Anionic and Steric Factors Governing Coordinative Unsaturation at Carbenic Phosphenium Centers

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Tetrachlorogallate and tetraphenylborate salts of the phosphenium cations $[(^iPr_2N)_2P]^+$ (**1**) and $[MeNCH_2CH_2N(Me)P]^+$ (**2**) are examined. Spectroscopic characterization confirms the ionic formulation for all compounds except for **2**$[BPh_4]$, which exists as the covalent alternative phosphine–borane $MeNCH_2CH_2N(Me)P(Ph){-}BPh_3$ (**5**) (crystal data: $C_{28}H_{30}BN_2P$, triclinic, $P\bar{1}$, $a = 9.710(1)$ Å, $b = 14.962(2)$ Å, $c = 9.610(2)$ Å, $\alpha = 105.45(1)°$, $\beta = 113.59(1)°$, $\gamma = 92.73(1)°$, $Z = 2$). The ionic borate **1**$[BPh_4]$ represents the first isolated phosphenium salt containing a "noncoordinating anion", and its stability with respect to the covalent alternative analogue **5** is postulated to rely upon the steric bulkiness of both cation and anion. Compound **1**$[BPh_4]$ reacts with chlorinated solvents within hours to give a number of products, one of which has been identified as the phosphonium salt $[(^iPr_2N)_2P(Cl)CH_2Cl][BPh_4]$ (**8**$[BPh_4]$) (crystal data: $C_{37}H_{50}BCl_2N_2P$, monoclinic, $P2_1/n$, $a = 10.049(3)$ Å, $b = 21.794(3)$ Å, $c = 16.391(3)$ Å, $\beta = 92.78(2)°$, $Z = 4$), the result of an oxidative addition of CH_2Cl_2 to the phosphenium center. In contrast, tetrachlorogallate salts of **1** and **2** are indefinitely stable in CH_2Cl_2 and $CHCl_3$ solutions. The crystal structures of **1**$[GaCl_4]$ (crystal data: $C_{12}H_{28}Cl_4GaN_2P$, tetragonal, $I4_1cd$, $a = 20.014(4)$ Å, $b = 20.014(4)$ Å, $c = 21.466(6)$ Å, $Z = 16$) and **2**$[GaCl_4]$ (crystal data: $C_4H_{10}Cl_4GaN_2P$, monoclinic, $P2_1$, $a = 6.489(3)$ Å, $b = 13.893(5)$ Å, $c = 7.066(5)$ Å, $\beta = 92.58(5)°$, $Z = 2$) reveal similar anionic arrays around the cation despite different space groups and cation size. The closest contacts occur between the phosphorus and chlorine centers but are in excess of the van der Waals radii. Nevertheless, electrostatic interactions are believed to be maintained to some degree in solution and are responsible for protection of the cationic center. Such interactions are expected to be weaker in the tetraphenylborate salt, which renders the phosphorus center susceptible to attack by solvent molecules that are small enough to infiltrate the steric shield allowing for formation of **8** and other products.

Introduction

Carbenes and their analogues represent important synthetic units in that they are small, simple molecules with coordinatively unsaturated sites and high reactivity.[1] The phosphorus analogues, known as phosphenium cations, are perhaps the most abundant and have been known for over 30 years. The first isolable salts[2–7] were reported long before the first stable carbenes,[8,9] over 40 cations have been identified in solution, and the chemistry of the phosphenium unit has been extensively investigated.[10,11] Nevertheless, few (less than 10) derivatives have been isolated and comprehensively characterized. Moreover, these compounds have characteristics that are common to most derivatives and are perhaps responsible for their stability: (1) Most salts contain the tetrachloroaluminate anion, and the remaining examples possess triflate anions.[7] (2) It is generally thought that the coordinative unsaturation and electron deficiency at phosphorus is satisfied by π-donation from the immediate atomic neighbor. Indeed, most derivatives possess at least one nitrogen center adjacent to the phosphenium site or are incorporated into an efficiently π-delocalized framework.[5,6,7,12] (3) Some derivatives possess sterically bulky substituents,[4] which may be responsible for kinetic stability.[13]

In an attempt to evaluate the importance of these factors in the existence and chemistry of the *carbenic* phosphenium site we have examined some of the properties of compounds containing the two previously reported phosphenium cations **1** and **2** (Chart 1) in the presence of anions $GaCl_4^-$ and BPh_4^-. Our observations reveal the combined role of steric shielding and the "coordinating"[14] nature of the anion on the stability and reactivity of the phosphenium cationic center.

