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Phosphinopnictonium Cations: High Yield and General Preparative Procedures for New Interpnictogen Frameworks Exploiting As→P and Sb→P Coordinate Bonds

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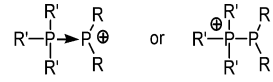
Abstract: Reactions of R_3Pn (Pn = As or Sb; R = Me, Et or Ph) with R'_2PCl or $R'PCl_2$ (R′ = Me, Et, Ph, Cy, ^{i}Pr), in the presence of a halide abstracting agent ($Me_3SiOSO_2CF_3$, $GaCl_3$, or $AlCl_3$), give salts with cations containing Pn−P bonds. The bond formation is envisaged to proceed by activation of the P−Cl bond and coordination of the pnictine to the resulting phosphorus cation (R'_2P^+ or $R'P^{2+}$, respectively). Salts of the first phosphinoarsonium cations, $[R_3As\text{-}PR'_2]^+$, and the first 2-phosphino-1,3-diarsonium dications, $[R_3AsP(R')AsR_3]^{2+}$, have been isolated and comprehensively characterized. In contrast, reactions involving Ph_3Sb give 2,3-diphosphino-1,4-distibonium dications, $[R_3SbP(R')P(R')SbR_3]^{2+}$, resulting from a single P−Cl activation (abstraction) at each of two phosphorus centers and reductive P−P coupling effected by Ph_3Sb. The analogous 2,3-diphosphino-1,4-diarsonium dication $[R_3AsP(R')P(R')AsR_3]^{2+}$ can be accessed from the 2,3-diphosphino-1,4-distibonium cation by a ligand exchange reaction, which also provides the phosphorus derivative 2,3-diphosphino-1,4-diphosphonium $[R_3PP(R')P(R')PR_3]^{2+}$. The versatile synthetic methodologies toward the new P−As and P−Sb frameworks demonstrate the potential for diversification and systematic expansion of interpnictogen compounds.

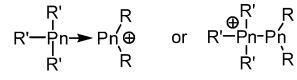
Interpnictogen compounds are promising as materials that exhibit new properties;[1] however, examples of compounds based on a Pn−Pn′ bonded backbone (Pn or Pn′ = P, As, Sb or Bi) are rare. The formation of P−P bonds using homoatomic coordination chemistry between neutral and cationic phosphorus centers represents a high yield and versatile new synthetic method that provides access to series of *catena*-phosphorus cations.[2−9] Application of this approach to the heavier pnictogen elements (As, Sb, Bi) offers the potential for diverse and extensive development of interpnictogen compounds.

The P→P homoatomic coordination chemistry is fundamentally described by reaction 1 involving the combination of a phosphine, a chlorophosphine and a halide abstracting agent (e.g., A = $Me_3SiOSO_2CF_3$, $AlCl_3$, $GaCl_3$). The reaction is envisaged to proceed by the heterolytic cleavage of the P−Cl bond and coincident or subsequent P→P coordination of the phosphine R_3P (Lewis donor) to the phosphenium R'_2P^+ center (Lewis acceptor) to give the salt $[R_3PPR'_2][anion]$. The P→P adduct can also be viewed as a phosphinophosphonium cation, as illustrated for $[R_3PPR'_2]^+$ by the molecular frameworks presented above reaction 1.[10]



$$R'_3P + R_2PCl + A \rightarrow [R'_3PPR_2][anion] \quad (1)$$

{anion = $[AlCl_4]^-$ or $[GaCl_4]^-$ or $[OSO_2CF_3]^-$ + Me_3SiCl}



$$R'_3Pn' + R_2PnCl + A \rightarrow [R'_3Pn'PnR_2][anion] \quad (2)$$

{anion = $[AlCl_4]^-$ or $[GaCl_4]^-$ or $[OSO_2CF_3]^-$ + Me_3SiCl} (2)

Reaction 2 describes the potential generic application of eq 1 to form bonds between the heavy pnictogen elements (Pn or Pn′ = P, As, Sb or Bi). This has been successfully exploited to obtain examples of pnictinophosphonium cations containing formal P→Pn coordinate bonds for Pn = As, Sb or Bi,[11,12] as well as examples of stibinoarsonium and bismuthinoarsonium

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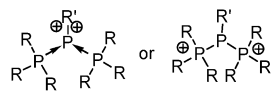
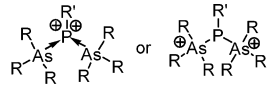
cations containing examples of As→Sb and As→Bi coordinate bonds, respectively.[13,14] Here we describe the preparation and characterization of the first examples of salts containing phosphinoarsonium and phosphinostibonium cations, representing the first compounds with formal As→P (Preliminary Communication)[15] and Sb→P coordinate bonds, in which the traditionally less basic pnictogen center is a donor on the more basic phosphorus center.

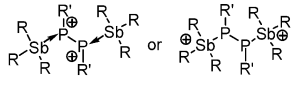
Consideration of the number of Pn′−Pn (Pn or Pn′ = As, Sb, Bi) bonds in an interpnictogen framework, the variety of connectivities (isomers) and the accommodation of more than one molecular charge, introduces potential for vast diversification. In this context, activation of both P−Cl bonds of a dichlorophosphine by a halide abstracting agent in the presence of a phosphine according to reaction 3 gives the 2-phosphino-1,3-diphosphonium framework $[R_3PP(R')PR_3]^{2+}$.[2,3] We have now evolved this methodology to prepare and characterize salts containing the first examples of phosphinodiarsonium dications according to reaction 4. In contrast, halide abstraction is accompanied by a reduction of the dichlorophosphine upon reaction with a stibine to give the first examples of diphosphinodistibonium dications according to reaction 5. Moreover, diphosphinodistibonium represents a precursor to diphosphinodiarsonium dications according to reaction 6, involving a ligand exchange process. The versatility and generality of these reactions bodes well for the extensive and diverse development of interpnictogen frameworks that provide opportunities for the discovery of new inorganic materials.



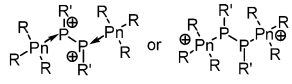
$$2R_3P + R'PCl_2 + 2AlCl_3 \rightarrow [R_3PP(R')PR_3][AlCl_4]_2 \quad (3)$$



$$2R_3As + R'PCl_2 + 2A \rightarrow [R_3AsP(R')AsR_3][anion]_2 \quad (4)$$
$$\{anion = [AlCl_4]^- \text{ or } [GaCl_4]^- \text{ or } [OSO_2CF_3]^- + Me_3SiCl\}$$



$$3Ph_3Sb + 2R'PCl_2 + 2AlCl_3 \rightarrow [Ph_3SbP(R')P(R')SbPh_3][AlCl_4]_2 + Ph_3SbCl_2 \quad (5)$$



$$[Ph_3SbP(R')P(R')SbPh_3]^{2+} + 2R_3Pn \rightarrow [R_3PnP(R')Pn(R')PnR_3]^{2+} + 2Ph_3Sb \quad (6)$$
(Pn = P, As)

Synthetic Procedures and Characterization Data

General. Reactions were carried out in an MBraun Glovebox under atmosphere of dry N_2. Solvents were dried on an MBraun solvent purification system and stored over 4 Å molecular sieves. MeCN was purchased from Aldrich and degassed with argon and stored over 4 Å molecular sieves. Et_2O was dried over sodium/benzophenone and distilled prior to use. Deuterated solvents were purchased from Aldrich and were used as received. Me_3As, Et_3As, Me_2PCl, and $MePCl_2$ were purchased from Strem Chemicals and used as received. $GaCl_3$ was purchased from Strem Chemicals and sublimed before use. $AlCl_3$ was purchased from Aldrich and sublimed before use. $Me_3SiOSO_2CF_3$ was purchased from Aldrich and distilled prior to use. All other chemicals were purchased from Aldrich and used as received.

NMR spectra were obtained at room temperature, unless otherwise stated, on a Bruker AVANCE 500 ^1H (500.13 MHz, 11.7 T) and Bruker/Tecmag AC250 ^1H (250.06 MHz, 5.9 T). Chemical shifts (δ) are reported in ppm. $^{13}C\{^1H\}$ (125.76 MHz) chemical shifts are referenced to $\delta_{TMS} = 0.00$ ppm, $^{31}P\{^1H\}$ (202.46 MHz, 101.26 MHz) chemical shifts are referenced to $\delta_{H3PO4(85\%)} = 0.00$ ppm. NMR spectra were obtained on aliquots of reaction mixture in appropriate deuterated solvent in a 5 mm tube. The tubes were capped and sealed with parafilm prior to removal from the inert atmosphere.

