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Phosphinoarsonium and Diarsonium Cations from Chloride-Abstraction-Induced Pnictogen Coupling

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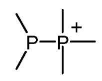
The first salts of phosphinoarsonium, diarsonium, and phosphinodiarsonium ions are obtained from reaction mixtures of a chlorophosphine, a tertiary arsine, and a chloride-abstracting agent. The versatile synthetic approach has implications in the development of a wide variety of interpnictogen compounds.

A variety of high-yield preparative reactions have been reported that provide a catalog of *catena*-phosphorus cations.[1–10] Together with the neutral[11–14] and anionic[11–13,15–24] analogues, *catena*-phosphorus compounds have the potential to achieve the extent and diversity of chemistry based on *catena*-carbon frameworks. The prototypical phosphinophosphonium **1**,[4] diphosphonium **4**,[25] and phosphinodiphosphonium **7**[1] ions as well as larger frameworks[5–10] have been substitutionally derivatized; however, diversification within the pnictogen skeleton is currently limited to derivatives of framework **2** (Pn = As,[26] Sb, Bi[27]). Triphosphorus cations of type **7** were first obtained from reaction mixtures of a dichlorophosphine, a tertiary phosphine, and aluminum chloride,[1] and we have now applied this approach more generally to prepare the first salts of phosphinoarsonium **3**, diarsonium **6**, and phosphinodiarsonium **9** ions.



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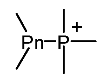

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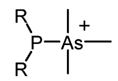
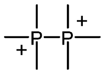
Pn = As, Sb or Bi



3(R)



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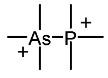

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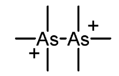

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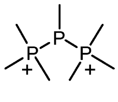

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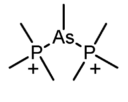

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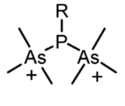

9(R)

^{31}P NMR spectra of reaction mixtures composed of $ClPR_2$ (R = Me, Ph), Me_3As, and $Me_3SiOSO_2CF_3$ (TMSOTf) in

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Table 1. ^{31}P NMR Data for Derivatives of **2**,[26,28,29] **3**, and **9**

compound	^{31}P{^{1}H} NMR	ref
[**2a**][PF_6]	19.0	26
[**2b**][BPh_4]	59.2	28
[**2c**][OTf]	6.0	29
[**3**(Ph)][OTf]	−2.2	[a]
[**3**(Me)][OTf]	−15.8	[a]
[**9**(Me)][$OTf]_2$	−15.1	[a]
[**9**(Ph)][$OTf]_2$	−6.2	[a]
[**9**(Et)][$OTf]_2$	−17.2	[a]
[**9**(Cy)][$OTf]_2$	−2.0	[a]
[**9**(^{i}Pr)][$OTf]_2$	2.7	[a]

[a] This work.

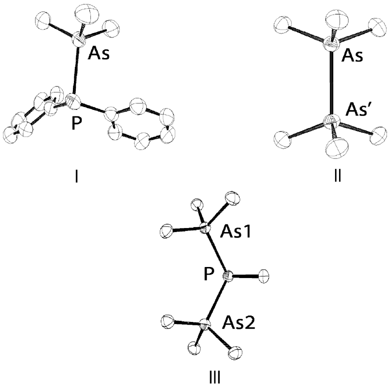
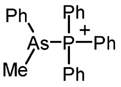
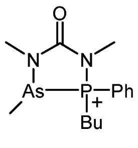


Figure 1. Representative solid-state views of the cation in [**3**(Ph)][OTf] (**I**), [**6**][$OTf]_2$ (**II**), and [**9**(Me)][$OTf]_2$ (**III**). Ellipsoids are at 50% probability. Hydrogen atoms not shown.

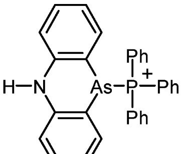
CH_2Cl_2 show the formation of a single phosphorus-containing species that has been isolated and comprehensively characterized as the trifluoromethanesulfonate (triflate) salt of phosphinoarsonium cations **3**(R) (R = Me, Ph). The analogous reaction of Cl_2PR (R = Me, Et, Ph, Cy, ^{i}Pr), Me_3As, and TMSOTf gives salts of phosphinodiarsonium cations **9**. In comparison, the combination of Cl_3P with Me_3As and TMSOTf gives hexamethyldiarsonium triflate [**6**][$OTf]_2$. Table 1 lists ^{31}P NMR data for derivatives of **3** and **9**, together with values for[**2a**]-[PF_6],[28] [**2b**][BPh_4],[26] and [**2c**][OTf].[29] X-ray crystallographic data confirm the identity of [**3**(Ph)][OTf], [**6**][$OTf]_2$, and [**9**(Me)][$OTf]_2$, and representative views of the cations in the solid state are shown in Figure 1. Selected structural parameters for the cations are listed in Table 2, together with comparative values for derivatives of the arsinophosphonium framework (**2**).[26,28,29]