Experimental Section

General Procedures. $NaBPh_4$ (Aldrich) was used without purification. Anhydrous $GaCl_3$ and $AlCl_3$ (Aldrich) were sublimed *in vacuo*, and PCl_3, $MeN(H)CH_2CH_2(H)NMe$, and $^iPr_2NH$ (Aldrich) were distilled before

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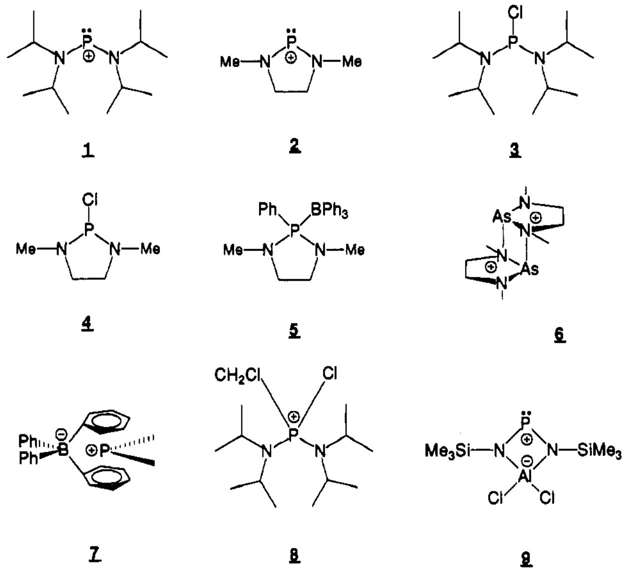
Chart 1



use. CH_2Cl_2, $CHCl_3$, CD_2Cl_2, and $CDCl_3$ were dried over P_2O_5 and CaH_2 and stored in evacuated bulbs. $(^iPr_2N)_2PCl$ and $Me\overline{NCH_2CH_2N(Me)P}Cl$ were prepared by literature methods.[15,16] Solids were handled in a VAC Vacuum/Atmospheres nitrogen-filled glove-box, while liquids were manipulated in a nitrogen-filled glovebag. Reactions were performed in an evacuated (10^{-3} Torr, ca. 0.133 Pa) reactor,[17] and all glass apparatuses were flame-dried before use. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Gottingen, Germany. Infrared spectra were recorded at Nujol mulls on CsI plates using a Nicolet 510P FT-IR spectrometer. $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-250 MHz, and ^{11}B NMR spectra were recorded on a Bruker AMX-400 MHz. NMR samples were flame-sealed in 5-mm Pyrex tubes. All chemical shifts are reported in ppm relative to external standards, 85% H_3PO_4 for ^{31}P, $BH_3{\cdot}Et_2O$ for ^{11}B, and TMS for ^1H and ^{13}C. Crystalline samples were obtained by slow removal of solvent from the reaction mixture within the reaction vessel by passing a cool stream of water over the empty adjacent compartment (or placing it over liquid nitrogen) and distilling the volatiles *in vacuo* (static). Crystals were washed with cool solvent by cold spot back-distillation.[17]

Preparation of $[(^iPr_2N)_2P][GaCl_4]$. A solution of $(^iPr_2N)_2PCl$ (1.02 g, 3.75 mmol) in CH_2Cl_2 was added to a solution of $GaCl_3$ (0.64 g, 3.6 mmol) in CH_2Cl_2 (total 30 mL) giving a clear yellow solution within a few seconds. After the solutions were stirred for approximately 3 h, solvent was removed *in vacuo* (dynamic) to half the volume, and the resulting precipitate was recrystallized from the warmed solution. Pale yellow crystals (two crops) were characterized as bis(diisopropylamino)phosphenium tetrachlorogallate: yield 1.22 g, 2.75 mmol, 76%; mp 127.5–128.5 °C. Anal. Calcd: C, 32.5; H, 6.4; N, 6.3. Found: C, 32.7, H, 6.4; N, 6.3. IR (cm^{-1}): 1399 (s), 1377 (s), 1337 (m), 1300 (m), 1209 (s), 1172 (sh), 1163 (sh), 1135 (br), 1060 (s), 1038 (s), 925 (s), 884 (w), 859 (w), 835 (w), 620 (w), 549 (m), 529 (m), 375 (s), 331 (sh), 305 (w), 281 (w), 256 (w), 248 (w). NMR (ppm in CD_2Cl_2): ^{31}P, 313; ^{13}C, 25.2 (d) ($^3J_{PC}$ = 8 Hz), 55.2 (s); ^1H, 1.52 (d, 24H) ($^3J_{HH}$ = 6.7 Hz), 4.20 (d of sept, 4H) ($^3J_{PH}$ = 2.6 Hz, $^3J_{HH}$ = 6.7 Hz). Approximate solubility in CH_2Cl_2: 0.03 g/mL. A single signal at 313 ppm was observed in the ^{31}P NMR spectrum of the reaction mixture. An NMR study has shown that $[(^iPr_2N)_2P][GaCl_4]$ is stable in a CH_2Cl_2 solution at room temperature for a period exceeding 1 year.