IR spectra were obtained on powdered and ground crystalline samples dissolved in CH_2Cl_2 and spotted on CsI plates. Data collection was on a Bruker Vector FT-IR spectrometer. Peaks are reported in wavenumbers (cm^{-1}) with ranked intensities in parentheses, where a value of one is indicative of the most intense peak in the spectrum. Melting points were recorded on an Electrothermal apparatus in sealed capillary tubes under N_2. Elemental analyses of selected samples were performed by Canadian Microanalytical Services Ltd. Delta, British Columbia, Canada.

Preparation of $[Ph_2PAsMe_3][OSO_2CF_3]$. Me_3As (10.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and Ph_2PCl (13.5 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min. The mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was recrystallized from CH_2Cl_2 by diffusion of ether vapor into the solution at room temperature, giving large white crystals that were isolated by decantation and washed with ether (3 × 3 mL). Yield: 40.9 mg, 90%; mp 88−90 °C; elemental analysis calcd. (found): C 42.30 (40.80), H 4.22 (4.22); FTIR (cm^{-1}, ranked intensities): 3164 (17), 2942 (16), 2627 (19), 2409 (20), 2292 (8), 2253 (4), 1438 (12), 1375 (15), 1262 (3), 1225 (14), 1157 (6), 1032 (2), 918 (10), 800 (18), 749 (7), 696 (11), 640 (1), 573 (13), 518 (9), 378 (5); ^1H NMR (CD_3CN, 500 MHz, 293 K): 1.79 (*s*, 9H), 7.61−7.71 (*m*, 10H); $^{13}C\{^1H\}$ NMR (CD_3CN, 125.8 MHz, 293 K): 14.2 (*s*), 119.1(*d*, $^1J_{PC} = 25$ Hz), 129.1 (*s*), 131.1 (*s*), 133.2 (*s*); $^{31}P\{^1H\}$ NMR (CD_3CN, 101.3 MHz, 293 K): −2.2 (*s*). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Me_2PAsMe_3][OSO_2CF_3]$. Me_3As (10.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and Me_2PCl (9 μL, ∼0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min. The mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was redissolved in CH_2Cl_2 and diffusion of ether vapor into the solution gave a white powder that was isolated by decantation and washed with ether (3 × 3 mL). Yield: 8.25 mg, 25%; mp. 100−102; FTIR (cm^{-1}, ranked intensities): 3017 (9), 2930 (10), 2875 (15), 1423 (8), 1259 (1), 1225 (5), 1155 (3), 1031 (2), 934 (7), 898 (6), 855 (13), 756 (12), 736 (11), 709 (14), 638 (4). $^{31}P\{^1H\}$NMR (CD_3CN, 101.3 MHz, 293 K): −15.8 (*s*); ^1H NMR ($CDCl_3$, 500 MHz, 293 K): 1.21 (*s*, 9H), 1.82 (*d*, 6H, $^2J_{PH} = 25$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 15.3 (*s*), 65.8 (*s*).

Preparation of $[Ph_2PAsPh_3][AlCl_4]$. Ph_3As (30.4 mg, 0.100 mmol) in CH_2Cl_2 (2 mL) was added to a mixture of $AlCl_3$ (26.7 mg, 0.200 mmol) and Ph_2PCl (13.5 μL, 0.100 mmol) in benzene

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(1 mL) and stirred for 10 min. The mixture exhibited a new signal in the $^{31}P\{^1H\}$ NMR spectra and low intensity signals at 58.1 (*d*, $^1J_{PP}$ = 182 Hz) and −17.8 (*d*, $^1J_{PP}$ = 182 Hz corresponding to $[Ph_2(Cl)PPPh_2][AlCl_4]$.[16] Addition of hexanes (3 mL) effected precipitation of a white solid that was redissolved in CH_2Cl_2 and precipitated by diffusion of hexane vapor into the solution. The solution was decanted and the solid was washed with ether (3 × 2 mL). Yield: 22.1 mg, 35%; mp 52−55 °C; FTIR (cm^{-1}, ranked intensities): 3155 (25), 3058 (7), 2993 (18), 2957 (15), 2927 (17), 2870 (20), 2670 (30), 2576 (28), 2326 (29), 1971 (23), 1898 (24), 1816 (22), 1777 (27), 1670 (26), 1582 (9), 1481 (6), 1438 (1), 1392 (19), 1337 (11), 1312 (12), 1265 (8), 1187 (10), 1163 (13), 1101 (4), 1024 (14), 997 (5), 919 (21), 740 (2), 688 (3), 619 (16); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 101.3 MHz, 293 K): 17.1 (*s*). ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): 7.29−7.49 (*m*, 25H), $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz, 293 K): 129.1 (*s*), 129.2 (*s*), 130.5 (*d*, $^1J_{PC}$ = 14 Hz), 132.5 (*d*, $^1J_{PC}$ = 15 Hz), 134.2 (*s,* 2C), 136.3 (*s*), 140.0 (*s*).

Preparation of $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$. Ph_3As (60.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $AlCl_3$ (39.8 mg, 0.300 mmol) and $MePCl_2$ (9.0 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min. The mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was isolated and recrystallized from CH_2Cl_2 by diffusion of ether vapor into the solution, giving pale-yellow crystals. Yield: 78.6 mg, 95%; mp: 35−37 °C; FTIR (cm^{-1}, CsI, ranked intensities): 3057 (16), 2988 (17), 2646 (20), 1481 (9), 1437 (5), 1393 (10), 1309 (18), 1190 (12), 1150 (13), 1074 (11), 997 (4), 876 (7), 834 (15), 766 (8), 738 (2), 694 (6), 533 (1), 493 (3), 409 (14), 317 (19; $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 101.3 MHz, 293 K): −18.3 (*s*);^1H NMR ($CDCl_3$, 500 MHz, 293 K): 2.23 (*d*, 3H, $^2J_{PH}$ = 25 Hz), 7.30−7.40 (*m*, 30H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 30.5 (*d*, $^1J_{PC}$ = 25 Hz), 118.2 (*s*), 129.2 (*s*), 133.3 (*s*), 139.8 (*s*). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$. Me_3As (21.4 μL, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and $MePCl_2$ (9 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min. The mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was isolated and recrystallized from CD_3CN by diffusion of ether vapor into the solution, giving pale-white crystals. Yield: 40.4 mg, 93%; mp 153−155; elemental analysis calcd. (found): C 18.60 (18.31), H 3.12 (3.63); FTIR (cm^{-1}, ranked intensities): 3369 (16), 3280 (18), 3092 (15), 2966 (19), 2261 (1), 2115 (13), 1274 (3), 1225 (9), 1192 (10), 1159 (7), 1101 (8), 1032 (2), 927 (14), 832 (4), 736 (20), 689 (13), 640 (6), 573 (12), 518 (11), 347 (5); $^{31}P\{^1H\}$ NMR (CD_3CN, 101.3 MHz, 293 K): −15.1 (*s*); ^1H NMR (CD_3CN, 500 MHz, 293 K): 1.49 (*d*, 3H, $^2J_{PH}$ = 25 Hz), 2.55 (*s*, 18H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 125.8 MHz, 293 K): 15.2 (*t*, $^1J_{PC}$ = 62.9 Hz), 21.5 (*s*). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Me_3AsP(Et)AsMe_3][OSO_2CF_3]_2$. Me_3As (21.4 μL, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and $EtPCl_2$ (12.3 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was recrystallized from CH_2Cl_2 by diffusion of ether vapor into the solution, giving blocklike white crystals. Yield: 55.1 mg, 93%; mp 122−24; FTIR (cm^{-1}, ranked intensities): 3021 (12), 2934 (14), 2305 (17), 1604 (18), 1463 (15), 1422 (11), 1261 (1), 1232 (3), 1160 (2), 1034 (4), 922 (6), 857 (13), 739 (8), 703 (10), 639 (5), 574 (9), 516 (7), 349 (16); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 101.3 MHz, 293 K): −17.2 (*s*); ^1H NMR (DMSO-d_6, 500 MHz, 293 K): 1.12 (*dt*, 3H, $^2J_{PH}$ = 69 Hz, $^3J_{HH}$ = 10 Hz), 1.75 (*dq*, 2H, $^2J_{PH}$ = 69 Hz, $^3J_{HH}$= 10 Hz), 2.55 (*s*, 18H); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 125.8 MHz, 293 K): 11.5 (*s*), 12.1 (*s*), 13.4 (*d*, $^1J_{PC}$ = 25 Hz). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Me_3AsP(^iPr)AsMe_3][OSO_2CF_3]_2$. Me_3As (21.4 μL, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and $^iPrPCl_2$ (12.3 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was recrystallized from $CDCl_3$ by diffusion of ether vapor in the solution, giving pale-white powder. Yield: 51.5 mg, 85%; mp 91−93; FTIR (cm^{-1}, ranked intensities): 3054 (9), 2986 (10), 2685 (15), 2305 (14), 1605 (18), 1421 (11), 1264 (1), 1232 (5), 1160 (4), 1040 (6), 896 (13), 740 (2), 705 (3), 643 (7), 579 (12), 514 (8), 349 (17), 286 (16); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 101.3 MHz, 293 K): 2.7 (*s*); ^1H NMR ($CDCl_3$, 500 MHz, 293 K): 1.46 (*dd*, 6H, $^3J_{HH}$ = 10 Hz, $^3J_{PH}$ = 20 Hz), 2.35 (*s*, 18H), 3.18 (*dsept*, 1H, $^3J_{HH}$ = 10 Hz, $^2J_{PH}$ = 5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 12.8 (*s*), 22.3 (*s*), 25.3 (*d*, $^1J_{PC}$ = 25 Hz). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Me_3AsP(Cy)AsMe_3][OSO_2CF_3]_2$. Me_3As (21.4 μL, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and $CyPCl_2$ (0.100 mmol, 12.3 μL) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. Addition of ether (3 mL) effected precipitation of a white solid that was redissolved in $CDCl_3$ and precipitated by diffusion of ether vapor into the solution, giving pale-white powder. Yield: 47.1 mg, 73%; mp 85−87 °C; FTIR (cm^{-1}, ranked intensities): 3029 (14), 2933 (7), 2870 (15), 1633 (13), 1454 (3), 1414 (6), 1360 (10), 1259 (2), 1151 (9), 1027 (8), 907 (16), 795 (17), 702 (4), 666 (1), 623 (11), 513 (12); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 101.3 MHz, 293 K): −2.0 (s); ^1H NMR ($CDCl_3$, 500 MHz 293 K): 1.33−1.37 (*m*, 2H), 1.96−2.00 (*m*, 4H), 2.12 (*t*, $^3J_{HH}$ = 15 Hz, 4H), 2.28 (*s*, 18H), 2.45−2.49 (*m*, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 10.5 (*s*), 24.1 (s), 26.1 (*s*), 32.2 (*s*), 34.2 (*d*, $^1J_{PC}$ = 25 Hz). The $^{31}P\{^1H\}$ NMR spectra observed for reaction mixtures are independent of the order that the reactants are combined.