2a



2b



2c

Table 2. Selected As−P Distances (Å), C−As−C and C−As−P Angles (deg) in [**3**(Ph)][OTf], [**6**][$OTf]_2$, [**9**(Me)][$OTf]_2$, [**2a**][PF_6],[28] [**2b**][BPh_4],[26] and [**2c**][OTf][29]

compound	As−Pn	C−As−Pn	As−P−As	As−P−C(R)
[**2a**][PF_6]	2.3480(5)	92.31(8) 97.04(6)		
[**2b**][BPh_4]	2.346(2) 2.341(2)			
[**2c**][OTf]	2.4121(5)	95.76(6) 99.38(5)		
[**3**(Ph)][OTf]	2.3239(7)	110.58(9) 113.72(10) 108.88(10)		*98.94(8)* *98.32(7)*
[**6**][$OTf]_2$	2.4109(3)	110.64(7)		
[**9**(Me)][$OTf]_2$	2.3267(6) 2.3283(6)	C1: 120.29(8) C2: 102.89(8) C3: 111.57(8) C5: 121.06(7) C6: 106.11(8) C7: 107.83(8)	106.80(2)	99.77(8) 99.63(8)

Chlorophosphines ($ClPR_2$, Cl_2PR) are activated by TMSOTf, which effects chloride abstraction and in the presence of the tertiary arsine Me_3As enables the formation of coordinate P ← As bonds in **3** and **9**, more appropriately described as a phosphinoarsonium bond. The consequential pnictogen coupling is a rational and high-yield synthetic approach to interpnictogen frameworks. The formation of the diarsonium cation **6** from Cl_3P, Me_3As, and TMSOTf represents a redox process that is induced by chloride abstraction and implicates the formation of phosphorus subchlorides or elemental phosphorus. This reaction contrasts those of Cl_3P, R_3P, and $AlCl_3$, which give [R_3PPPR_3]-[$AlCl_4$].[2,3] We are currently targeting derivatives of framework **5** through alkylation of framework **3** and framework **8** through reactions of dichloroarsines with tertiary phosphines in the presence of a halide-abstracting agent.

^{31}P NMR chemical shifts for derivatives of **3** and **9** occur in a narrow range that is typical of phosphine centers in phosphinophosphonium cations.[4] Indeed, the chemical shifts of the phosphonium centers in derivatives of **2** are only slightly more positive.[26,28,29] The As−P bond lengths in **3**(Ph) and derivatives of **9** are very consistent and are slightly shorter than those in derivatives of arsinophosphonium **2** cations. The pyramidal environments for the phosphorus centers in **3**(Ph) and **9**(Me), with angles of close to 100°, are typical of phosphine centers, and the As−P−As angles in **9**(Me) are predictably larger than As−P−C angles because of steric interactions between the terminal substituents on arsenic. For the same reasons, the arsonium centers in **3**(Ph) and in **9**(Me) are also substantially distorted from a tetrahedral geometry. The eclipsed conformation of the diarsonium cation **6** reveals an As−As bond length [2.4109(3) Å] that is only slightly shorter than that in a neutral diarsine ([MesC(O)]$_2$As−As[C(O)Mes]$_2$ = 2.4300(8) Å).[30] For comparison, a larger difference is observed between the Sb−Sb bond length in the hexamethyldistibonium dication [2.7624(11) and 2.7867(12) Å] and in tetramethyldistibine [2.862(2), 2.830(1), and 2.838(1) Å].[31]

In summary, reaction mixtures of chlorophosphines with Me_3As and TMSOTf result in P−As bond formation via chloride abstraction to give the first examples of phosphi-

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noarsonium cations. Similarly, dichlorophosphines give the first phosphinodiarsonium dications. In contrast, trichlorophosphine oxidizes Me_3As to give the first diarsonium dication. This versatile synthetic approach has implications in the development of a wide variety of interpnictogen compounds.

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Supporting Information Available: All experimental details including crystallographic information files (CIF) for all of the compounds presented above. This material is available free of charge via the Internet at http://pubs.acs.org.

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