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Arsinophosphonium Cations from Arsenium-phosphine and -bisphosphine Coordination Chemistry

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A new 14π-electron tricyclic organoarsenium cation (5-hydrophenarsazinium, AN, $C_{12}H_9AsN^+$) has been prepared in situ and used as a Lewis acceptor with trimethylphosphine, triphenylphosphine, bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)methane (dmpm), and 1,4-bis(diphenylphosphino)benzene (dppb) ligands. Solid-state structures and spectroscopic characterization data are reported for complexes of the general formula $[AN–PMe_3]^+$, $[AN–PPh_3]^+$, $[AN–dppm]^+$, $[AN–dppm–AN]^{2+}$, $[AN–dmpm–AN]^{2+}$, and $[AN–dppb–AN]^{2+}$ as tetrachlorogallate salts. Depending on reaction stoichiometry, dppm forms adducts at one or both of the donor sites. Structural comparisons with analogous complexes of phosphenium cations provide interesting similarities and differences.

Introduction

The coordination chemistry of electron-rich (lone-pair bearing) phosphorus centers as Lewis acceptors[1] is well established and provides a new approach to forming bonds between phosphorus and carbon,[2−9] nitrogen,[10−18] oxygen,[19] phosphorus,[17,20−28] sulfur,[19] chlorine,[8] gallium,[29] bromine,[8] or selenium.[19] Solid-state structural characterization data or NMR data that have been reported for examples of complexes involving electron-rich arsenic Lewis acceptors[30−40]

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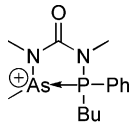
highlight the potential for application of this methodology to arsenic chemistry. Moreover, the intramolecular phosphine complex, **1**,[39]



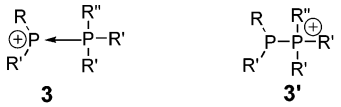
1

and the prototypical arsenium−phosphine complexes, **2**,[40]

2 **2′**

a: Pn = As; R = Me, R' = R'' = Ph
b: Pn = As; R = Me, R' = Ph, R'' = 2-(MeO)C_6H_4

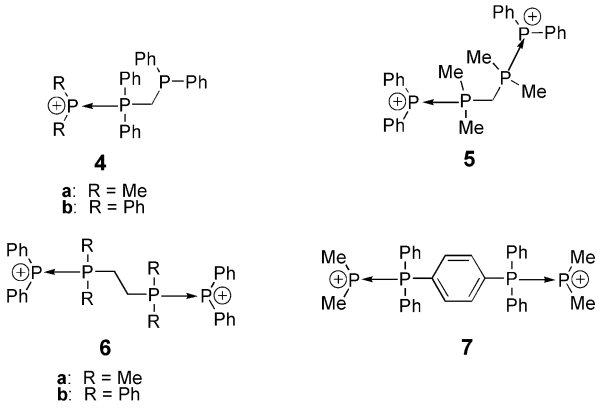
are analogues of the phosphenium-phosphine cations, **3**,[41,20] and were first proposed as "arsinophosphonium" cations, **2′**, for solids with appropriate elemental composition that were isolated from reactions of dialkylhaloarsines with triarylphosphines.[42]



3 **3'**

R = Me, Ph; R' = Me, Ph; R'' = Me, Ph, Cl

The extensive ligand exchange chemistry that has been observed for derivatives of **3′** [15,20,29,43] defines the reactivity of the phosphorus derivatives as ligand stabilized phosphenium cations, **3**, but the coordination sphere of the phosphenium Lewis acceptor is apparently restricted to a single ligand. Nevertheless, the coordination chemistry of phosphenium cations has been extended using bisphosphine ligands dppm, dmpm, dppe, dmpe, dpph, and dppb, which give triphosphorus monocations, **4**, and tetraphosphorus dications, **5**, **6**, and **7**,[20] depending on the ligand backbone and the steric crowding of the donor and the acceptor sites.



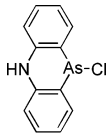
4 **5**

a: R = Me
b: R = Ph

6 **7**

a: R = Me
b: R = Ph

Attempts to isolate complexes of the diphenylarsenium cation have been unsuccessful, but the closely related tricyclic 5-hydrophenarsazinium cation (AN, $[C_{12}H_9AsN]^+$) has been prepared in situ from 10-chloro-5-hydrophenarsazine (ANCl **8**)[44] and a number of arsinophosphonium, arsinophosphoniumphosphine, and bisarsinobisphosphonium tetrachlorogallate salts have been isolated and comprehensively characterized.



8
ANCl

Cations with the abbreviated formulas $[AN-PR_3]^+$ (R = Me, Ph), $[AN-dppm]^+$, $[AN-dppm-AN]^{2+}$, $[AN-dmpm-AN]^{2+}$, and $[AN-dppb-AN]^{2+}$ demonstrate a versatile Lewis acid behavior for the new 14π-electron arsenium cation (AN). The complexes exploit a new avenue of phosphorus−arsenic chemistry in a rational and systematic manner, offering interesting structural comparisons, and the observation that both $[AN-dppm]^+$ and $[AN-dppm-AN]^{2+}$ demonstrate some control of ligand stoichiometry.