Preparation of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$. $AlCl_3$ (39.8 mg, 0.300 mmol) was added to a mixture of $PhPCl_2$ (27.4 μL, 0.200 mmol) and Ph_3Sb (106.0 mg, 0.300 mmol) in CH_2Cl_2 (2 mL) and stirred for 2.5 h, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. The solution became pale yellow and crystals were obtained by layering hexane on the solution and storing at −25 °C. The solid was washed with ether (3 × 2 mL). The solid was recrystallized by diffusion of ether into a solution in CH_2Cl_2, giving pale-yellow crystals. Yield: 52%, 63.0 mg; mp: 127−129 °C.; elemental analysis: calcd (found): C 45.69 (43.37), H 3.19 (3.16); light sensitive; $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_2Cl_2): −29.2 (*s*); ^1H NMR (500 MHz, 293 K, CD_2Cl_2): 7.35−7.39 (*m*, 30 H), 7.45−7.49 (*m*, 10 H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_2Cl_2): 131.2 (*s*), 131.6 (*s*), 132.1 (*s*), 132.6 (*s*), 134.9 (*s*), 135.2 (*s*), 135.8 (*s*), 136.3 (*s*); FTIR (cm^{-1}, CsI, ranked intensities): 3054 (4), 2987 (9), 2685 (15), 2305 (12), 1479 (13), 1437 (6), 1422 (7), 1265 (2), 1066 (14), 966 (11), 896 (8), 740 (1), 705 (3), 493 (5), 286 (10). Reaction mixtures prepared by addition of Ph_3Sb to a mixture of $AlCl_3$ and $PhPCl_2$ showed no evidence for the formation of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$.

Preparation of $[Ph_3SbP(Me)P(Me)SbPh_3][AlCl_4]_2$. $AlCl_3$ (39.8 mg, 0.300 mmol) was added to a mixture of $MePCl_2$ (18.0 μL, 0.200 mmol) and Ph_3Sb (106.0 mg, 0.300 mmol) in CH_2Cl_2 (2 mL) and stirred for 2 h in the dark, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. A pale yellow powder precipitated on standing that was isolated and recrystallized by diffusion of ether into a solution in CH_2Cl_2 to give pale-yellow crystals. Yield: 48%, 54.5 mg; mp: Decomposed above 205 °C; light sensitive; FTIR (cm^{-1}, CsI, ranked intensities): 3055 (13), 2982 (22), 2876 (21),

(16) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712–4717.

1699 (20), 1652 (16), 1575 (18), 1558 (19), 1478 (7), 1436 (3), 1334 (12), 1096 (17), 1065 (9), 1018 (14), 730 (1), 687 (4), 492 (2), 444 (5), 384 (10), 326 (15), 280 (8), 247 (11); $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_2Cl_2): −78.8 (*s*); ^1H NMR (500 MHz, 293 K, CD_2Cl_2): 7.51−7.92 (*m*, 30 H), 2.91 (*s*, 6H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_2Cl_2): 29.7 (*s*), 132.4 (*s*), 132.5 (*s*), 135.3 (*s*), 136.2 (*s*); Reaction mixtures prepared by addition of Ph_3Sb to a mixture of $AlCl_3$ and $MePCl_2$ showed no evidence for the formation of $[Ph_3SbP(Me)P(Me)SbPh_3][AlCl_4]_2$.

Preparation of $[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$. Ph_3As (151.5 mg, 0.500 mmol) in CH_2Cl_2 (4 mL) was added dropwise to a solution of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ (251 mg, 0.200 mmol) in CH_2Cl_2 (2 mL) and stirred for 10 min and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. The reaction mixture was concentrated and diffusion of ether vapor into the solution at −25 °C gave pale-white crystals that were washed with ether (3 × 3 mL). Yield: 68%, 158 mg; mp: 153−155 °C; FTIR (cm^{-1}, CsI, ranked intensities): 3055 (9), 1965 (22), 1887 (21), 1815 (20), 1577 (10), 1480 (6), 1436 (3), 1334 (11), 1307 (13), 1265 (19), 1185 (12), 1162 (14), 1067 (7), 1021 (8), 997 (5), 802 (18), 733 (2), 688 (4), 564 (17), 491 (1), 329 (16), 288 (15); $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_2Cl_2): −11.9 (*s*); ^1H NMR (500 MHz, 293 K, CD_2Cl_2): 7.12 (*d*, J_{HH} = 7 Hz, 8H), 7.34−7.55 (*m*, 25 H), 7.56 (*t*, J_{HH} = 6 Hz, 5H), 7.68−7.88 (*m*, 32H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, $CDCl_3$): 131.7 (*s*), 131.9 (*s*), 132.1 (*s*), 133.1 (*s*), 134.9 (*s*), 135.5 (*s*), 135.6 (*s*), 135.8 (*s*).

Preparation of $[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$. Me_3As (53.5 μL, 0.500 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ (251 mg, 0.200 mmol) in CH_2Cl_2 (3 mL) and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. The reaction mixture was concentrated and pale-white crystals were formed by diffusion of ether vapor into a solution in CH_2Cl_2 at −25 °C. Crystals were washed with ether (3 × 3 mL). Yield: 82%, 130 mg; mp: 182−184 °C; elemental analysis calcd (found): C 27.23 (27.64), H 3.56 (3.54); FTIR (cm^{-1}, CsI, ranked intensities): 3943 (20), 3055 (3), 2986 (4), 2305 (12), 1650 (16), 1575 (17), 1478 (8), 1436 (6), 1331 (15), 1265 (2), 1184 (18), 1065 (19), 997 (19), 912 (3), 895 (11), 739 (1), 704 (5), 494 (7), 456 (9), 288 (10); $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_3CN): −31.6 (*s*); ^1H NMR (500 MHz, 293 K, CD_3CN): 1.33 (*s*, 18H), 7.60−7.68 (*m*, 10H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_3CN): 10.0 (*s*), 129.7 (*s*), 132.0 (*s*), 134.1 (*s*), 140.1 (*s*).