Preparation of $[(^iPr_2N)_2P][BPh_4]$. A solution of $(^iPr_2N)_2PCl$ (0.54 g, 2.0 mmol) in CH_2Cl_2 (~10 mL) was added to a suspension of $NaBPh_4$ (0.68 g, 2.0 mmol) in CH_2Cl_2 (~10 mL), and the reaction mixture was stirred for 1 h. The resulting yellow solution was separated from the white precipitate through a sintered glass frit, and a fraction of the solvent was removed *in vacuo* (dynamic) until a yellow solid began to precipitate from solution. A layer of hexane (~10 mL) was distilled onto the mixture, and the solution was warmed (60 °C) to redissolve the solid. Removal of the volatiles *in vacuo* (static) within 3 h resulted in yellow crystalline plates, which were washed with fresh hexane and characterized as bis(diisopropylamino)phosphenium tetraphenylborate: yield 0.89 g, 1.6 mmol, 81%; decompsn pt above 114 °C. Anal. Calcd: C, 78.5; H, 8.8; N, 5.1. Found: C, 78.4; H, 8.8; N, 5.0. IR (cm^{-1}): 1937 (w), 1883 (w), 1815 (w), 1759 (w), 1701 (w), 1673 (w), 1648 (w), 1582 (s), 1562 (w), 1481 (s), 1430 (s), 1400 (sh), 1390 (sh), 1347 (s), 1306 (m), 1268 (m), 1203 (s), 1182 (m), 1157 (s), 1132 (s), 1104 (s), 1066 (m), 1046 (s), 1028 (s), 947 (sh), 932 (s), 884 (w), 848 (m), 813 (w), 747 (s), 707 (s), 628 (m), 610 (s), 545 (m), 527 (m), 492 (w), 466 (m), 350 (w), 307 (w), 266 (w), 256 (w). NMR (ppm in CD_2Cl_2): ^{31}P, 308; ^{13}C, 25.0 (d) ($^3J_{PC}$ = 8 Hz), 55.2 (s), 164.4 (q), 136.3 (s), 125.6 (s), 121.8 (s); ^1H, 1.27 (d, 24H) ($^3J_{HH}$ = 6.8 Hz), 3.92 (d of sept, 4H) ($^3J_{PH}$ = 2.0 Hz, $^3J_{HH}$ = 6.7 Hz), 6.94 (t), 7.08 (t), 7.46 (s); ^{11}B, -7.0.

Preparation of $[Me\overline{NCH_2CH_2N(Me)P}][GaCl_4]$. A solution of $Me\overline{NCH_2CH_2N(Me)P}Cl$ (1.7 g, 11 mmol) in CH_2Cl_2 (5 mL) was added to a solution of $GaCl_3$ (2.0 g, 11 mmol) in CH_2Cl_2 (8 mL), and the mixture was stirred for 5 h. The ^{31}P NMR spectrum of the reaction mixture showed a single signal at 269 ppm. Slow removal of solvent *in vacuo* (static) resulted in the precipitation of a white crystalline solid which was characterized as 1,3-dimethyl-1,3-diaza-2-phospholidinium tetrachlorogallate: yield 2.4 g, 7.1 mmol, 62%; mp 95–97 °C. Anal. Calcd: C, 14.6; H, 3.1; N, 8.5. Found: C, 14.7; H, 3.1; N, 8.4. IR (cm^{-1}): 1356 (s), 1310 (m), 1253 (s), 1204 (s), 1143 (s), 1077 (m), 1036 (s), 1013 (s), 964 (s), 849 (m), 742 (s), 593 (s), 492 (m), 382 (s), 325 (s). NMR (ppm in CD_2Cl_2): ^{13}P, 269; ^{13}C, 35.3 (d) ($^2J_{PC}$ = 19 Hz), 56.0 (d) ($^2J_{PC}$ = 9 Hz); ^1H, 3.25 (d, 6H) ($^3J_{PH}$ = 11.6 Hz), 4.03 (d, 4H) ($^3J_{HH}$ = 4.4 Hz).