Experimental Section

General. All manipulations were carried out in a N_2-filled Innovative Technologies drybox. Solvents were purified using an MBraun Solvent Purification System and were degassed with three freeze−pump−thaw cycles prior to use. Arsenic trichloride was purchased from BDH. Triphenylphosphine, gallium chloride, trimethylsilyltrifluoromethanesulfonate (TMS-OTf), bis(diphenylphosphino)methane (dppm), and bis(dimethylphosphino)methane (dmpm) were purchased from Aldrich Chemical Co., and 1,4-bis(diphenylphosphino)benzene (1,4-dppb) was purchased form Kodak Chemical Company. All reagents were used as received without further purification. 10-Chloro-5-hydrophenarsazine (ANCl **8**, "adamsite") was prepared by a literature procedure.[44] IR spectra were recorded

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Table 1. Crystal Data

	[AN−PMe_3] **9a** [$GaCl_4$]	[AN−PMe_3] **9a** [OTf]	[AN−PPh_3] **9b** [OTf]
formula	$C_{15}H_{18}AsCl_4GaNP$	$C_{16}H_{18}AsF_3NO_3PS$	$C_{31}H_{24}AsF_3NO_3PS$
fw (g mol^{-1})	529.71	467.26	653.46
cryst syst	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	*Pbca*	$P\bar{1}$
a (Å)	8.9063(6)	12.4041(11)	10.9114(6)
b (Å)	10.4349(7)	14.4224(13)	11.2816(6)
c (Å)	11.5512(7)	21.608(2)	14.0864(8)
α (deg)	87.2939(9)	−	68.8860(10)
β (deg)	83.2283(9)	−	69.0570(10)
γ (deg)	80.7053(8)	−	66.4330(10)
V ($Å^3$)	1051.61(12)	3865.5(6)	1435.75(14)
Z	2	8	2
D_c (Mg m^3)	1.673	1.606	1.512
R1 ($I > 2\sigma(I)$)	0.0276	0.0899	0.0330
wR2 ($I > 2\sigma(I)$)	0.0643	0.0890	0.0759
GOF	1.072	1.049	1.030

	[AN−dppm] **10** [$GaCl_4$]	[AN−dppm−AN] **11a** [$GaCl_4]_2$	[AN−dmpm−AN] **11b** [$GaCl_4]_2$	[AN−dppb−AN]**12** [$GaCl_4]_2$ [CH_2Cl_2]
formula	$C_{37}H_{31}AsCl_4GaNP_2$	$C_{49}H_{40}As_2Cl_8Ga_2N_2P_2$	$C_{29}H_{32}As_2Cl_8Ga_2N_2P_2$	$C_{55}H_{44}As_2Cl_{10}Ga_2N_2P_2$
fw (g mol^{-1})	838.01	1291.65	1043.39	1438.64
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.8267(8)	11.9023(6)	10.2840(9)	12.973(2)
b (Å)	11.0873(8)	12.1996(6)	11.5340(10)	21.727(3)
c (Å)	16.9738(12)	19.0401(10)	17.5873(15)	21.088(3)
α (deg)	93.6919(10)	80.5845(9)	75.9930(10)	−
β (deg)	105.8446(10)	79.7616(9)	85.1000(10)	97.109(2)
γ (deg)	107.4575(10)	78.9139(9)	76.6770(10)	−
V ($Å^3$)	1845.9(2)	2645.8(2)	1968.7(3)	5898.2(16)
Z	2	2	2	4
D_c (Mg m^3)	1.508	1.621	1.760	1.620
R1 ($I > 2\sigma(I)$)	0.0501	0.0627	0.0503	0.0528
wR2 ($I > 2\sigma(I)$)	0.1026	0.1207	0.0734	0.0831
GOF	1.034	1.064	0.993	1.026

on a Bruker VECTOR 22 FT-IR using Nujol mulls and are reported with ranked intensities in parentheses. Solution NMR data were obtained on a Bruker AC-250 NMR spectrometer at room temperature unless otherwise indicated. Chemical shifts are reported in ppm relative to a reference standard [TMS (^{1}H); 85% H_3PO_4 (^{31}P)] and *J* values are reported in Hz. Unless otherwise indicated, crystalline samples were obtained by vapor diffusion, in which the sample (0.050 to 0.100 g) was dissolved in a minimal amount of CH_2Cl_2 in an uncapped 1 dram vial that was placed inside a 4 dram vial containing Et_2O, hexane, or pentane (2 mL). The larger vial was capped tightly, and the system was allowed to stand at room temperature. Crystals were mounted under oil (perfluoropolyether or Paratone). X-ray diffraction data (Table 1) were collected at 193(2) K on a Bruker PLATFORM diffractometer with a sealed tube generator and a SMART 1000 CCD detector using graphite-monochromated Mo Kα ($\lambda = 0.71073$) radiation.

Preparative Procedures and Characterization Data. [AN−PMe_3][$GaCl_4$]. A solution of $GaCl_3$ (0.032 g, 0.18 mmol) in CH_2Cl_2 (2 mL) was added to a solution of ANCl (0.050 g, 0.18 mmol) in CH_2Cl_2 (5 mL). PMe_3 (1.0 M in hexane, 180 μL, 0.18 mmol) was added after 1 h, and the mixture was stirred for 48 h. The solvent was reduced in vacuo to 2 mL, and the addition of hexanes gave a white precipitate. Crystallization was by hexane vapor diffusion into a CH_2Cl_2 solution. Yield: 0.089 g, 93%. mp: 152 °C. Elemental analyses were not determined. IR (cm^{-1}): 300 (13), 361 (15), 375 (1), 445 (3), 560 (10), 802 (6), 958 (2), 1027 (4), 1235 (14), 1261 (8), 1342 (11), 1576 (5), 1595 (9), 2360 (12), 3375 (7). ^{1}H NMR (CD_2Cl_2): δ 8.2 (s, 1H, NH), 7.6−7.1 (m, 8H, aromatic), 1.6 (d, 9H, CH_3, $^2J_{PH} = 13.7$ Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 7.

