cl_2 (15 mL) while a solution of $[PPh_4P][I]$ (0.070 g; 0.150 mmol) in CH_2Cl_2 (5 mL) was added via cannula. A solution of Me_3NO (0.068 g; 0.900 mmol) in CH_2Cl_2 (5 mL) was then added immediately via cannula, and the clear orange solution became cloudy yellow. The mixture was stirred for 1 h. The white precipitate that formed was removed by filtration to afford a clear yellow filtrate. The solvent was removed in vacuo, and the yellow solid was washed with PhMe (5 mL) and Et_2O (5 mL) to remove $dppeO_2$. The yellow solid was dissolved in a minimal amount of CH_2Cl_2 and upon slow evaporation yielded 0.083 g of a yellow crystalline solid in 52% yield. mp 204−205 °C (dec). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 23.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 136.2 (s), 135.0 (s), 131.2 (s), 118.0 (d, $^1J_{C-P} = 89$). ^1H NMR (CD_2Cl_2) δ: 7.93 (m, 1H), 7.79 (m, 2H), 7.62 (m, 2H). IR (cm^{-1}): 1584.3 (w), 1435.6 (m), 1186.6 (m), 1175.3 (m), 1122.8 (m), 1107.1 (m), 996.2 (w), 763.07 (w), 753.28 (m), 740.83 (m), 730.13 (m), 694.17 (m), 531.84 (m), 512.21(w).

X-ray Crystallography. Each crystal was covered in Nujol and placed rapidly into the cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using the SMART[15] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 30 s per frame. The data were collected at −100 °C. Details of crystal data, data collection, and structure refinement are listed in Table 1 and selected metrical parameters are compiled in Tables 2 and 3. Data reductions were performed using the SAINT[16] software, and the data were corrected for absorption using SADABS.[17] The structures were solved by direct methods using SIR97[18] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97[19] and the WinGX[20] software package, and thermal ellipsoid plots were produced using SHELXTL.[21]

Powder X-ray diffraction experiments were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using Cu Kα radiation ($\lambda = 1.54186$ Å).

Results and Discussion

As^{I} Salt Structure. We have recently reported the preparation of the univalent arsenic iodide salt [(dppe)As][I] (**1**) from the treatment of AsI_3 with 1,2-bis(diphenylphosphino)ethane (dppe) in methylene chloride.[12] While the purity of **1** was confirmed by both spectroscopic and microanalytical methods, we have yet to obtain crystalline material of the salt suitable for a single-crystal X-ray diffraction experiment. The powder X-ray diffraction spectrum of "as prepared" pure **1** did not exhibit any peaks and suggests that it is noncrystalline.

In an attempt to obtain X-ray quality single crystals of **1**, the reaction mixture of dppe and AsI_3 was allowed to stir overnight before removal of the volatile substances. ^{31}P NMR spectrum of a CD_2Cl_2 solution of the solid thus obtained exhibited two peaks that are attributable to coordinated dppe fragments: the peak at 60.4 ppm was consistent with the expected shift for the cation $[(dppe)As]^{+1}$; however, identity of the component that gives rise the much broader peak at −13.6 ppm was unclear. Fortunately, concentration of such reaction mixtures consistently results in the deposition of orange prism-shaped crystals amenable to crystallographic study. The results of such diffraction experiments allow for

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Table 1. Summary of X-ray Crystallographic Data for Compounds **2**−**5**