Preparation of $Me\overline{NCH_2CH_2N(Me)P}(Ph)\text{–}BPh_3$. A solution of $Me\overline{NCH_2CH_2N(Me)P}Cl$ (0.16 g, 1.0 mmol) in CH_2Cl_2 was added quickly to a suspension of $NaBPh_4$ (0.37 g, 1.1 mmol) in CH_2Cl_2 (total CH_2Cl_2 of 7 mL), and the mixture was stirred for 12 h at room temperature. The resulting precipitate was separated from the solution by decantation. A single signal at 80 ppm was observed in the ^{31}P NMR spectrum of the reaction mixture after 10 min. Slow removal of the solvent *in vacuo* (static) yielded crystals of 2-phenyl-1,3-dimethyl-1,3-diazaphospholidine–triphenylboron: yield 0.23 g, 0.52 mmol, 49%; mp 168–173 °C. Chemical analyses were not obtained. IR (cm^{-1}): 1960 (w), 1891 (w), 1816 (w), 1588 (w), 1335 (m), 1304 (w), 1255 (m), 1229 (w), 1206 (m), 1198 (m), 1164 (m), 1128 (s), 1100 (s), 1069 (w), 1035 (s), 1002 (w), 976 (w), 937 (s), 862 (m), 849 (sh), 803 (w), 751 (sh), 743 (s), 715 (s), 704 (s), 697 (sh), 686 (sh), 635 (m), 619 (m), 609 (m), 526 (s), 487 (m), 462 (m), 438 (m), 283 (w), 229 (w). NMR (ppm in CD_2Cl_2): ^{31}P, 82; ^{13}C, 34.9 (d) ($^2J_{PC}$ = 7 Hz), 52.1 (s), 125.9 (s), 126.9 (s), 128.3 (d), 131.0 (s), 131.8 (d), 136.7 (s); ^1H, 2.07 (d, 6H), ($^3J_{PH}$ = 10.8 Hz), 2.98 (m, 2H), 3.15 (m, 2H), 7.30 (m, 20H); ^{11}B, 0.2.

Isolation of $[(^iPr_2N)_2P(Cl)CH_2Cl][BPh_4]$.[18] In one experiment, a solution of $(^iPr_2N)_2PCl$ (0.27 g, 1.0 mmol) in CH_2Cl_2 was added quickly to a mixture of $NaBPh_4$ (0.34 g, 1.0 mmol) in $CHCl_3$ (1:1 CH_2Cl_2:$CHCl_3$). After 10 days slow removal of solvent from the orange solution *in vacuo* (static) gave 20–30 small rectangularly shaped crystals, which were characterized by X-ray crystallography as $[(^iPr_2N)_2P(Cl)CH_2Cl][BPh_4]$ ($^{31}P\{^1H\}$ 57 ppm). Other attempts (5) to isolate this material have been unsuccessful yielding only $[^iPr_2NH_2][BPh_4]$.[19]

^{31}P NMR Study of $[(^iPr_2N)_2P][BPh_4]$ in CH_2Cl_2 and $CHCl_3$. Equimolar mixture (0.3 mmol) of $(^iPr_2N)_2PCl$ and $NaBPh_4$ in three different solvent systems (1 mL) were treated in an ultrasonic bath and examined by ^{31}P NMR spectroscopy at 2-h intervals. Observations are presented as ^{31}P NMR chemical shifts with relative signal heights in parentheses. CH_2Cl_2: 2 h, 312; 4 h, 312 (100), 338 (5), and more than 10 minor peaks 100–0; 6 h, 312 (100), 58 (20), 45 (25), and 13 (20); 8 h, 13 and minor peaks 100–0. ^{11}B NMR: −7.0 characteristic of BPh_4^-. $CHCl_3$: 2 h, 150 (100), 132 (<5), 122 (<5), 62 (5), 59 (5), 16 (<5), 14 (<5); 4 h, 162 (100), 62 (15), 59 (20); 6 h, 172 (100), 62 (20), 59 (30) and minor peaks

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(19) Crystallographic characterization: $C_{30}H_{36}BN$, MW = 419.42, space group = $P2_1/n$, a = 12.889(6) Å, b = 13.405(5) Å, c = 14.912(8) Å, β = 98.81(4)°, V = 2546(2) Å^3, Z = 4, D_c = 1.094 g/cm^3, F_{000} = 912, R = 0.0453, R_w = 0.0448, GOF = 2.201.

Table 1. Crystallographic Data

	1[GaCl$_4$]	**2**[GaCl$_4$]	**5**	**8**[BPh$_4$]
formula	$C_{12}H_{28}Cl_4GaN_2P$	$C_4H_{10}Cl_4GaN_2P$	$C_{28}H_{30}BN_2P$	$C_{37}H_{50}BCl_2N_2P$
M_n	442.87	328.64	436.34	635.51
space group	$I4_1cd$	$P2_1$	$P\bar{1}$	$P2_1/n$
system	tetragonal	monoclinic	triclinic	monoclinic
lattice reflcns: θ/deg (no.)	(25) 10–12	(21) 4–8	(24) 34.8–40.7	(25) 24.65–31.82
temp/°C	18	18	18	18
a/Å	20.014(4)	6.489(3)	9.710(1)	10.049(3)
b/Å	20.014(4)	13.893(5)	14.962(2)	21.794(3)
c/Å	21.466(6)	7.066(5)	9.610(2)	16.391(3)
α/deg			105.45(1)	
β/deg		92.58(5)	113.59(1)	92.78(2)
γ/deg			92.73(1)	
V/Å^3	8598(6)	636.3	1214.3	3585(1)
Z	16	2	2	4
D_c/Mg m^{-3}	1.3684	1.715	1.193	1.177
λ(Mo Kα)/Å	0.709 26	0.710 69	0.710 69	0.710 69
μ/cm^{-1}	18.45	30.86	1.26	2.50
standard reflcns	–10,0,–6/–8,8,0/6,8,–6	–1,3,–1/0,2,0/0,4,0	1,–2,0/1,–1,0/2,–1,0	0,0,–2/–1,0,–1/–1,–2,–1
R	0.0540	0.0516	0.0417	0.0541
R_w	0.0640	0.0516	0.0422	0.0569
goodness of fit	0.8434	1.2504	2.46	1.8590