[AN−PMe_3][OTf]. PMe_3 (1.0 M in hexane, 77 μL, 0.077 mmol) was added to a solution of [AN−PPh_3][OTf] (0.050 g, 0.077 mmol) in CH_2Cl_2 (5 mL). The solvent was reduced in vacuo to 2 mL, and the addition of hexane gave an off-white precipitate. Crystallization was by Et_2O vapor diffusion into a CH_2Cl_2 solution. Yield 0.043 g, 91%. mp: 183−184 °C. Elemental analyses were not determined. IR (cm^{-1}): 450 (15), 517 (13), 636 (8), 750 (7), 962 (5), 1028 (4), 1156 (2), 1224 (6), 1249 (1), 1282 (3), 1344 (9), 1522 (14), 1576 (10), 1601 (11), 3314 (12). ^{1}H NMR (CD_2Cl_2): δ 8.2 (s, 1H, NH), 7.6−7.1 (m, 8H, aromatic), 1.5 (d, 9H, CH_3, $^2J_{PH} = 13.7$ Hz). ^{31}P-{^{1}H} NMR (CH_2Cl_2): δ 7.

[AN−PPh_3][OTf]. TMS−OTf (0.33 mL, 1.80 mmol) was added to ANCl (0.499 g, 1.80 mmol) in CH_2Cl_2 (15 mL). Ph_3P (0.473 g, 1.80 mmol) in CH_2Cl_2 (10 mL) was added after 1 h and stirred for 5 h. Solvent was removed in vacuo giving a yellow precipitate that was filtered and washed with 2 × 10 mL hexane. Crystallization was by Et_2O vapor diffusion into a CH_2Cl_2 solution. Yield: 1.06 g, 90%. mp: 170−171 °C. Elemental analyses were not determined. IR (cm^{-1}): 495 (14), 517 (13), 634 (10), 692 (12), 720 (18), 746 (5), 755 (7), 995 (15), 1029 (3), 1096 (11), 1151 (4), 1223 (6), 1257 (1), 1282 (2), 1346 (9). ^{31}P{^{1}H} NMR: δ 6.

[AN−dppm][$GaCl_4$]. Dppm (0.038 g, 0.10 mmol) in CH_2Cl_2 (2 mL) was added to a solution of ANCl (0.028 g, 0.10 mmol) in CH_2Cl_2 (2 mL) and $GaCl_3$ (0.018 g, 0.10 mmol) in CH_2Cl_2 (2 mL).

Table 2. Selected As−P and As−C Distances (Å), C−As−C and C−As−P Angles (deg), and the Shortest Intermolecular and Intramolecular Distances (Å) Between the Centroids of AN and Aryl Planes and Angles (deg) between the Planes for Derivatives of **1**, **2**, **9**, **10**, **11**, and **12**

	As−P	As−C	C−As−C	C−As−P	AN···AN (angle)	iPh···AN (angle)	ref
1 [BPh_4]	2.346(2)	1.975(7) 1.877(5) (As−N)	98.8(3) (C−As−N)	96.6 (3) 83.9(2) (N−As−P)			39
[PhMeAs−PPh_3] **2a** [PF_6]	2.3480(5)	1.959(2) 1.955(2)	101.73(7)	92.31(8) 997.04(6)			40
[PhMeAs−PPh_2 {2-(MeO)C_6H_4}] **2b** [PF_6]	2.3703(5)	1.956(2) 1.957(2)	100.35(8)	95.59(6) 96.99(5)			40
[AN−PPh_3] **9b** [OTf]	As1−P1 2.4121(5)	As1−C1 1.913(2) As1−C7 1.914(2)	C1−As1−C7 97.31(8)	C1−As1−P1 95.76(6) C7−As1−P1 99.38(5)	3.361 (0)		*a*
[AN−PMe_3] **9a** [$GaCl_4$]	As1−P1 2.3393(6)	As1−C11 1.928(2) As1−C21 1.934(2)	C11−As1−C21 97.36(9)	C11−As1−P1 94.30(6) C21−As1−P1 94.03(6)	3.334 (0)		*a*
[AN−PMe_3] **9a** [OTf]	As1−P1 2.342(1)	As1−C1 1.937(4) As1−C1 1.931(4)	C21−As1−C11 96.9(2)	C11−As1−P1 95.9(1) C21−As1−P1 94.1(1)	3.322 (0)		*a*
[AN−dppm] **10** [$GaCl_4$]	As1−P1 2.3753(8)	As1−C1 1.922(3) As1−C12 1.928(3)	C1−As1−C12 97.5(1)	C1−As1−P1 93.82(9) C12−As1−P1 94.29(9)	3.402 (0)	3.683 (22.7)	*a*
[AN−dppm−AN] **11a** [$GaCl_4$]$_2$	As1−P1 2.414(1) As2−P2 2.417(1)	As1−C11 1.928(4) As1−C21 1.920(4) As2−C41 1.921(5) As2−C31 1.924(5)	C21−As1−C11 97.8(2) C41−As2−C31 97.2(2)	C11−As1−P1 94.1(1) C21−As1−P1 92.6(1) C41−As2−P2 93.2(1) C31−As2−P2 91.7(1)	3.335 (0)	3.502 (15.5) 3.437 (18.0)	*a*
[AN−dmpm−AN] **11b** [$GaCl_4$]$_2$	As1−P1 2.3755(8) As2−P2 2.3663(9)	As1−C1 1.931(3) As1−C7 1.927(3) As2−C21 1.917(3) As2−C27 1.919(3)	C11−As1−C11 97.1(1) C21−As2−C27 97.6(1)	C1−As1−P1 91.09(9) C7−As1−P1 95.78(9) C21−As2−P2 94.62(9) C27−As2−P2 93.72(9)	3.371 (0)		*a*
[AN−dppb−AN] **12** [$GaCl_4$]$_2$ [b]	As1A−P1A 2.3925(8)	As1A−C11A 1.926(4) As1A−C21A 1.930(3)	C11A−As1A−C21A 97.7(1)	C11A−As1A−P1A 96.08(9) C21A−As1A−P1A 92.54(9)	3.503 (4.2)	A 3.632 (20.6) B: 3.641 (20.5)	*a*

[a] This work. [b] One of two essentially identical asymmetric units.