Preparation of $[Et_3AsP(Ph)P(Ph)AsEt_3][AlCl_4]_2$. Et_3As (70.0 μL, 0.500 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ (251 mg, 0.200 mmol) in CH_2Cl_2 (3 mL) and stirred for 10 min, giving a white precipitate. The white solid was dissolved in CD_3CN and exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. The powder was washed with CH_2Cl_2 (3 × 3 mL) and recrystallized by diffusion of ether vapor into a CH_2Cl_2 solution giving pale yellow crystals. Yield: 67%, 114 mg; mp: 172−174 °C; FTIR (cm^{-1}, CsI, ranked intensities): 3055 (19), 2969 (12), 2938 (13), 2878 (22), 1964 (24), 1891 (25), 1818 (26), 1576 (23), 1479 (6), 1456 (8), 1437 (3), 1408 (15), 1388 (14), 1335 (18), 1238 (17), 1164 (16), 1067 (9), 1931 (10), 996 (5), 810 (21), 734 (2), 688 (4), 491 (1), 445 (7), 287 (11), 256 (20); $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_3CN): −36.1 (*s*); ^1H NMR (500 MHz, 293 K, CD_3CN): 1.44 (*t*, $^3J_{HH}$ = 8 Hz, 18 H), 2.99 (*q*, $^3J_{HH}$ = 8 Hz, 12H), 7.75 (*bs*, 6 H), 8.10 (*bs*, 4H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_3CN): 17.2 (*s*), 26.5 (*s*), 128.8 (*s*), 129.0 (*s*), 131.2 (*s*), 136.5 (*s*).

Preparation of $[Me_3AsP(^iPr)P(^iPr)AsMe_3][AlCl_4]_2$. Me_3As (53.5 μL, 0.500 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$ (0.200 mmol) in CH_2Cl_2 (3 mL) and stirred for 10 min, giving a white precipitate. The white solid was dissolved in CD_3CN and exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra. The powder was washed with CH_2Cl_2 (3 × 3 mL). Yield: 71%, 103 mg; mp: 129−130 °C; FTIR (cm^{-1}, CsI, ranked intensities): 3055 (1), 2987 (3), 2305 (18), 1644 (14), 1477 (11), 1434 (6), 1265 (4), 1154 (20), 1065 (17), 996 (15), 918 (16), 895 (13), 738 (2), 703 (7), 685 (10), 609 (19), 490 (5), 455 (12), 287 (9), 254 (8); $^{31}P\{^1H\}$ NMR (101.3 MHz, 293 K, CD_3CN): −27.2 (*s*); ^1H NMR (500 MHz, 293 K, CD_3CN): 1.35 (*dd*, $^3J_{HH}$ = 18 Hz, $^4J_{HP}$ = 7 Hz), 1.49 (*s*, signals at 1.35 and 1.49 overlap, total integration 30H); 2.77 (*sept*, not well resolved, connectivity confirmed through 2D COSY, 2H). ^{13}C NMR$\{^1H\}$ (125.8 MHz, 293 K, CD_3CN): 10.4 (*s*), 18.6 (*s*), 31.5 (*s*).

NMR Identification of Compounds Prepared in Situ. $[Ph_2PAsMe_3][GaCl_4]$. Me_3As (10.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $GaCl_3$ (52.8 mg, 0.300 mmol) and Ph_2PCl (13.5 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: 1.0 (*s*);^1H NMR (CD_2Cl_2, 500 MHz, 293 K): 2.02 (*s*, 9H), 7.37−7.70 (*m*, 10H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.8 MHz, 293 K): 31.2 (*s*), 126.1 (*s*), 132.5 (*s*), 133.6 (*s*), 135.1 (*s*).

$[Ph_2PAsEt_3][OSO_2CF_3]$. Et_3As (14.0 μL, 0.100 mmol) in benzene (2 mL) was added to a solution of $Me_3SiOSO_2CF_3$ (52.1 μL, 0.200 mmol) and Ph_2PCl (13.5 μL, 0.100 mmol) in benzene (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: −15.1 (*s*); ^1H NMR (C_6D_6, 500 MHz, 293 K): 1.73 (*t*, 9H, $^3J_{HH}$ = 30 Hz), 1.26 (*q*, 6H, $^3J_{HH}$ = 10 Hz), 6.96−7.00 (*m*, 2H), 7.11−7.17 (*m*, 4H), 7.48 (*t*, 4H, $^3J_{HH}$ = 10 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.8 MHz, 293 K): 10.6 (*s*), 16.4 (*s*), 128.6 (*s*), 130.1 (*s*), 131.5 (*d*, $^2J_{PC}$ = 25 Hz), 139.0 (*d*, $^1J_{PC}$ = 63 Hz).

$[Cy_2PAsMe_3][OSO_2CF_3]$: Me_3As (10.7 μL, 0.100 mmol) in benzene (1 mL) was added to a solution of TMSOTf (25 μL, 0.300 mmol) and Cy_2PCl (22,1.5 μL, 0.100 mmol) in benzene (1 mL) and stirred for one hour, resulting in a clear colorless solution. The mixture exhibited two signals in the $^{31}P\{^1H\}$ NMR spectra: 24.6 (*s*) ($[Cy_2PAsMe_3][OSO_2CF_3]$, 70%), and 131.4 (*s*) Cy_2PCl (30%).

$[^iPr_2PAsMe_3][OSO_2CF_3]$. Me_3As (10.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) was added to a solution of TMSOTf (25 μL, 0.300 mmol) and $^iPr_2PCl$ (15.9 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for one hour, resulting in a clear colorless solution. The mixture exhibited two signals in the $^{31}P\{^1H\}$ NMR spectra: 28.1 (*s*) ($[^iPr_2PAsMe_3][OSO_2CF_3]$, 50%), and 137.8 (*s*) $^iPr_2PCl$ (50%).

$[Et_2PAsMe_3][OSO_2CF_3]$. Me_3As (10.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) was added to a solution of TMSOTf (25 μL, 0.300 mmol) and Et_2PCl (μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for one hour, resulting in a clear colorless solution. The mixture exhibited signals in the $^{31}P\{^1H\}$ NMR spectra that are assigned to three compounds: −5.1 (*s*) ($[Et_2PAsMe_3][OSO_2CF_3]$, 30%), $[Et_2PCl$-$PEt_2][OSO_2CF_3]$ (40%), and 119.0 (*s*) Et_2PCl (20%), $[Et_2PAsMe_3]$-$[OSO_2CF_3]$ −5.1 (broad).

$[Ph_3AsP(Ph)AsPh_3][AlCl_4]_2$. Ph_3As (60.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $AlCl_3$ (39.8 mg, 0.300 mmol) and $PhPCl_2$ (13.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: −4.1 (*s*); ^1H NMR ($CDCl_3$, 500 MHz, 293 K): 7.25−7.99 (*m*, 35H).$^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 118.2 (*s*), 129.7 (*s*), 130.1 (*s*), 130.9 (*s*), 131.1 (*s*), 134.2 (*s*), 134.5 (*s*), 140.6 (*s*).

$[Ph_3AsP(Et)AsPh_3][AlCl_4]_2$. Ph_3As (60.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $AlCl_3$ (39.8 mg, 0.300 mmol) and $EtPCl_2$ (10.1 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: −7.7 (*s*); ^1H NMR ($CDCl_3$, 500 MHz, 293 K): 1.59 (*t*, 3H, $^3J_{HH}$ = 10 Hz), 4.55, (*q*, 2H, $^3J_{HH}$ = 10 Hz), 7.41−7.62 (*m*, 20H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 12.3 (*s*),71.8(*s*), 129.2(*s*), 129.8(*s*), 132.1(*s*), 133.8(*s*).

$[Ph_3AsP(^iPr)AsPh_3][AlCl_4]_2$. Ph_3As (60.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $AlCl_3$ (39.8 mg, 0.300 mmol) and $^iPrPCl_2$ (12.3 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: 7.7 (*s*); ^1H NMR ($CDCl_3$, 500 MHz, 293 K): 1.26 (*d*, 6H, $^3J_{HH}$ = 20 Hz), 2.70 (*sept*, 1H, $^3J_{HH}$ = 21 Hz) 7.5−8.0 (*m*, 30H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.8 MHz, 293 K): 23.9 (*d*, $^2J_{PC}$ = 15 Hz), 33.0 (*d*, $^1J_{PC}$ = 49 Hz).