at 135 and 0; 8 h, 153 (100), 62 (35), 59 (55); 24 h, 145 and minor signals. ^{11}B NMR: –7.0. $CH_2Cl_2/CHCl_3$ (~1:1): 2 h, 217 (100), 59 (5), 16 (5); 4 h, 226 (100), 59 (15), 16 (10), and minor peaks between 100–0; 6 h, 218 (100), 59 (50), 45 (20), 16 (25), and minor peaks between 100–0; 8 h, 196 (50), 59 (100), 45 (55), 15 (35), and more than 10 minor peaks between 100–0; 24 h, 169 (50), 59 (100), and more than 10 peaks (5–80) between 100–0. Similar activity was observed with 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and 1,2-dichlorobenzene.

^{31}P NMR Study of Reactions between [(^{i}Pr$_2$N)$_2$P][A] and 2,3-Dimethyl-1,3-butadiene, [A] = [GaCl$_4$] or [BPh$_4$]. Rapid reaction with the appearance of a single signal at 67 ppm corresponding to the previously reported cycloaddition product.[20]

^{31}P NMR Study of $\overline{N(SiMe_3)PN(SiMe_3)Al}Cl_2$ in CH_2Cl_2 and $CHCl_3$. Slow reaction in $CHCl_3$ resulted in the appearance of a signal at 37 ppm and half-life of approximately 1 month. No reaction observed with CH_2Cl_2.

X-ray Crystallography. Crystals suitable for crystallography were obtained as described in the text for each compound and were selected and mounted in Pyrex capillaries in the drybox. Data were collected at room temperature on Enraf-Nonius CAD-4 (Mo Kα, λ = 0.709 26 Å) and Rigaku (Mo Kα, λ = 0.710 69 Å) diffractometers with a graphite monochromator, using the $\omega/2\theta$ scan technique. Unit cell parameters were obtained from the setting angles of a minimum of 20 accurately centered reflections; the choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures. All pertinent crystallographic data are summarized in Table 1. The stability of the crystals was monitored using three standard reflections; no significant decay was observed. Data were corrected for Lorentz and polarization effects by routine procedures; empirical absorption corrections were applied.[21] Scattering factors[22] were corrected for anomalous dispersion.

Structures were solved by direct method[23] to find the heavy atoms with the remaining atoms located from difference direct method[24] and/or difference Fourier syntheses. Hydrogen atoms were placed geometrically (C–H = 1.08 Å) and refined isotropically or not refined [U_{iso}(H) = 1.2B_{eq}(C)]. The models were refined using least-squares techniques based on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight.[25,26] Either a unit or SHELX weighting scheme was used during refinement. Final atomic coordinates for **1**[GaCl$_4$], **2**[GaCl$_4$], **5**, and **7**[BPh$_4$] are presented in Tables 2–5. Selected bond lengths and angles for **1**[GaCl$_4$], **2**[GaCl$_4$], and **5** are presented in Table 6.

Table 2. Positional Parameters and Isotropic Temperature Factors for [(^{i}Pr$_2$N)$_2$P][GaCl$_4$] (**1**[GaCl$_4$])