After 1 h, the solvent was reduced in vacuo to 2 mL, and the addition of Et_2O (10 mL) gave a yellow precipitate, which was recrystallized by liquid−liquid diffusion (CH_2Cl_2/hexane). Yield: 0.051 g, 61%. mp: 179−180 °C. Anal. Calcd for $C_{37}H_{31}AsCl_4GaNP_2$ (Found): C, 53.03 (52.92); H, 3.73 (3.52); N, 1.67 (1.57). IR (cm^{-1}): 461 (4), 480 (19), 502 (7), 519 (13), 586 (17), 658 (16), 687 (2), 891 (14), 997 (15), 1027 (8), 1105 (5), 1160 (9), 1235 (12), 1307 (18), 1351 (20), 1513 (10), 1574 (6), 1595 (1), 2725 (11), 3358 (3). ^{1}H NMR (CD_2Cl_2): δ 8.2 (s, 1H, NH), 7.6−6.6 (m, 28H, aromatic), 2.9 (t, 2H, CH_2, $^2J_{PH}$ = 6.3 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2, 200 K): δ 11 (d, $^2J_{PP}$ = 75 Hz), −30 (d, $^2J_{PP}$ = 75 Hz).

[AN−dppm−AN][GaCl$_4$]$_2$. $GaCl_3$ (0.035 g, 0.20 mmol) in CH_2Cl_2 (2 mL) was added to a ANCl (0.056 g, 0.20 mmol) in CH_2Cl_2 (2 mL). The resulting purple solution was then slowly added dropwise to a solution of dppm (0.038 g, 0.01 mmol) in CH_2Cl_2 (2 mL). Orange crystalline material slowly precipitated. Yield 0.099 g, 77%. mp 223 °C. Anal. Calcd for $C_{49}H_{40}As_2C_{l8}Ga_2N_2P_2$ (Found): C, 45.56 (45.04); H, 3.12 (2.88); N, 2.17 (1.95). IR (cm^{-1}): 453 (6), 494 (15), 585 (11), 685 (3), 890 (14), 1024 (10), 1063 (12), 1102 (4), 1164 (7), 1235 (8), 1317 (13), 1515 (9), 1573 (5), 1596 (1), 3357 (2). ^{1}H NMR (CD_2Cl_2): δ 8.2 (s, 2H, NH), 7.6−6.8 (m, 36H, aromatic), 3.0 (t, 2H, CH_2, $^2J_{PH}$ = 9.5 Hz). ^{31}P-{^{1}H} NMR (CH_2Cl_2): δ 4.

[AN−dmpm−AN][GaCl$_4$]$_2$. $GaCl_3$ (0.018 g, 0.10 mmol) in CH_2Cl_2 (2 mL) was added to ANCl (0.028 g, 0.10 mmol) in CH_2Cl_2 (5 mL). The resulting purple solution was then added dropwise to a solution of dmpm (0.014 g, 0.10 mmol) in CH_2Cl_2 (5 mL), giving a pale yellow solution which was stirred for 24 h. Crystallization by liquid−liquid diffusion (CH_2Cl_2/hexane) gave yellow crystals. Yield 0.05 g, 60%. mp 174−175 °C. Elemental analyses were not determined. IR (cm^{-1}): 801 (14), 893 (1), 952 (6), 1025 (3), 1178 (8), 1261 (4), 1507 (11), 1541 (15), 1559 (12), 1576 (5), 1595 (2), 1653 (9), 3375 (10), 3750 (13), 3853 (7). ^{1}H NMR (CD_2Cl_2): δ 8.2 (s, 2H, NH), 7.7−7.1 (m, 16H, aromatic), 1.4 (d, 12H, CH_3, $^2J_{PH}$ = 5 Hz), 2.0 (t, 2H, CH_2, $^2J_{PH}$ = 7 Hz). ^{31}P{^{1}H} NMR (CH_2Cl_2, 200 K): δ 16, −43.

[AN−dppb−AN][GaCl$_4$]$_2$. A solution of dppb (0.045 g., 0.10 mmol) in CH_2Cl_2 (2 mL) was added to ANCl (0.028 g, 0.10 mmol) in CH_2Cl_2 (2 mL) and $GaCl_3$ (0.018 g, 0.1 mmol) in CH_2Cl_2 (2 mL). Red-orange crystals formed when the solution stood at room temperature. Yield: 0.046 g, 51. mp: 253−254 °C. Anal. Calcd for $C_{54}H_{42}As_2Cl_8Ga_2N_2P_2$ (Found): C, 47.91 (45.92); H, 3.13 (3.08); N, 2.07 (1.95). IR (cm^{-1}): 282 (12), 374 (2), 441 (10), 496 (13),

Table 3. Comparison of P−C−P−Pn and C−Pn−P−C Torsional Angles (deg) for derivatives of **4**, **5**, **7**, **10**, **11**, and **12**