Table 1. Crystal Data for $[Me_3AsPPh_2][OSO_2CF_3]$, $[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$, $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$, and Derivatives of $[R'_3PnP(R)P(R)PnR'_3][AlCl_4]_2$ (Pn = As or Sb)

	$[Me_3AsPPh_2][OSO_2CF_3]$	$[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$	$[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$	$[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$	$[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$	$[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$	$[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$
empirical formula	$C_{16}H_{19}AsF_3O_3PS$	$C_9H_{21}As_2F_6O_6PS_2$	$C_{37}H_{33}Al_2As_2C_{18}P$	$C_{48}H_{40}Al_2C_{18}P_2Sb_2$	$C_{42}H_{44}Al_2C_{18}P_2Sb_2{\bullet}CH_2Cl_2$	$C_{48}H_{40}Al_2As_2C_{18}P_2$	$C_{18}H_{28}Al_2As_2C_{18}P_2$
formula weight	454.26	584.19	996.00	1259.80	1276.70	1166.14	793.74
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	P (No. 2)	P (No. 2)	$P2_1/c$ (No. 14)
a (Å)	11.7585 (8)	13.4659 (12)	20.132 (3)	11.5699 (5)	10.142 (2)	11.327 (3)	28.143 (4)
b (Å)	12.8289 (9)	11.5349 (11)	14.3110 (18)	10.8660 (5)	11.858 (3)	11.345 (3)	15.696 (2)
c (Å)	12.9423 (9)	14.0530 (13)	15.4865 (19)	21.0827 (9)	22.810 (5)	20.433 (6)	11.3857 (15)
α (deg)	90	90	90	90	81.329 (3)	90.271 (4)	90
β (deg)	96.4800 (10)	109.1230 (10)	101.1671 (18)	101.3290 (10)	79.316 (3)	98.929 (4)	97.8153 (17)
γ (deg)	90	90	90	90	85.433 (3)	90.595 (4)	90
V (Å^3)	1939.9 (2)	2062.4 (3)	4377.3 (9)	2598.8 (2)	1276.70	2593.7 (13)	4982.9 (12)
D_c (g cm^{-3})	1.555	1.881	1.511	1.610	1.593	1.493	1.587
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	193	193	193	173	173	173	173
GoF	1.044[a]	1.043[a]	1.049[a]	1.044[a]	1.208[a]	1.066[a]	1.047[a]
$R1$	0.0335[b]	0.0283[b]	0.0376[b]	0.0232[b]	0.0861[b]	0.0813[b]	0.0425[b]
$wR2$	0.0889[c]	0.0748[c]	0.0978[c]	0.0620[c]	0.2094[c]	0.2448[c]	0.1104[c]

[a] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0496P)^2 + 0.7515P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$). [b] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Coordinate Bonds between the Heavy Pnictogen Elements[a]

	ref		ref		ref		ref
P→P	4, 5	As→P		Sb→P		Bi→P	
P→As	11, 12	**As→As**	19	Sb→As		Bi→As	
P→Sb	12	**As→Sb**	13	**Sb→Sb**	20	Bi→Sb	
P→Bi	12	**As→Bi**	13	Sb→Bi		Bi→Bi	

[a] Bold font highlights bonds for which examples of representative compounds have been isolated and characterized.

$[Ph_3AsP(Cy)AsPh_3][AlCl_4]_2$. Ph_3As (60.4 mg, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $AlCl_3$ (39.8 mg, 0.300 mmol) and $CyPCl_2$ (12.3 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the reaction mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: 3.8 (*s*).

$[Me_3AsP(Ph)AsMe_3][OSO_2CF_3]_2$. Me_3As (21.4 μL, 0.200 mmol) in CH_2Cl_2 (1 mL) was added to a solution of $Me_3SiOSO_2CF_3$ (75.4 μL, 0.300 mmol) and $PhPCl_2$ (13.7 μL, 0.100 mmol) in CH_2Cl_2 (1 mL) and stirred for 10 min, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: −6.2 (*s*); ^1H NMR (CD_3CN, 500 MHz, 293 K): 1.95 (*s*, 18H), 7.61−7.81 (*m*, 5H); $^{13}C\{^1H\}$ NMR (CD_3CN, 125.8 MHz, 293 K): 12.5 (*s*), 130.7 (*s*), 131.2 (*s*), 134.1 (*s*), 137.8 (*d*, $^1J_{PC}$ = 25 Hz).

$[Ph_3SbP(Et)P(Et)SbPh_3][AlCl_4]_2$. $AlCl_3$ (39.8 mg, 0.300 mmol) was added to a solution of $EtPCl_2$ (20.2 μL, 0.200 mmol) and Ph_3Sb (106.0 mg, 0.300 mmol) in CH_2Cl_2 (2 mL) and stirred for 2 h in the dark, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra; −58.2 (*s*); ^1H NMR (500 MHz, 293 K, CD_2Cl_2): 1.29 (*dt*, $^2J_{PH}$ = 15 Hz, $^3J_{HH}$ = 7 Hz, 6H), 2.37 (*dq*, $^3J_{HH}$ = 7 Hz, $^4J_{PH}$ = 13 Hz, 4H), 7.46−7.49 (*m*); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_2Cl_2): 14.3 (*s*), 23.1 (*s*), 125.1 (*s*), 127.9 (*s*), 128.8 (*s*), 137.5 (*s*).

$[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$. $AlCl_3$ (39.8 mg, 0.300 mmol) was added to a solution of $^iPrPCl_2$ (24.6 μL, 0.200 mmol) and Ph_3Sb (106.0 mg, 0.300 mmol) in CH_2Cl_2 (2 mL) and stirred for 2 h in the dark, and the mixture exhibited one signal in the $^{31}P\{^1H\}$ NMR spectra: −31.7 (*s*), ^1H NMR (500 MHz, 293 K, CD_2Cl_2): 1.55 (*dd*, $^3J_{HH}$ = 30 Hz, $^4J_{PH}$ = 10 Hz, 12H), 2.50 (*m*, 2H), 7.32−7.55 (*m*, 30 H); $^{13}C\{^1H\}$ NMR (125.8 MHz, 293 K, CD_2Cl_2): 20.2 (*s*), 39.2 (*s*), 130.1 (*s*), 132.5 (*s*), 135.6 (*s*), 137.2 (*s*).

Crystallography. X-ray diffraction data for $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$, $[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$ and $[Ph_2PasMe_3][OSO_2CF_3]$ were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer. Data for $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$, $[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$, $[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$, and $[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$ were collected on Bruker D8/APEX II CCD diffractometer. All data collections employed graphite-monochromated Mo Kα (0.71073 Å) radiation. Crystals were selected under oil, mounted on glass fibers, and placed in a cold stream of N_2. Structures were solved by direct methods[17] ($[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$) or Patterson location of heavy atoms[18] (all others) and refined using full matrix least-squares on F^2.[17] Refinement details are summarized in Table 1.

Results and Discussion

While the bond energies of bonds between the pnictogen elements are viable, reports of compounds containing bonds between heavy pnictogen elements are rare, perhaps due to the limited availability of synthetic approaches for Pn′-Pn bond formation. Application of the generic reaction eq 2 using phosphines as ligands on pnictogenium centers has enabled the facile preparation of compounds containing P→Pn coordinate bonds[4,12,15] as well as compounds containing As→As,[19] As→Sb,[13,14] As→Bi,[13,14] and Sb→Sb coordinate bonds.[20] Nevertheless, only half of the possible interpnictogen coordinate bonds have been identified in examples of representative compounds, as illustrated by the bolded entries in Table 2, which lists all possible coordinate bonds between pnictogen elements. Moreover, all examples of isolated compounds containing a Pn′→Pn coordinate bond involve a pnictogen donor center (Pn′) that is a stronger base than the pnictogen acceptor center (Pn).