	2	**3**·$2CH_2Cl_2$	**4**·$2CH_2Cl_2$	**5**
formula	$[(dppe)As][(dppe)As_2I_7]$	$[(dppe)As]_2[SnCl_6]\cdot 2CH_2Cl_2$	$[(dppe)O_2H]_2[As_6I_8]\cdot 2CH_2Cl_2$	$[PPh_4]_2[As_6I_8]$
empirical formula	$C_{52}H_{48}As_3I_7P_4$	$C_{54}H_{52}As_2Cl_{10}P_4Sn$	$C_{27}H_{27}As_3Cl_2I_4O_2P_2$	$C_{24}H_{20}As_3I_4P$
formula weight	1909.84	1447.87	1248.69	1071.73
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions:				
a (Å)	19.1484(15)	10.8800(7)	11.7825(7)	11.7453(6)
b (Å)	18.8443(15)	11.6470(7)	12.4177(7)	11.9257(6)
c (Å)	16.6084(13)	12.9540(8)	13.1465(7)	12.0263(6)
α (deg)	90	69.144(1)	79.601(1)	75.273(1)
β (deg)	91.508(2)	79.827(1)	88.659(1)	77.412(1)
γ (deg)	90	81.868(1)	74.866(1)	65.189(1)
vol ($Å^3$)	5990.9(8)	1504.33(16)	1825.71(18)	1466.89(13)
Z	4	1	2	2
ρ (calcd) ($g\cdot cm^{-3}$)	2.117	1.598	2.271	2.426
μ (mm^{-1})	5.411	2.102	6.370	7.673
F(000)	3560	722	1160	980
θ range (deg)	1.06 to 27.52	1.88 to 27.50	1.73 to 27.52	1.76 to 27.52
reflns collected/unique	56704/13767	13130/6553	17948/8338	14454/6718
R_{int}	0.0489	0.0286	0.0239	0.0295
data/restraints/parameters	13767/0/595	6553/0/344	8338/0/365	6718/0/309
GOF on F^2	1.040	1.284	1.068	1.023
R1 indices[a] $[I > 2\sigma(I)]$	0.0436	0.0518	0.0325	0.0316
wR2 indices[a] (all data)	0.0985	0.1084	0.0835	0.0831
largest difference map peak and hole ($e\cdot Å^{-3}$)	1.610 and −0.690	1.347 and −1.220	1.208 and −1.168	1.449 and −1.261

[a] $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $wR2(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2\}^{1/2}$ where *w* is the weight given each reflection.

Table 2. Selected Metrical Parameters for **2** and **3**

parameter	$[(dppe)As][(dppe)As_2I_7]$ (**2**) cation	anion	$[(dppe)As]_2[SnCl_6]$ (**3**)
	Distances (Å)		
As−P(1)	2.2559(17)	2.5383(15)	2.2519(12)
As−P(2)	2.2542(18)	2.5275(14)	2.2509(12)
P(1)−C(1)	1.852(6)	1.810(5)	1.816(4)
P(2)−C(2)	1.851(6)	1.821(5)	1.819(4)
C(1)−C(2)	1.391(9)	1.520(8)	1.533(6)
As(2)−I(1)		2.7838(7)	
As(2)−I(2)		2.8636(7)	
As(2)−I(3)		3.1641(7)	
As(2)−I(4)		3.1307(6)	
As(3)−I(2)		3.3229(7)	
As(3)−I(3)		3.3749(8)	
As(3)−I(4)		3.1182(7)	
As(3)−I(5)		2.6741(7)	
As(3)−I(6)		2.6442(7)	
As(3)−I(7)		2.6373(7)	
	Angles (°)		
P(1)−As−P(2)	85.44(6)	82.60(5)	85.63(4)
As−P(1)−C(1)	106.0(2)	103.02(18)	106.42(14)
As−P(2)−C(2)	105.6(2)	103.95(18)	107.88(14)
P(1)−C(1)−C(2)	109.3(4)	112.4(4)	107.5(3)
P(2)−C(2)−C(1)	108.9(4)	112.0(4)	107.4(3)

Table 3. Selected Metrical Parameters for **4** and **5**

parameter	$[(dppe)O_2H]_2[As_6I_8]$ (**4**)	$[PPh_4]_2[As_6I_8]$ (**5**)
	Distances (Å)	
O(1)−P(1)	1.533(3)	
O(2)−P(2)	1.521(3)	
P(1)−C(1)	1.804(4)	
P(2)−C(2)	1.803(4)	
C(1)−C(2)	1.539(5)	
As(1)−I(1)	2.7136(5)	2.6951(7)
As(2)−I(2)	2.6862(5)	2.6608(7)
As(3)−I(3)	2.6367(6)	2.6911(6)
As(1)−I(4)	4.1676(5)	4.1033(6)
As(2)−I(4)	3.1472(6)	3.1578(7)
As(3)−I(4)	4.0500(5)	3.9981(6)
As(1)−As(2)	2.4656(6)	2.4709(7)
As(2)−As(3)	2.4599(6)	2.4563(8)
As(3)−As(1a)	2.4563(6)	2.4708(8)
	Angles (°)	
As(1)−As(2)−As(3)	96.46(2)	100.90(3)
As(2)−As(3)−As(1a)	98.73(2)	101.62(3)
As(3)−As(1a)−As(2a)	97.47(2)	97.68(3)
avg As−As−I(terminal)	89.74	89.29