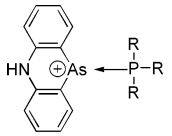
	P−C−P−Pn	CA−Pn−P−C	C−Pn−P−C	ref
[Me_2P-dppm] **4a** [OTf]	P(3)−C(3)−P(2)−P(1) −52.3(2)	C(1)−P(1)−P(2)−C(3) −147.4(2)	C(2)−P(1)−P(2)−C(3) −44.9(2)	43
[Me_2P-dppm] **4a** [$GaCl_4$]	P(3)−C(3)−P(2)−P(1) 60.4(2)	C(1)−P(1)−P(2)−C(3) 65.3(2)	C(2)−P(1)−P(2)−C(3) 167.4(2)	43
[Ph_2P-dppm] **4b** [OTf]	P(1)−C(1)−P(2)−P(3) −61.3(1)	C(51)−P(3)−P(2)−C(1) −163.6(1)	C(61)−P(3)−P(2)−C(1) −54.7(1)	43
[Ph_2P-dmpm-PPh_2] **5** [$GaCl_4$]$_2$	P(1′)−C(1)−P(1)−P(2) −38.05(6) P(1)−C(1)−P(1′)−P(2′) −38.05(6)	C(11)−P(2)−P(1)−C(1) 166.3(2) C(11′)−P(2′)−P(1′)−C(1) 166.3(2)	C(21)−P(2)−P(1)−C(1) −86.8(2) C(21′)−P(2′)−P(1′)−C(1) −86.8(2)	43
[Ph_2P-dmpm-PPh_2] **5** [OTf]$_2$	P(3)−C(1)−P(2)−P(1) −68.6(2) P(2)−C(1)−P(3)−P(4) 170.1(1)	C(11)−P(1)−P(2)−C(1) −106.3(1) C(31)−P(4)−P(3)−C(1) −79.7(1)	C(21)−P(1)−P(2)−C(1) 143.9(1) C(41)−P(4)−P(3)−C(1) 167.8(1)	43
[Me_2P-dppb-PMe_2] **7** [$GaCl_4$]$_2$		C(11)−P(1)−P(2)−C(1) −42.0(4) C(61)−P(4)−P(3)−C(4) 165.6(4) C(71′)−P(5′)−P(6′)−C(7′) 164.8(7) C(71)−P(5)−P(6)−C(7) 164.8(7)	C(12)−P(1)−P(2)−C(1) 60.3(4) C(62)−P(4)−P(3)−C(4) 63.5(4) C(72)−P(5)−P(6)−C(7) 67.2(6) C(72′)−P(5′)−P(6′)−C(7′) 67.2(6)	43
[AN−dppm] **10** [$GaCl_4$]	P(2)−C(20)−P(1)−As −176.1(1)	C(1)−As−P(1)−C(20) 65.2(1)	C(12)−As−P(1)−C(20) −163.0(1)	*a*
[AN−dppm−AN] **11a** [$GaCl_4$]$_2$	P(2)−C(1)−P(1)−As(1) −176.6(2) P(1)−C(1)−P(2)−As(2) −174.3(2)	C(11)−As(1)−P(1)−C(1) −179.2(2) C(31)−As(2)−P(2)−C(1) −74.7(2)	C(21)−As(1)−P(1)−C(1) −81.2(2) C(41)−As(2)−P(2)−C(1) −172.0(2)	*a*
[AN−dmpm−AN] **11b** [$GaCl_4$]$_2$	P(2)−C(40)−P(1)−As(1) 166.8(1) P(1)−C(40)−P(2)−As(2) 161.9(1)	C(1)−As(1)−P(1)−C(40) 174.5(2) C(21)−As(2)−P(2)−C(40) 70.5(2)	C(7)−As(1)−P(1)−C(40) 77.3(2) C(27)−As(2)−P(2)−C(40) −27.5(1)	*a*
[AN−dppb−AN] **12** [$GaCl_4$]$_2$ [b]		C(11A)−As(1A)−P(1A) −C(51A) −46.8(1)	C(21A)−As(1A)−P(1A)−C(51A) 51.2(1)	*a*

[a] This work. [b] One of two essentially identical asymmetric units.

519 (1), 577 (4), 693 (6), 801 (5), 1023 (3), 1098 (7), 1164 (15), 1261 (8), 1573 (14), 1595 (9), 3357 (11). The compound is sparingly soluble, and NMR data could not be obtained.

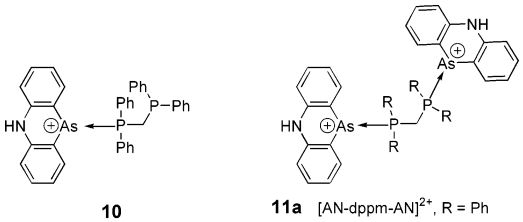
Results and Discussion

The bisphosphines dppm, dmpm, dppe, dmpe, dpph, and dppb are traditionally employed as chelate ligands or bridging ligands for transition metals. They have recently been used to effect ligand exchange of the phosphine in phosphenium−phosphine **3** (phosphinophosphonium cations **3′**) to give phosphenium−bisphosphine **4** (phosphinophosphoniumphosphine **4′**) and bisphosphenium−bisphosphine **5**, **6**, and **7** cations (bisphosphinobisphosphonium **5′**, **6′**, and **7′**).[43] Tetrachlorogallate salts of arsenium−bisphosphine **10** (arsinophosphoniumphosphine **10′**) and bisarsenium−bisphosphine **11** and **12** (bisarsinobisphosphonium **11′**, **12′**) have now been prepared using an in situ generation of arsenium cation AN, and the comparative characterization data for the prototypical arsenium−phosphine **9** cations (arsinophosphonium **9′**), prepared in the same manner, provide a systematic means of developing new As−P bonded compounds.



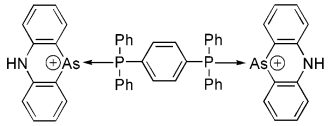
9
[AN-PR_3]$^+$ **a**: R = Me
b: R = Ph

Yellow solutions of 10-chloro-5-hydrophenarsazine (**8** ANCl, "adamsite")[44] react rapidly with trimethylsilyltrifluoromethanesulfonate (TMSOTf) or gallium chloride to give purple solutions. Attempts to isolate and characterize products from these reactions have been unsuccessful. Nevertheless, introduction of Ph_3P, Me_3P, or the tethered bisphosphines dppm, dmpm, or dppb, has enabled isolation of complexes containing the cationic unit AN with phosphine or bisphosphine ligands, which exhibit similar ^{31}P NMR chemical shifts to the quantitative products observed by ^{31}P NMR spectroscopy in each reaction mixture. Except in the case of reactions involving dppm, the ^{31}P NMR spectra of the reaction mixtures are independent of the imposed reaction stoichiometry, and chemical shifts for all derivatives of **9**,