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Table 3. $^{31}P\{^1H\}$ and ^1H NMR Data for Derivatives of $[R'_3PnP(R)PnR'_3][AlCl_4]_2$, $[R'_3PnP(R)PnR'_3][OSO_2CF_3]_2$, $[R'_3PnP(R)P(R)PnR'_3][AlCl_4]_2$, and $[R'_3PnP(R)P(R)PnR'_3][OSO_2CF_3]_2$

	$\delta^{31}P\{^1H\}$ (ppm)	δ ^1H (ppm), [integ.][a]	ref
$[Me_3AsPPh_2][OSO_2CF_3]$	−2.2 (*s*)	7.61−7.71 [10]	*d*
$[Me_3AsPMe_2][OSO_2CF_3]$	−15.8 (*s*)	1.82 [6]	*d*
$[Me_3AsPPh_2][GaCl_4]$[e]	1.0 (*s*)	7.37−7.70 [10]	*d*
$[Me_3AsPCy_2][OSO_2CF_3]$	24.6 (*s*)	N/A	*d*
$[Me_3AsPEt_2][OSO_2CF_3]$	−5.1 (*s*)	N/A	*d*
$[Me_3AsP^iPr_2][OSO_2CF_3]$	28.1 (*s*)	N/A	*d*
$[Et_3AsPPh_2][OSO_2CF_3]$[e]	−15.1 (*s*)	1.73 [9], 1.26 [6]	*d*
$[Ph_3AsPPh_2][AlCl_4]$	17.1 (*s*)	N/A[b]	*d*
$[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$	−15.1 (s)	1.49 [3]	*d*
$[Me_3AsP(Ph)AsMe_3][OSO_2CF_3]_2$	−6.2 (s)	7.8−8.0 [5]	*d*
$[Me_3AsP(Et)AsMe_3][OSO_2CF_3]_2$	−17.2 (s)	1.12 [3], 1.75 [2]	*d*
$[Me_3AsP(Cy)AsMe_3][OSO_2CF_3]_2$	−2.0 (s)	1.35 [2], 1.98 [4], 2.12 [4], 2.47 [1]	*d*
$[Me_3AsP(^iPr)AsMe_3][OSO_2CF_3]_2$	2.7(s)	1.46 [6], 3.18 [1]	*d*
$[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$	−18.3 (*s*)	2.23 [3]	*d*
$[Ph_3AsP(Ph)AsPh_3][AlCl_4]_2$[e]	−4.1 (*s*)	N/A[b]	*d*
$[Ph_3AsP(Et)AsPh_3][AlCl_4]_2$[e]	−7.7 (*s*)	1.59 [3], 4.55, [2]	*d*
$[Ph_3AsP(Cy)AsPh_3][AlCl_4]_2$[e]	3.8 (*s*)	N/A	*d*
$[Ph_3AsP(^iPr)AsPh_3]$ $[AlCl_4]_2$	7.7 (*s*)	1.26 [6], 2.70 [1]	*d*
$[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$	−29.2 (*s*)	N/A[b]	*d*
$[Ph_3SbP(Me)P(Me)SbPh_3][AlCl_4]_2$	−78.8 (*s*)	2.91 [6]	*d*
$[Ph_3SbP(Et)P(Et)SbPh_3][AlCl_4]_2$[e]	−58.2 (*s*)	5.02 [6], 5.38 [4]	*d*
$[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$[e]	−31.7 (s)	1.55 [12], 2.50 [2]	*d*
$[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$	−11.9 (*s*)	N/A[b]	*d*
$[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$	−31.6 (*s*)	7.60−7.68 [10]	*d*
$[Et_3AsP(Ph)P(Ph)AsEt_3][AlCl_4]_2$	−33.4 (*s*)	7.75 [6], 2,99 [4]	*d*
$[Me_3AsP(^iPr)P(^iPr)AsMe_3][AlCl_4]_2$	−27.2 (*s*)	see exptl section	*d*
$[Ph_3PP(Ph)P(Ph)PPh_3][OSO_2CF_3]_2$	−33 (*m*), 24 (*m*)	N/A[b]	9
$[Me_3PP(Ph)P(Ph)PMe_3][OSO_2CF_3]_2$	−52 (*m*), 25 (*m*)	7.74 [4], 7.84 [2], 8.05 [4]	9
$[Ph_3PP(Me)P(Me)PPh_3][OSO_2CF_3]_2$	−71 (*m*), 26 (*m*)	0.76 [6]	9
$[Me_3PP(Me)P(Me)PMe_3][OSO_2CF_3]_2$	−73 (*m*), 26 (*m*)	1.93 [6]	9
$[Ph_3PP(Et)P(Et)PPh_3][OSO_2CF_3]_2$	−54 (*m*), 24 (*m*)	1.93 [4], 0.55 [6]	9
$[Ph_3PP(^iPr)P(^iPr)PPh_3][OSO_2CF_3]_2$	−26 (*m*), 22 (*m*)	0.93 [12], 3.26 [2]	9
$[Me_3PP(Cy)P(Cy)PMe_3][OSO_2CF_3]_2$	−34 (*m*), 20 (*m*)	N/A[c]	9

[a] Integrations are relative to signals for R′. [b] Indistinguishable aromatic regions. [c] Not reported. [d] This work. [e] Not isolated.

The use of a cationic charge at the acceptor site offers the potential to extrapolate coordination chemistry as a synthetic methodology to access compounds with interpnictogen coordinate bonds that have not yet been observed (Table 2). Consequently, the implementation of reaction 2 has broad scope in terms of the discovery of new interpnictogen compounds. To this end we have used three component reaction mixtures of a chlorophosphine, a pnictine, and a halide abstracting agent as a versatile and high yield approach to the first compounds containing coordinate As→P and Sb→P bonds, representing the first examples of bonds involving the less basic pnictogen center (As or Sb) as the donor to the more basic pnictogen center (P).

Reaction mixtures composed of chlorophosphines ($ClPR'_2$, R′ = Me, Ph, ^{i}Pr, Cy), Me_3As and $Me_3SiOSO_2CF_3$ in CH_2Cl_2 exhibit one product signal in the $^{31}P\{^1H\}$ NMR spectra, independent of the imposed reaction stoichiometry (Table 3). For R′ = Ph, the compound has been isolated and crystallographically characterized as $[Me_3AsPPh_2][OSO_2CF_3]$, and the structure of the cation in the solid state is shown in Figure 1. The compound can be described as a salt of a phosphinoarsonium cation formed according to reaction 2 (Pn = P, Pn′ = As). The cation may also be considered as a complex of an arsine ligand on a phosphenium cationic Lewis acceptor, as illustrated by molecular frameworks presented above reaction 2. Reaction mixtures containing the less basic Ph_3As (relative to Me_3As) with $AlCl_3$ as the halide abstracting agent show analogous formation of the As→P bond. However, no reaction is observed in mixtures of chlorophosphines, Ph_3As and $Me_3SiOSO_2CF_3$ probably demonstrating the kinetic limitations of $Me_3SiOSO_2CF_3$ as a chloride abstracting agent.

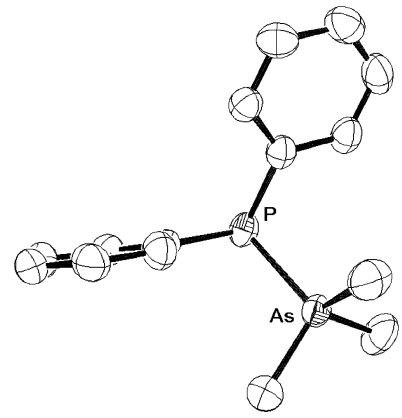

Figure 1. Crystallographic view of the cation in $[Me_3AsPPh_2][OSO_2CF_3]$. Ellipsoids presented at 50%, hydrogen atoms and counteranions removed for clarity. All nonlabeled atoms are carbon.

Reaction mixtures composed of dichlorophosphines ($R'PCl_2$, R′ = Ph, Et, ^{i}Pr, Me, Cy), Ph_3As and $AlCl_3$ in CH_2Cl_2 exhibit one product signal in the $^{31}P\{^1H\}$ NMR spectra (Table 3), independent of the imposed reaction stoichiometry. For *R* = Me, the product has been isolated and crystallographically characterized as the 2-phosphino-1,3-diarsonium tetrachloroaluminate $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$, which is spectroscopically identical to the compound identified in the reaction mixture, and implicates reaction 4. Integrated ^1H NMR data (Table 3) for all derivatives of $[Ph_3AsP(R)AsPh_3][AlCl_4]_2$ are consistent with the solid state structure of the cation in $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$, which is illustrated in Figure 2a,

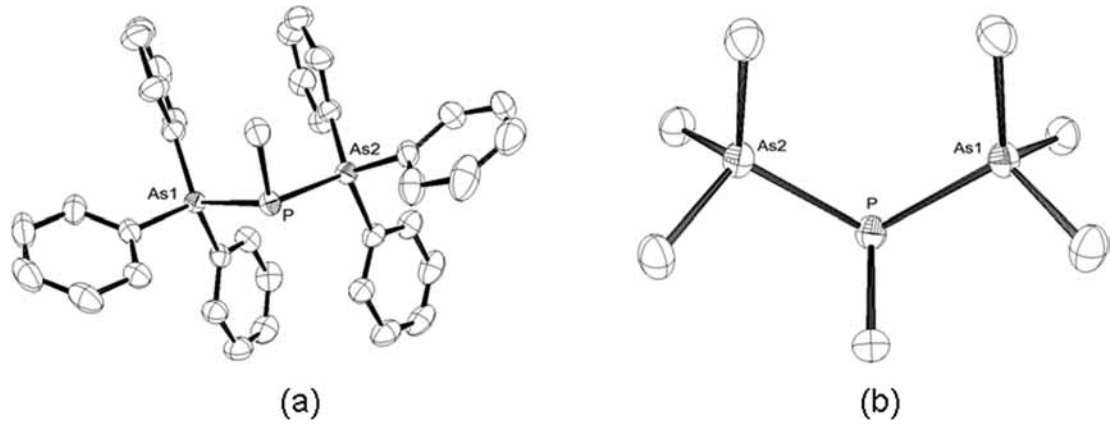

Figure 2. Crystallographic views of the dications in (a) $[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$ and in (b) $[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$. Ellipsoids presented at 50%, hydrogen atoms and counteranions removed for clarity. All nonlabeled atoms are carbon.