atom	x/a	y/b	z/c	U_{eq}/Å^2
Ga1	0.24940(11)	–0.00893(9)	0.07560(0)	0.0555
Cl4	0.23068(11)	0.05822(9)	–0.00040(0)	0.1059
Cl3	0.25905(11)	0.05067(9)	0.15964(0)	0.1091
Cl2	0.34099(11)	–0.06058(9)	0.06081(0)	0.1450
Cl1	0.16702(11)	–0.07627(9)	0.08749(0)	0.1242
P1	0.2797(2)	0.0301(2)	0.3377(3)	0.0516
N1	0.2039(3)	0.0518(3)	0.3452(7)	0.0294
C1	0.1419(4)	0.0109(6)	0.3457(8)	0.0774
C2	0.1029(4)	0.0142(6)	0.2839(8)	0.0786
C3	0.1001(4)	0.0303(6)	0.4031(8)	0.1017
C4	0.1922(7)	0.1253(3)	0.3483(7)	0.0643
C5	0.2219(7)	0.1524(3)	0.4094(7)	0.0858
C6	0.2195(7)	0.1612(3)	0.2901(7)	0.0877
N2	0.2939(3)	–0.0470(4)	0.3229(8)	0.0563
C7	0.3665(4)	–0.0662(7)	0.3252(8)	0.0828
C8	0.4061(4)	–0.0278(7)	0.2753(8)	0.0950
C9	0.3965(4)	–0.0558(7)	0.3906(8)	0.0906
C10	0.2471(6)	–0.1006(5)	0.3013(8)	0.0589
C11	0.2669(6)	–0.1344(5)	0.2398(8)	0.1015
C12	0.2432(6)	–0.1557(5)	0.3508(8)	0.1060

Table 3. Positional Parameters and Isotropic Temperature Factors for [Me$\overline{NCH_2CH_2N(Me)P}$][GaCl$_4$] (2[GaCl$_4$])

atom	x/a	y/b	z/c	U_{eq}/Å^2
Ga1	0.1938(3)	0.8001(0)	0.2510(3)	0.0757
Cl1	0.5249(7)	0.8073(14)	0.2449(7)	0.1097
Cl2	0.0830(23)	0.9313(11)	0.1116(22)	0.1269
Cl3	0.0728(22)	0.6770(12)	0.1144(24)	0.1379
Cl4	0.1073(8)	0.8079(16)	0.5419(7)	0.1312
P1	0.3448(13)	0.5352(9)	0.5571(13)	0.1324
N1	0.4353(25)	0.5044(16)	0.3656(23)	0.0907
N2	0.5227(24)	0.6047(17)	0.6311(26)	0.1089
C1	0.6455(29)	0.5382(20)	0.3288(33)	0.1410
C2	0.6985(29)	0.5888(20)	0.5097(28)	0.0910
C3	0.3540(35)	0.4374(19)	0.2177(31)	0.1395
C4	0.5318(37)	0.6567(21)	0.8131(28)	0.1406

Results and Discussion

Preparation and Characterization of Phosphenium Salts. The halide ion abstraction or metathesis reactions of halophosphines

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Table 4. Positional Parameters and Isotropic Temperature Factors for $\mathrm{Me\overline{NCH_2CH_2N(Me)P}Ph{-}BPh_3}$ (5)

atom	*x*	*y*	*z*	*B*(eq)/Å^2
P1	0.27506(8)	0.21891(5)	0.31639(9)	2.61(2)
N1	0.2874(3)	0.1051(2)	0.2421(3)	3.27(8)
N2	0.3615(3)	0.2574(2)	0.2207(3)	3.7(1)
C1	0.5589(3)	0.2924(2)	0.5997(3)	2.86(9)
C2	0.6373(3)	0.2293(2)	0.5377(4)	3.7(1)
C3	0.7901(4)	0.2515(3)	0.5710(4)	4.7(1)
C4	0.8717(4)	0.3406(3)	0.6678(5)	5.2(1)
C5	0.7986(4)	0.4052(3)	0.7308(5)	5.2(1)
C6	0.6458(4)	0.3821(2)	0.6977(4)	3.8(1)
C7	0.3373(3)	0.1787(2)	0.6158(3)	2.77(9)
C8	0.2010(4)	0.1663(2)	0.6328(3)	3.4(1)
C9	0.1560(4)	0.0890(3)	0.6683(4)	4.7(1)
C10	0.2476(6)	0.0214(3)	0.6912(4)	5.8(2)
C11	0.3845(5)	0.0331(2)	0.6818(4)	5.3(1)
C12	0.4293(4)	0.1101(2)	0.6443(4)	4.0(1)
C13	0.3146(3)	0.3588(2)	0.6294(3)	2.88(9)
C14	0.3395(4)	0.3844(2)	0.7891(4)	3.9(1)
C15	0.2942(5)	0.4632(3)	0.8607(5)	5.3(1)
C16	0.2223(5)	0.5207(2)	0.7733(6)	5.6(1)
C17	0.1977(4)	0.4994(2)	0.6169(5)	5.0(1)
C18	0.2433(4)	0.4199(2)	0.5453(4)	3.8(1)
C19	0.0745(3)	0.2273(2)	0.2123(3)	2.74(8)
C20	−0.0286(4)	0.2117(3)	0.2720(4)	5.1(1)
C21	−0.1826(4)	0.2107(3)	0.1860(5)	5.8(2)
C22	−0.2354(4)	0.2244(2)	0.0402(4)	4.1(1)
C23	−0.1348(4)	0.2416(3)	−0.0198(4)	4.4(1)
C24	0.0196(4)	0.2434(2)	0.0654(4)	3.9(1)
C25	0.2933(4)	0.0927(3)	0.0880(4)	4.6(1)
C26	0.3918(4)	0.1815(3)	0.1102(4)	5.1(1)
C27	0.4435(5)	0.3519(3)	0.2666(5)	5.7(2)
C28	0.1849(4)	0.0287(2)	0.2399(4)	4.5(1)
B1	0.3793(4)	0.2678(2)	0.5614(4)	2.7(1)