10
[AN-dppm]$^+$

11a [AN-dppm-AN]$^{2+}$, R = Ph
11b [AN-dmpm-AN]$^{2+}$, R = Me



12
[AN-dppb-AN]$^{2+}$

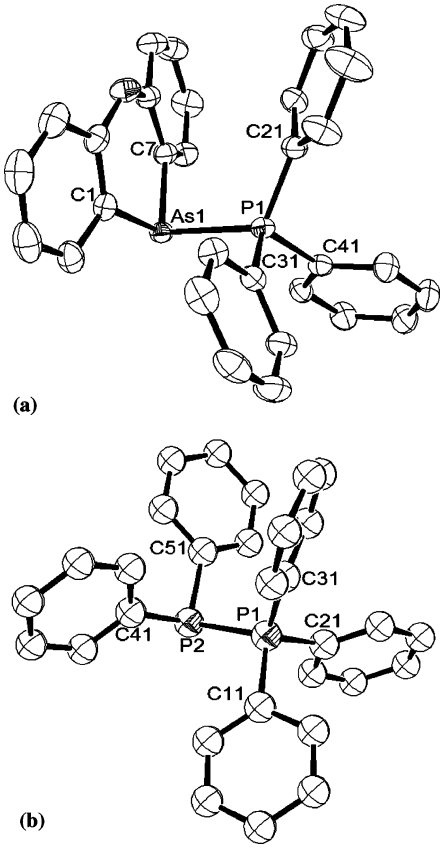


Figure 1. Representative structural view of the cation in (a) [AN−PPh_3] **9b** [OTf] and (b) [Ph_2P−PPh_3] **3** (R = R′ = R″ = Ph) [OTf].[20] Ellipsoids are drawn to 50% probability. Hydrogen atoms are not shown.

10, **11**, and **12** are consistent with the distinctive shifts for phosphorus analogues **4**, **5**, **6**, and **7**[20] and the phosphonium cations (e.g., Ph_4P^+, δ 20).[45]

X-ray crystallographic studies (Table 1) have confirmed the ionic formulations for tetrachlorogallate (gallate) and trifluoromethanesulfonate (triflate) salts of [AN−PMe_3] (**9a**), [AN−PPh_3] (**9b**), [AN−dppm] (**10**), [AN−dppm−AN] (**11a**), [AN−dmpm−AN] (**11b**), and [AN−dppb−AN] (**12**). Table 2 lists P−As distances and angles at the arsenic center for each compound together with values for the related cations in **1** [BPh_4],[39] **2a** [PF_6], and **2b** [PF_6],[40] which contain examples of previously reported As−P coordinate bonds. Table 3 provides a comparison of important torsional angles for cations involving bisphosphine ligands with arsenium or phosphenium cation acceptors.

The cations in [AN−PMe_3]**9a**[$GaCl_4$] and [AN−PMe_3]-**9a**[OTf] are essentially identical, indicating that the anion has no influence on the structure of the cation. A representative view of cation **9b** in [AN−PPh_3][OTf] is shown in Figure 1a, and it confirms the interaction of the donor phosphine center with the arsenic center with an approach that is perpendicular to the plane of AN and analogous to those in the phosphorus derivatives **3**, as shown in Figure 1b for [Ph_2P−PPh_3][$GaCl_4$]. Consequently, the arsenic centers adopt a pyramidal geometry in all compounds, with

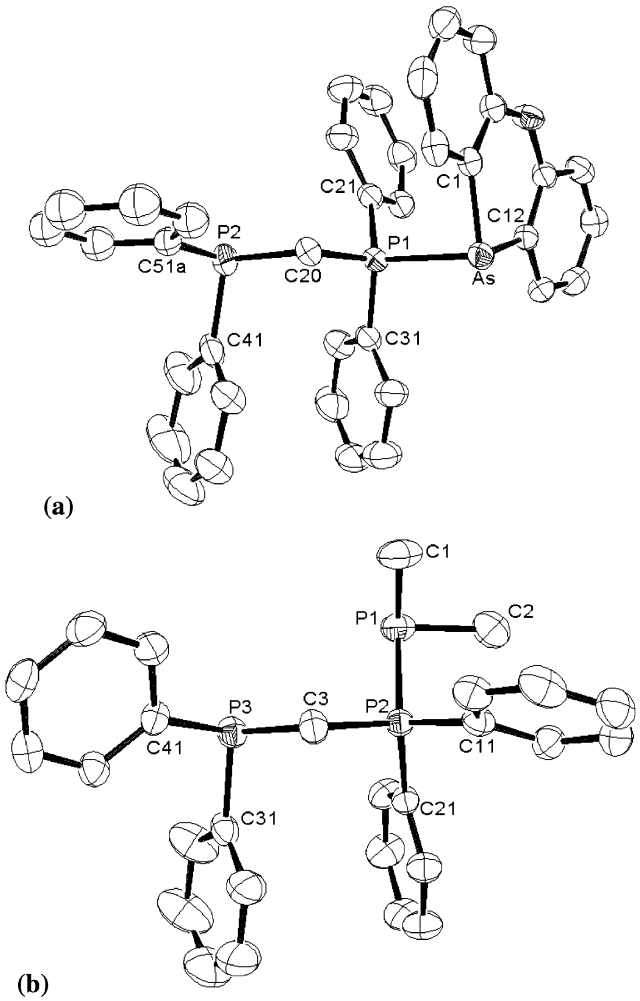


Figure 2. Representative structural views of the cations in (a) [AN−dppm] **10** [$GaCl_4$] and (b) [Me_2P-dppm] **4a** [$GaCl_4$].[43] Ellipsoids are drawn to 50% probability. Hydrogen atoms are not shown.