the identification of both peaks in the ^{31}P NMR spectrum and reveal that the salt obtained under these reaction conditions is $[(dppe)As][(dppe)As_2I_7]$ (**2**), as shown in eq 1

$$2dppe + 3AsI_3 \xrightarrow{-I_2} \underset{\mathbf{2}}{[(dppe)As][(dppe)As_2I_7]} \qquad (1)$$

The mixed valence salt $[(dppe)As][(dppe)As_2I_7]$ crystallizes in the space group $P2_1/c$ and exhibits no unusually short cation−anion contacts. The asymmetric unit of **2**, depicted in Figure 1, consists of a single As^I cation, $[(dppe)As]^{+1}$, and an unprecedented dinuclear As^{III} monoanion, $[(dppe)As_2I_7]^{-1}$. The metrical parameters of the "(dppe)As" fragment in each of the ions, listed in Table 1, are distinct and emphasize the differences in the bonding between the diphosphines and the As^I and As^{III} centers. In particular, the P−As distances in the cation (2.2559(17) Å and 2.2542(18) Å) are considerably shorter than the corresponding distances in the anion (2.5383(15) Å and 2.5275(14) Å). It should be noted that the average As−P single bond distance from the Cambridge Structural Database[22] is 2.341 Å and the longest distance previously reported was 2.394 Å.[23] While the steric

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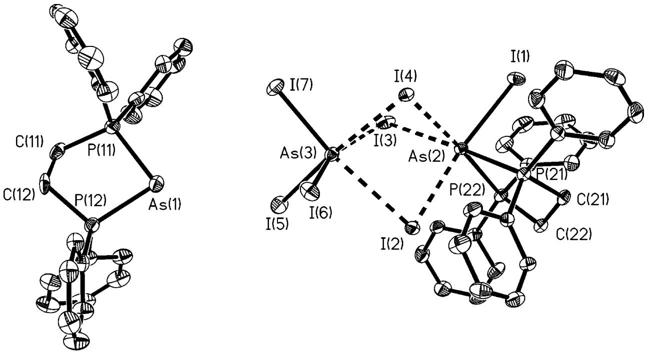

Figure 1. Thermal ellipsoid plot (30% probability surface) of the molecular structure of [(dppe)As][(dppe)As_2I_7] (**2**); hydrogen atoms are omitted for clarity. Selected metrical parameters for this salt are listed in Table 2.

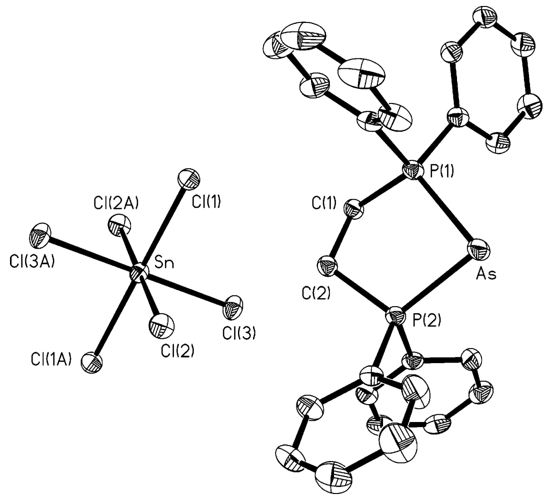

Figure 2. Thermal ellipsoid plot (30% probability surface) of a cation and anion of $[(dppe)As]_2[SnCl_6]\cdot 2CH_2Cl_2$, ($\mathbf{3}\cdot 2CH_2Cl_2$). Hydrogen atoms and a molecule of methylene chloride have been removed for clarity. Selected metrical parameters for this salt are listed in Table 2.