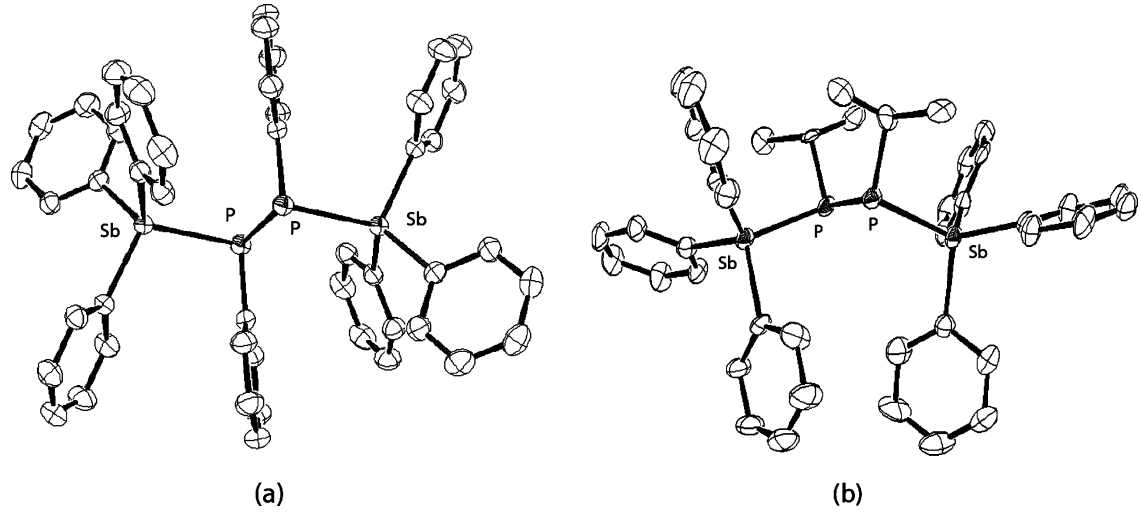

Figure 3. Crystallographic views of the dications in (a) $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ and in (b) $[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$. Ellipsoids presented at 50%, hydrogen atoms and counteranions removed for clarity. All nonlabeled atoms are carbon.

and can be described as a phosphinodiarsonium cation. Alternatively, the cation can be described as a complex of two arsine ligands on a formal $R'P^{2+}$ dication (phosphinidenium) Lewis acceptor, as illustrated by molecular frameworks presented above eq 4. In contrast to phosphenium[21,22,22−25] and arsenium cations,[26−29] examples of salts containing phosphinidenium dications have not been reported.

As for mixtures of $ClPR'_2$, Ph_3As and $Me_3SiOSO_2CF_3$, mixtures of $R'PCl_2$ with Ph_3As and $Me_3SiOSO_2CF_3$ show no evidence of reaction in the $^{31}P\{^1H\}$ NMR spectra after 24 h. Nevertheless, the more basic ligand Me_3As enables formation of derivatives of $[Me_3AsP(R')AsMe_3][OSO_2CF_3]_2$ (R′ = Me, Ph, Et, ^{i}Pr, Cy) using reaction 4 as evidenced by $^{31}P\{^1H\}$ NMR spectra (Table 3) of reaction mixtures. The identity of the triflate salts is also confirmed by the solid state structure of $[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$, the cation of which is shown in Figure 2b. It has not been possible to identify the chlorophosphinoarsonium cation $[R'_3AsP(Cl)R]^+$ intermediate, which is inevitable in these reactions based on the observed products, even though salts of the corresponding chlorophosphinophosphonium cations have been previously isolated.[4]

Reaction mixtures composed of dichlorophosphines ($R'PCl_2$, R = Ph, Et, ^{i}Pr, Me), Ph_3Sb and $AlCl_3$ in CH_2Cl_2 also exhibit one product signal in the $^{31}P\{^1H\}$ NMR spectra, independent of the imposed reaction stoichiometry. In contrast to reaction mixtures involving arsine donors, crystallographic characterization of the product from the reaction of $PhPCl_2$ (or $^iPrPCl_2$), Ph_3Sb and $AlCl_3$ reveal the first salts of 2,3-diphosphino-1,4-distibonium cations, resulting from reaction 5. Views of the solid state structures of the dications in $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ and $[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$ are shown in Figure 3. Other derivatives of $[Ph_3SbP(R')P(R')SbPh_3][AlCl_4]_2$ have been prepared *in situ* as evidenced by $^{31}P\{^1H\}$ NMR spectra (Table 3) of reaction mixtures. Integrated ^1H NMR data

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Table 4. Selected Interatomic Distances in Phosphinopnictonium Compounds

	P−P (Å)	Pn−P (Å)	ref
$[Me_3AsPPh_2][OSO_2CF_3]$	−	2.3239(7)	*d*
$[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$	−	2.3267(6), 2.3283(6)	*d*
$[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$	−	2.3247(7), 2.3198(7)	*d*
$[Ph_3PP(Ph)P(Ph)PPh_3][OSO_2CF_3]_2$	2.258(1), 2.221(1)	N/A	9
$[Me_3PP(Ph)P(Ph)PMe_3][OSO_2CF_3]_2$	2.2041(9), 2.2318(12)	N/A	9
$[Ph_3PP(Me)P(Me)PPh_3][OSO_2CF_3]_2$	2.206(13), 2.2284(12)	N/A	9
$[Me_3PP(Me)P(Me)PMe_3][OSO_2CF_3]_2$	2.192(2), 2.243(2), 2.191(2)	N/A	9
$[Ph_3PP(Et)P(Et)PPh_3][OSO_2CF_3]_2$	2.2048(8), 2.2153(11)	N/A	9
$[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$[a]	2.221(4), 2.241(5)	2.379(2), 2.365(2)	*d*
$[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$[c]	2.2271(12), 2.2215(18)	2.3106(10), 2.3199(9), 2.3118(10)	*d*
$[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$	2.226(4)	2.523(3), 2.503(3)	*d*
$[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$[b]	2.2357(10)	2.5387(5)	*d*

[a] Two independent cations, both inversion-symmetric. [b] Cation is inversion-symmetric. [c] Two independent cations, one is inversion-symmetric. [d] This work.

Table 5. Selected Angles in Phosphinopnictonium Compounds

	Pn−P−Pn (deg)	Pn−P−P−Pn (deg)	ΣR−Pn−Pn (deg)	ref
$[Me_3AsPPh_2][OSO_2CF_3]$	−	−	301.1	*d*
$[Me_3AsP(Me)AsMe_3][OSO_2CF_3]_2$	106.80(2)	−	306.2	*d*
$[Ph_3AsP(Me)AsPh_3][AlCl_4]_2$	102.77(3)	−	304.0	*d*
$[Ph_3PP(Ph)P(Ph)PPh_3][OSO_2CF_3]_2$	97.20(3)[b]	180	299.5	9
$[Me_3PP(Ph)P(Ph)PMe_3][OSO_2CF_3]_2$	96.41(3)[b]	180	295.2	9
$[Ph_3PP(Me)P(Me)PPh_3][OSO_2CF_3]_2$	96.66(4), 91.45(4)	−159.98(4)	298.4 303.9	9
$[Me_3PP(Me)P(Me)PMe_3][OSO_2CF_3]_2$	95.20(3), 94.45(3)	−126.72(3)	295.2 298.7	9
$[Ph_3PP(Et)P(Et)PPh_3][OSO_2CF_3]_2$	95.83(3)[b]	−142.35(3)	309.3	9
$[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$[a]	95.16(12), 96.60(13)	180.0, 180.0	293.8 295.7	*d*
$[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$[c]	97.58(4), 94.54(4), 95.86(5)	173.36(3), 180.0	295.7 294.7 294.8	*d*
$[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$	93.63(13), 93.77(13)	−5.0(6)	306.7 308.5	*d*
$[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$[b]	93.62(3)	180.0	290.5	*d*

[a] Two independent cations, both inversion-symmetric. [b] Cation is inversion-symmetric. [c] Two independent cations, one is inversion-symmetric. [d] This work.