angles close to 90° (range 91.1−99.4°). The As−P distance is slightly shorter in [AN−PMe_3] **9a** [$GaCl_4$] and [AN−PMe_3] **9a** [OTf] than in [AN−PPh_3] **9b** [OTf], consistent with the relative inductive basicity of the respective phosphine ligands. The pyramidal geometry about the three-coordinate arsenic center in all cations is consistent with an arsine-like environment, and the donor phosphorus centers have a phosphonium-like distorted tetrahedral geometry. The As−P distances in [AN−PMe_3] **9a** and [AN−PPh_3] **9b** are the same as those in **2a** [PF_6] and **2b** [PF_6].[40]

Differences in As−C bond lengths between **2a**, **2b**, **9a**, and **9b**, as well as differences in the angles (C−As−C and C−As−P) at arsenic, can be rationalized in terms of the restrictions imposed by the heterocyclic framework of AN. The As−C bonds are slightly shorter in derivatives of **9** than those in **2a** and **2b**[40] because of the involvement of the arsenic center in the π framework of anthracenic unit AN. In addition, the C−As−C angle is slightly smaller in **9a** and **9b**, and the C−As−P angles are larger than those in **2a** and **2b**,[40] which represent complexes of acyclic arsenium acceptors. Although the As−P distance in **1**[BPh_4][39] is comparable with the those described above, it is not reasonable to compare the other structural features as the arsenic center

(45) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley-Interscience: Toronto, 1972.

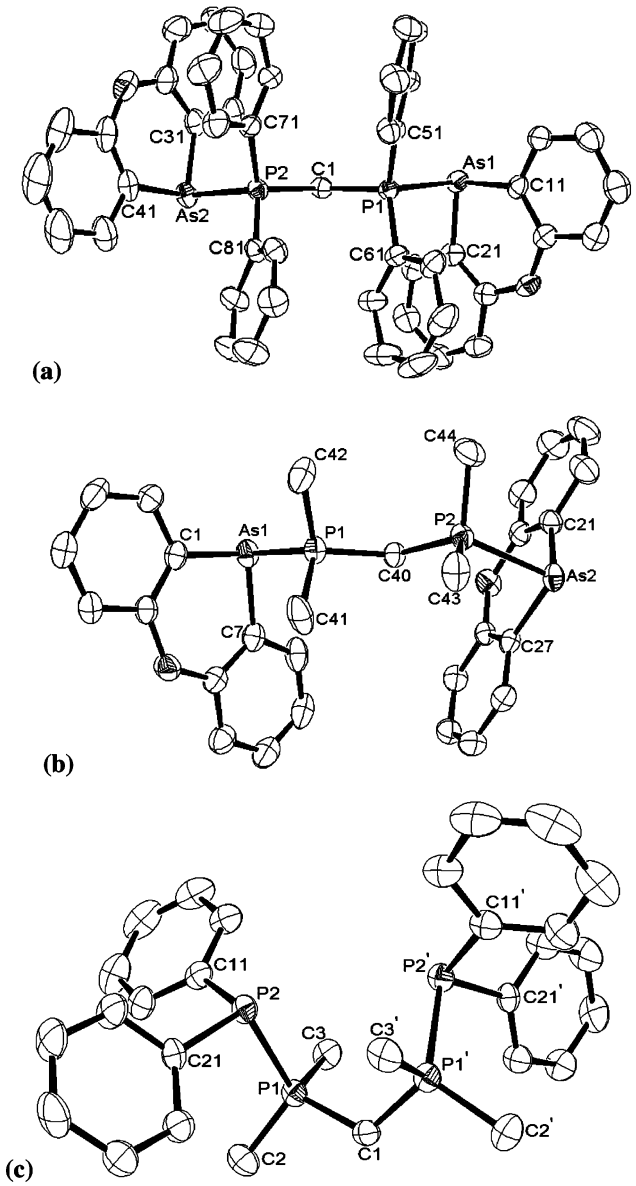


Figure 3. Representative structural views of the cations in (a) [AN−dppm−AN] **11a** $[GaCl_4]_2$, (b) [AN−dmpm−AN] **11b** $[GaCl_4]_2$, and (c) $[Ph_2P$-dmpm-$PPh_2]$ **5** $[GaCl_4]_2$.[43] Ellipsoids are drawn to 50% probability. Hydrogen atoms are not shown.