Table 5. Positional Parameters and Isotropic Temperature Factors for $[(^i\mathrm{Pr_2N})_2\mathrm{P(Cl)CH_2Cl}][\mathrm{BPh_4}]$ (**8**[$\mathrm{BPh_4}$])

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/Å^2
B1	1.2121(7)	−0.1691(3)	0.2789(4)	0.0384
C1	1.229(6)	−0.0933(2)	0.2649(3)	0.0411
C2	1.2099(6)	−0.0673(2)	0.1873(3)	0.0538
C3	1.2079(7)	−0.0037(3)	0.1758(4)	0.0673
C4	1.2176(7)	0.0348(3)	0.2427(4)	0.0708
C5	1.2287(7)	0.0100(3)	0.3199(4)	0.0665
C6	1.2300(7)	−0.0534(2)	0.3311(3)	0.0532
C7	1.2973(6)	−0.1937(2)	0.3607(3)	0.0429
C8	1.4208(5)	−0.1674(2)	0.3855(3)	0.0474
C9	1.5019(6)	−0.1920(3)	0.4483(3)	0.0645
C10	1.4570(7)	−0.2417(3)	0.4911(3)	0.0672
C11	1.3364(7)	−0.2685(3)	0.4688(4)	0.0628
C12	1.2577(6)	−0.2437(3)	0.4054(4)	0.0559
C13	1.0516(5)	−0.1810(2)	0.2823(3)	0.0418
C14	0.9702(5)	−0.1935(3)	0.2125(3)	0.0473
C15	0.8316(6)	−0.1991(3)	0.2137(4)	0.0586
C16	0.7690(6)	−0.1922(3)	0.2871(4)	0.0613
C17	0.8460(6)	−0.1795(3)	0.3573(4)	0.0625
C18	0.9839(6)	−0.1742(3)	0.3537(3)	0.0551
C19	1.2804(6)	−0.2073(2)	0.2050(3)	0.0449
C20	1.3917(6)	−0.1859(3)	0.1649(3)	0.0568
C21	1.4545(7)	−0.2203(3)	0.1061(4)	0.0792
C22	1.4054(8)	−0.2778(3)	0.0839(4)	0.0862
C23	1.2974(7)	−0.3011(3)	0.1235(4)	0.0807
C24	1.2353(6)	−0.2660(2)	0.1824(3)	0.0558
P1	0.73056(17)	0.02252(8)	0.21692(9)	0.0404
N1	0.7403(4)	0.0406(1)	0.3126(2)	0.0393
C25	0.7510(6)	−0.0111(3)	0.3733(3)	0.0697
C26	0.8878(7)	−0.0158(3)	0.4148(5)	0.0927
C27	0.6353(8)	−0.0216(4)	0.4263(5)	0.1170
C28	0.6974(5)	0.1034(2)	0.3379(3)	0.0546
C29	0.5512(6)	0.1092(3)	0.3582(4)	0.0762
C30	0.7898(7)	0.1307(3)	0.4052(4)	0.0847
N2	0.7542(4)	0.0803(2)	0.1569(2)	0.0467
C31	0.8961(6)	0.1032(2)	0.1560(3)	0.0655
C32	0.9541(8)	0.0953(3)	0.0725(4)	0.0934
C33	0.9120(7)	0.1690(3)	0.1875(4)	0.0771
C34	0.6587(7)	0.1120(3)	0.0980(4)	0.0781
C35	0.6098(9)	0.0726(3)	0.0252(4)	0.0944
C36	0.5437(7)	0.1433(3)	0.1372(5)	0.0982
Cl1	0.5532(1)	−0.0150(0)	0.1874(1)	0.0743
C37	0.8490(6)	−0.0393(2)	0.1998(3)	0.0471
Cl2	0.83460(24)	−0.06175(9)	0.09605(11)	0.0850