(Table 3) for derivatives of $[R_3SbP(R')P(R')SbR_3][AlCl_4]_2$ are consistent with the 2,3-diphosphino-1,4-distibonium formula.

Formation of the 2,3-diphosphino-1,4-distibonium bis(tetrachloroaluminate) salts from the assembly of two molecules of $R'PCl_2$ with two molecules of Ph_3Sb and two molecules of $AlCl_3$ involves a chloride abstraction from the phosphine with subsequent coordination of a stibine to the resulting chlorophosphenium cation and reductive P−P coupling of two cationic phosphorus centers. There is no evidence for the intermediate existence of the chlorophosphinostibonium cation $[Ph_3SbP(Cl)R']^+$, perhaps indicating that the P−P reductive coupling reaction precedes the chloride abstraction and Sb→P coordination. Formation of $[Ph_3SbP(R')P(R')SbPh_3]^{2+}$ is analogous to that reported for reactions of a dichlorophosphine with a phosphine and $MeSi_3OSO_2CF_3$ to give derivatives of $[R_3PP(R')P(R')PR_3][OSO_2CF_3]_2$, examples of which are listed in Tables 3, 4, and 5.[9] Analogous reaction mixtures containing Ph_3Bi in place of Ph_3Sb render yellow reaction mixtures which show many signals in the $^{31}P\{^1H\}$ NMR spectra, but it has not been possible to isolate or identify the products.

We attribute the distinct difference in outcome for reactions 4 and 5 to the relative redox properties of arsenic and antimony. In contrast to Ph_3Sb, R_3As is an ineffective reducing agent. Adjustment of the stoichiometry of the reaction mixtures described by reactions 4 and 5 does not influence the cations formed. It has not been possible to observe derivatives of $[Ph_3SbP(R')SbPh_3][AlCl_4]_2$ or $[R_3AsP(R')P(R')AsR_3][AlCl_4]_2$ in these reactions. Nevertheless, as the basicity of Ph_3Sb is lower than that of R_3As (R = Me, Et, Ph) or Ph_3P, reactions of $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ with excess Ph_3P or R_3As (R = Me, Et, Ph) result in quantitative formation of $[Ph_3PP(Ph)P(Ph)PPh_3][AlCl_4]_2$ and $[R_3AsP(Ph)P(Ph)AsR_3][AlCl_4]_2$, respectively, according to reaction 6, as evidenced by the $^{31}P\{^1H\}$ NMR spectra of reaction mixtures. The solid state structures of $[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$ and $[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$ have been determined by X-ray crystallography and views of the structures of the dications are shown in Figure 4. It was not possible to observe the anticipated nonsymmetric cation in salts of the form $[R_3AsP(R')P(R')SbR_3][AlCl_4]_2$ for a reaction stoichiometry with less than the 2 equiv of arsine or phosphine. Instead, the reaction mixture contains unreacted $[Ph_3SbP(R)P(R')SbPh_3][AlCl_4]_2$ and the symmetric 2,3-diphosphino-1,4-diarsonium cation $[R_3AsP(R')P(R')AsR_3]^{2+}$, suggesting that the inevitable nonsymmetric intermediate $[R_3AsP(R')P(R')SbPh_3]^{2+}$ is more susceptible to ligand exchange than $[Ph_3SbP(R')P(R')SbPh_3]^{2+}$.

Selected solid state structural parameters for $[Me_3AsPPh_2]^+$ and derivatives of $[R_3AsP(R')AsR_3]^{2+}$ and $[R_3PnP(R')P(R')PnR_3]^{2+}$ (Pn = P, As, Sb) are presented in Tables 4 (bond lengths) and Table 5 (bond angles). In all cases, the terminal pnictonium environments adopt the predictable distorted tetrahedral geometry as shown in Figures 1−4. The trigonal pyramidal geometry for the phosphine centers exhibit smaller Pn−P−Pn angles in $[Me_3AsPPh_2]^+$ and derivatives of

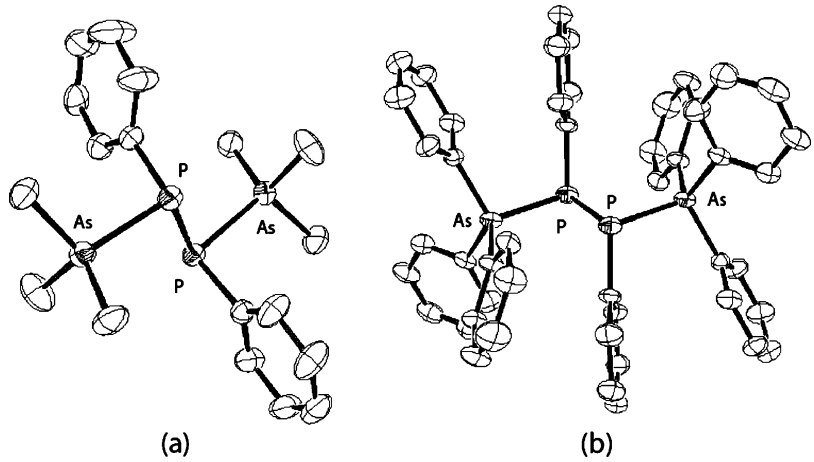

Figure 4. Crystallographic views of the dications in (a) $[Me_3AsP(Ph)P(Ph)AsMe_3][AlCl_4]_2$ and in (b) $[Ph_3AsP(Ph)P(Ph)AsPh_3][AlCl_4]_2$. Ellipsoids presented at 50%, hydrogen atoms and counteranions removed for clarity. All nonlabeled atoms are carbon.

$[R_3PnP(R')P(R')PnR_3]^{2+}$ than in derivatives of $[R_3AsP(R')AsR_3]^{2+}$, likely due to the steric imposition of the two arsonium centers. All of the interpnictogen bond lengths are within a narrow range, are typical for single bonds and are essentially independent of the molecular charge or the substitution (Table 4). The cation in $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ (Figure 2a) adopts an *R,S* configuration and a torsional angle of 180.0° for the Sb−P−P−Sb framework, consistent with the P−P−P−P framework of the phosphorus analogue $[Ph_3PP(Ph)P(Ph)PPh_3][OSO_2CF_3]_2$.[9] The cation in $[Ph_3SbP(^iPr)P(^iPr)SbPh_3][AlCl_4]_2$ (Figure 2b) shows an *S,S* configuration with an eclipsed conformation [C−P−P−C torsional angle = −5.0(6)°], consistent with the calculated gas phase structure of $[H_3PP(^iPr)P(^iPr)PH_3]^{2+}$.[9] Only one isomer is observed in the solid state structure for both derivatives of $[Ph_3SbP(R)P(R)SbPh_3]^{2+}$, consistent with the observed $^{31}P\{^1H\}$ NMR spectra (Table 3). The solid state structures for both derivatives of $[R_3AsP(Ph)P(Ph)AsR_3]^{2+}$ adopt anti conformations consistent with the structures of the dications in $[Ph_3SbP(Ph)P(Ph)SbPh_3][AlCl_4]_2$ and $[Ph_3PP(Ph)P(Ph)PPh_3][OSO_2CF_3]_2$.

Conclusion

Reactions of chlorophosphines or dichlorophosphine with arsines (R_3As, R = Me, Et, Ph) or Ph_3Sb in the presence of a chloride ion abstracting agent ($AlCl_3$, $GaCl_3$, $Me_3SiOSO_2CF_3$) provide a versatile one pot synthetic approach to interpnictogen frameworks containing two, three or four pnictogen centers. The compounds represent the first examples of salts containing phosphinoarsonium, 2-phosphino-1,3-diarsonium, 2,3-diphosphino-1,4-diarsonium and 2,3-diphosphino-1,4-distibonium cations. The bonding in the cations can be viewed as interpnictogen coordination and are the first examples of As→P and Sb→P bonding. As such, the complexes demonstrate the possibility of the interaction between a donor that is a weaker base than the acceptor by virtue of a cationic charge on the acceptor. The high yield and generic nature of these new preparative reactions bodes well for the discovery of interpnictogen compounds representing building blocks in the development of new materials.

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Supporting Information Available: CIF files with crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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