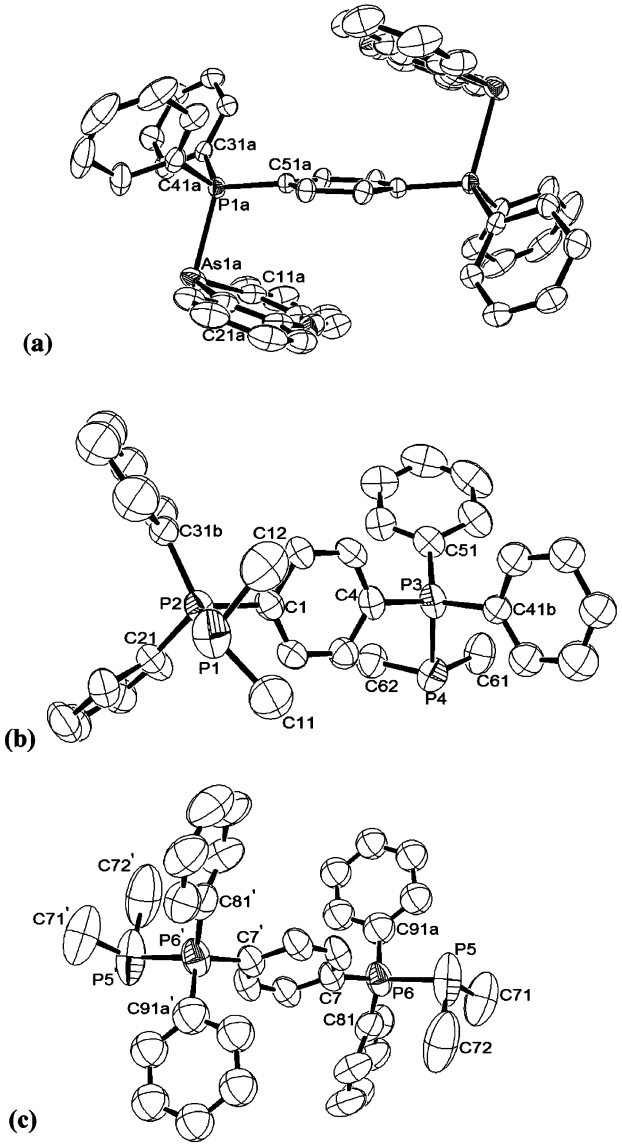


Figure 4. Representative structural views of the cations in (a) [AN−dppb−AN] **12** $[GaCl_4]_2$, (b) gauche-$[Ph_2P$-dppb-$PPh_2]$ **7** $[GaCl_4]_2$,[43] and (c) *anti*-$[Ph_2P$-dppb-$PPh_2]$ **7** $[GaCl_4]_2$. Ellipsoids are drawn to 50% probability. Hydrogen atoms are not shown.

in this compound is bound to a nitrogen center and is encumbered by the intramolecular coordinative cyclic arrangement.

A representative view of monocation **10** in the solid-state structure of [AN−dppm][$GaCl_4$] is shown in Figure 2a, and it illustrates the interaction of arsenic with a single phosphorus donor and the consequential pendant tricoordinate phosphine. The structure of this arsenium−bisphosphine cation is analogous to that of cation **4a** in [Me_2P-dppm]-[$GaCl_4$], shown in Figure 2b.[43] The As−P and As−C distances, as well as the angles at arsenic in **10**, are within the narrow range exhibited in **1**[BPh_4],[39] **2a** [PF_6],[40] **2b** [PF_6],[40] **9a** [$GaCl_4$], **9a** [OTf], and **9b** [OTf]. The conformation of the P−C−P−Pn backbones in **4a** and **10** are notably different, with the P−C−P−P angle of 61.3(1)° in **4a** best considered gauche, while **10** adopts an anti arrangement involving a P−C−P−As torsional angle of 176.6(2)°, perhaps resulting from the alignment and intramolecular stacking of one of the phenyl substituents at P(1) with the central ring of AN. Nevertheless, it is interesting to note that intermolecular distances between the centroids of the AN units are generally shorter than intramolecular distances between the aryl centroid and that of the AN unit (Table 2).

Figure 3 shows representative views of the dications in [AN−dppm−AN] **11a** $[GaCl_4]_2$ and [AN−dmpm−AN] **11b** $[GaCl_4]_2$, confirming association of two arsenium centers by the tethered bisphosphine (dppm or dmpm) ligand in each case. Both dications adopt an anti−anti conformation with P−C−P−As torsional angles close to 180°. The anti conformation is extended to include the carbon centers attached to arsenic to give an anti−anti−anti conformation for **11b** and an anti−anti−anti−anti conformation for **11a**, with C(41), As(2), P(2), C(1), P(1), As(1), and C(11) essentially coplanar, as illustrated in Figure 3a. In addition, the tricyclic arsine units adopt an anti conformation with

respect to each other. Intramolecular interplane interactions between the phenyl substituents of the ligand and the plane of the arsenium cation are evident in **11a**, while the methyl substituents in **11b** apparently allow for more flexibility of the As−P−C−P−As backbone. By comparison with **11b**, bisphosphenium−bisphosphine **5** adopts a gauche−gauche conformation in the gallate salt, illustrated in Figure 3c, and a gauche−anti conformation in the triflate salt. We rationalize the differences between **11b** and **5** in terms of the greater steric flexibility allowed by two phenyl substituents at the phosphorus acceptor centers relative to that of the tricyclic unit AN.

The existence of both a monocationic arsenium−bisphosphine **10** and a dicationic bisarsenium−bisphosphine **11a**, employing the dppm ligand, indicates the potential to stoichiometrically control the association of arsenium centers by bifunctional ligands. In contrast, dppm is observed to form only phosphenium−bisphosphine cations, **4**, and the sterically less inhibited dmpm is observed to form only bisphosphenium−bisphosphine cations, **5**.[43] We speculate that the slightly longer As−P coordinate bonds in comparison to the P−P coordinate bonds provides for sufficient relief of the steric strain within the ligand to enable incorporation of the second Lewis acid.

The structure of cation **12** in $[AN-dppb-AN][GaCl_4]_2$ is shown in Figure 4a together with views of the gauche and anti conformations of cation **7** in $[Me_2P\text{-}dppb\text{-}PMe_2][GaCl_4]_2$. The arsine units (AN) of **12** adopt a distinct anti conformation with respect to the benzo plane of the ligand backbone, and the endo orientation of the AN units implies the existence of interplane stacking. In comparison, **7** displays both anti (Figure 4b) and gauche (Figure 4c) conformations.

Conclusions

The facile in situ preparation of a tricyclic arsenium species provides a versatile synthetic approach to arsinophosphonium, and the first arsinophosphoniumphosphine and bisarsinobisphosphonium salts. Spectroscopic and structural data show that the tricyclic (anthracenic) arsenium cation engages bifunctional ligands in pendant and tethered complexation. The new complexes highlight a versatile approach to As−P bond formation, and the demonstrated control of stoichiometry with bifunctional tethering ligands bodes well for the development of extended arrays and the potential for extrapolation to supramolecular or coordination polymeric systems.

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Supporting Information Available: 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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