consequences of the high coordination number of the As atom in the anion results in a significantly increased As−P distance, the shorter AS−P distance in the cation is consistent with the presence of π back-bonding between the As^I center and the dppe ligand. Such an interpretation of the bonding in the cation is in accordance with the results of computational investigations.[12] The larger P−As−P angle in the cation (85.44(6)° vs 82.60(5)° in the anion) is consistent with the shorter P−As distances and the constraints of the dppe ligand. Overall, the structure of the cation is identical to that found in the salt $[(dppe)As]_2[SnCl_6]$ (**3**), depicted in Figure 2, which we have synthesized for comparison by the reduction of $AsCl_3$ with $SnCl_2$ in the presence of the diphosphine.[13]

The structure of the anion, while unique, is clearly related to those of polyanions of the type $[As_2X_8]^{-2}$ and $[As_2X_9]^{-3}$.[24,25] Each arsenic atom in the anion exhibits a distorted octahedral coordination environment composed of three terminal ligands and three bridging iodide anions; the lone pairs of electrons on these As^{III} centers are not stereochemically active. The presence of three bridging ligands allows the overall structure of the anion to be described as being composed of two face-sharing AsL_6 octahedra. Predictably, the distances to the terminal iodide anions (As(2)−I(1): 2.7838(7) Å; range for As(3) terminal I atoms: 2.6373(7)-2.6741(7) Å) are significantly shorter than those to the bridging ligands (range for As(2) to μ-I: 2.8636(7)-3.1641(7) Å; range for As(3) to μ-I: 3.1182(7)- 3.3749(8) Å). Overall, the metrical parameters of the anion in **2** are consistent with the analogous values reported for $[As_2I_8]^{-2}$ [26] (unfortunately $[As_2I_9]^{-3}$ has not yet been reported) and do not require further comment.

It should be noted that the production of **1** or **2** in such reactions appears to be highly dependent on the concentration of the reagents in solution. Obviously, if a stoichiometry of $3AsI_3$ to 2dppe is used in a dilute reaction, the reaction produces **2** in high yield. However, when equimolar amounts of AsI_3 and dppe are mixed, the proportion of **1** and **2** obtained is determined by the concentration of the solution. If the solution is adequately dilute, such that the AsI_3 is completely dissolved, only **1** is formed. While the actual process involved in the formation of the anion is unclear, the composition of the ion suggests that two equivalents of AsI_3 interact with an iodide anion and one dppe ligand to produce the dinuclear anion.

Oxidative Ligand Cleavage. Whereas the salt **3** appears to be relatively stable when exposed to the atmosphere, **1** is air-sensitive. Although such sensitivity is predictable, the actual product of the decomposition is unexpected and suggests a new and unique use for such molecules. When a solution of **1** in methylene chloride was exposed to the atmosphere, large prism-shaped crystals formed after 7 days. The ^{31}P NMR spectrum of a CD_2Cl_2 solution of this solid exhibited a single signal at 32 ppm, indicative of the oxidation of dppe; however, the composition of the solid remained unclear.

A single-crystal X-ray diffraction experiment revealed that the solid obtained is the new salt $[Ph_2P(O)CH_2CH_2P(OH)Ph_2]_2[As_6I_8]$ (**4**). The salt is composed of oxidized and monoprotonated dppe cations and a heterocubane dianion $[As_6I_8]^{-2}$. The molecular structures of the cations and anion are shown in Figure 3. Two cations form a centrosymmetric dimer by way of intermolecular hydrogen bonding interactions (the H atom was found in the Fourier difference map and refined isotropically; the O(1)−O(2a) distance is 2.416(4) Å) and have no unusually close interactions with the dianion. While such hydroxyphosphonium−phosphine oxide cations are quite rare, the metrical parameters and overall structure are as one would expect.[27]

The dianion is composed of an As_6I_6 ring arranged in a chair conformation (with each terminal iodine ligand in an equatorial position) and is rendered dianionic by the μ_3-iodide anions that cap each face of the ring. The metrical parameters for the centrosymmetric dianion, compiled in Table 3, are essentially identical to those reported for the only other

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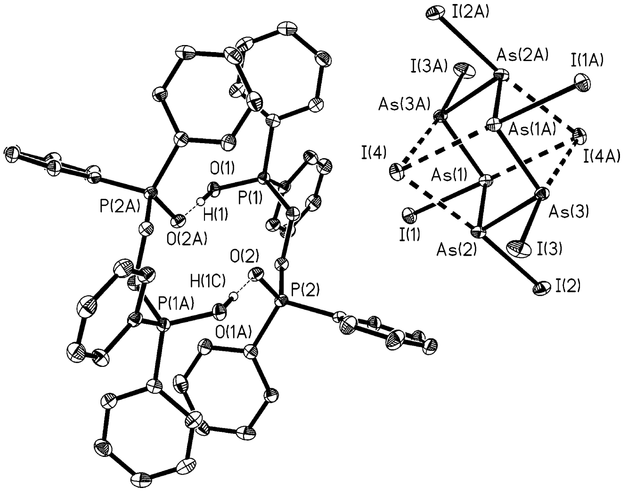


Figure 3. Thermal ellipsoid plot (30% probability surface) of a cation and anion of $[Ph_2P(O)CH_2CH_2P(OH)Ph_2]_2[As_6I_8]\cdot 2CH_2Cl_2$ (**4**$\cdot 2CH_2Cl_2$). Most of the hydrogen atoms and a molecule of methylene chloride have been removed for clarity. Selected metrical parameters for this salt are listed in Table 3.

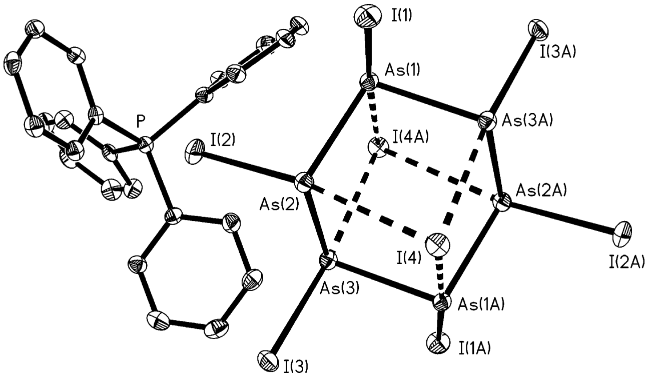
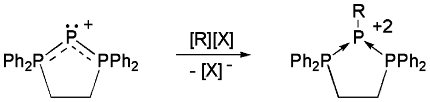


Figure 4. Thermal ellipsoid plot (30% probability surface) of a cation and anion of $[PPh_4]_2[As_6I_8]$ (**5**). Hydrogen atoms have been removed for clarity. Selected metrical parameters for this salt are listed in Table 3.

Scheme 1. "Typical" Oxidation of a P^I Center by Various Oxidants[a]



[a] R = proton or methyl cations; X = halide, tetrachloroaluminate, or trifluoromethanesulfonate anions.

examples of such anions.[28,29] For example, the As−As distances range from 2.4599(11) Å to 2.4657(11) Å; the As−I distances to the terminal I atoms range from 2.6367(6) Å to 2.7136(5) Å. The As−I distances to the bridging iodide anions are longer and range from 3.1472(6) Å to 4.1676(5) Å and attest to the distorted arrangement of the heterocubane core.

While the mechanism of the formation of **4** remains unclear, the nature of the salt components are important for the insight that they provide into the reactivity, and potential utility, of compounds such as **1**. Most importantly, the dianion is composed of six As^I centers, which are clearly not oxidized in the process. Consequently, the oxidation appears to happen exclusively at the dppe ligand. Together, the results suggest that the oxidation of the dppe ligand releases intact As^I-I fragments; these fragments can then cyclize to produce the As_6I_6 ring (cf. As_6Ph_6 or the other organoarsenic analogues[30]). Overall, the components of the decomposition product suggested to us that selective oxidation of the stabilizing ligand may be used to effect the controlled release of arsinidene fragments.

To test our hypothesis, we undertook a more rational synthesis of a salt of the heterocubane dianion. In this vein, the reaction of six equivalents of **1** with 12 equiv of trimethylamine-*N*-oxide in the presence of 2 equiv of tetraphenylphosphonium iodide results in the formation of $[PPh_4]_2[As_6I_8]$ (**5**) in high yield (eq 2). It should be noted that the only other reported syntheses of such anions resulted from the unintended reduction of $[As_2SBr_5]^{-1}$ or AsI_3 by transition metal complexes, making the method described herein the only rational synthesis of such a cluster:

$$\underset{\mathbf{1}}{6[(dppe)As][I]} + 12Me_3NO + 2[PPh_4][I] \xrightarrow[-12Me_3N]{-6dppeO_2} \underset{\mathbf{5}}{[PPh_4]_2[As_6I_8]} \quad (2)$$

Recrystallization of the salt from methylene chloride produced yellow crystals of **5** that were suitable for X-ray diffraction. The structure of the salt is depicted in Figure 4, and there are no unusually short cation−anion contacts. The geometry of the tetraphenylphosphonium cation is typical of the type and the structure of the $[As_6I_8]^{-2}$ anion is identical to that described for **4**, as evidenced by the metrical parameters listed in Table 3.

It should be noted that the oxidation of the dppe ligand is in stark contrast to the results observed in the oxidation reactions performed initially by Schmidpeter et al.[31] and more recently by Dillon and Olivey[32] for analogous P^I compounds. The oxidation of triphosphenium cations with $H[AlCl_4]$, alkylhalides, and methyl trifluoromethanesulfonate sometimes results in the oxidation of the dicoordinate P^I atom to give a P^{III} compound, as illustrated in Scheme 1, while the reactions reported herein clearly involve the oxidation of the dppe ligand.

A simplistic rationale for this differing reactivity is suggested by the electronic structures of both the cation and the particular oxidizing agent used in each reaction. As illustrated in Figure 5,[33−34] density functional theory calculations on the model compound $[(Me_2PCH_2CH_2PMe_2)As]^{+1}$ reveal that whereas the highest occupied molecular orbital (HOMO) is based primarily on the dicoordinate As atom, the lowest unoccupied molecular orbital (LUMO) of the cation is based primarily on the stabilizing ligand.[12] In this light, lone-pair bearing ("nucleophilic") oxidizing agents such as Me_3NO, oxygen or other elemental chalcogens may tend to attack the stabilizing ligand, as observed in the reactions

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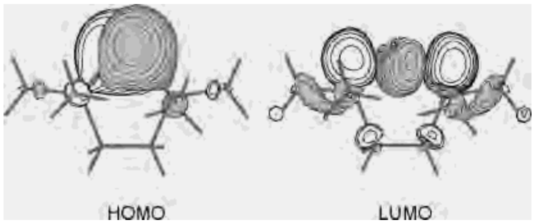

Figure 5. MOLDEN[33] depictions of the highest-occupied and lowest-unoccupied molecular orbitals for the model cation $[(Me_2PCH_2CH_2PMe_2)As]^{+1}$ calculated at the B3PW91/6-311+G(3df,2p)//B3PW91/6-31G(d) level of theory using the G98 suite of programs.[34]

producing **4** and **5**. In contrast, non-lone-pair bearing ("electrophilic") oxidizing agents, such as a proton or a methyl cation, tend to react with the univalent dicoordinate pnictogen atom. While additional work is required to prove this hypothesis, such a reactivity model suggests that a high level of control over the nature of the products obtained in such reactions may be attainable.

Furthermore, we believe that the "release" chemistry (oxidative or otherwise) described above may well be relatively general for compounds such as **1**. For example, the planar phosphonium and arsonium cations reported by Driess and co-workers definitely result from a similar cleavage of the ligands and liberation of "free" P^I or As^I cations.[35,36] It should be noted that for arsenic, salts containing the cation found in **1** with robust anions appear to be stable indefinitely in inert atmospheres. As such, these salts are potentially more practical As^I precursors than salts containing the relatively short-lived $[As(P(NMe_2)_3)_2]^{+1}$ cations.

Conclusions

We have discovered convenient and mild methods for the preparation, stabilization, and delivery of As^I cations and related arsinidenes. While the solid-state structure of **1** remains unavailable, the structure of the mixed valence salt **2** confirms the structure of the cation and highlights the differences in the bonding of dppe ligands to As^I and As^{III} centers. More importantly, initial observations and experiments indicate that compounds such as **1** may be used as sources of As^I species. In particular, the reaction of our improved As^I source **1** with Me_3NO results in the formation of clusters composed of As^I-I fragments. We are currently investigating the application of similar reactions for the synthesis of new reagents for the controlled formation of interesting clusters and the deposition of layers of group 15 elements.

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Supporting Information Available: Summary of computational results and crystallographic data in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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