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg)

param	**1**[$\mathrm{GaCl_4}$] ($\mathrm{C_{12}H_{28}Cl_4GaN_2P}$)	**2**[$\mathrm{GaCl_4}$] ($\mathrm{C_4H_{10}Cl_4GaN_2P}$)	**5** ($\mathrm{C_{37}H_{50}BCl_2N_2P}$)
P–N$_1$	1.587(12)	1.56(2)	1.616(5)
P–N$_2$	1.601(13)	1.58(2)	1.622(5)
N$_1$–P–N$_2$	117.0(7)	99.0(11)	113.3(3)
Σ angles of N$_1$	359.9(16)	360(3)	357.2(8)
Σ angles of N$_2$	359.7(17)	358(3)	359.9(8)

are well documented[10,11] and were used to obtain the first isolable phosphenium derivatives including **1**[$\mathrm{AlCl_4}$] (which has been structurally characterized)[4] and **2**[$\mathrm{PF_6}$] (which has been spectroscopically characterized).[2] We have employed the same approach to attempt the preparation of compounds containing these cations (**1** and **2**) with tetrachlorogallate and tetraphenylborate anions, from the corresponding reactions of **3** and **4** with $\mathrm{GaCl_3}$ and $\mathrm{NaBPh_4}$, respectively.

Studies of the reaction mixtures by ^{31}P NMR spectroscopy show a single signal in each case indicating that all reactions proceed in a quantitative fashion. A solid material has been isolated from each reaction corresponding to the species identified in each reaction mixture. Spectroscopic and crystallographic data (Crystals of **1**[$\mathrm{BPh_4}$] decay in the X-ray beam, and a structure has not yet been obtained) have confirmed the formation of a phosphenium cation in all but one case. The reactions of **4** with $\mathrm{NaBPh_4}$ provides the covalent phosphine–borane **5** (crystallographic view shown in Figure 1) rather than the intended ionic isomer **2**[$\mathrm{BPh_4}$].

The ionic nature of **1**[$\mathrm{GaCl_4}$], **1**[$\mathrm{BPh_4}$], and **2**[$\mathrm{GaCl_4}$] is evident from the typical[10,11] deshielded ^{31}P NMR resonances (**1**, ~300 ppm; **2**, ~260 ppm), with respect to **3** (141 ppm) and **4** (169 ppm). In contrast, a relatively shielded signal at 82 ppm is observed for compound **5** (rather than **2**[$\mathrm{BPh_4}$]). In the solid state the IR bands characteristic of the anions and the observation of discrete ions in the crystal structures of **1**[$\mathrm{GaCl_4}$] and **2**[$\mathrm{GaCl_4}$] provide further support for the ionic formulation.

The structural features of the cation in **1**[$\mathrm{GaCl_4}$] are consistent with those previously reported for the isostructural tetrachloroaluminate salt.[4] The molecular fragment corresponding to cation **2** has been used as a phosphorus bound ligand to $\mathrm{CpMo(CO)_2^-}$, for which the crystal structure has been reported.[27] However, the structure of the free cation **2** is reported here for the first time in the tetrachlorogallate salt (Figure 2a) and reveals similarities to the more sterically constrained cation **1**. Most important is the observation of a monomeric existence for the cation in the structure of **2**[$\mathrm{GaCl_4}$], in contrast to the arsenic analogue which adopts a dimeric structure in the solid-state **6**.[28] The monomeric structures for salts of **1** could be rationalized in terms of the steric sheilding present in the cation, but cation **2** has a more exposed phosphenium site capable of secondary interaction. We conclude that the nitrogen–phosphorus π-interaction is preferred over the inter-ring σ-bonding present in the arsenic dimer **6**.

There is recent interest in "noncoordinating anions"[14,29,30] and their role in the stability and reactivity of the cation. Compound

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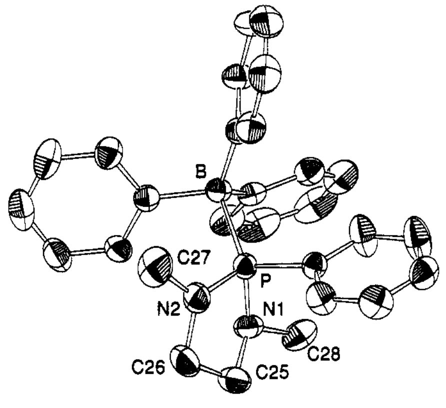
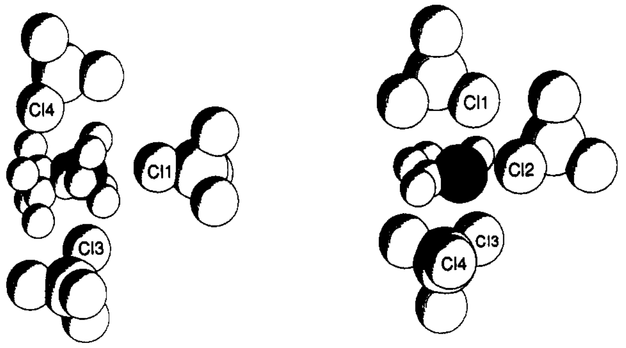


Figure 1. ORTEP view of Compound **5**.



(a) (b)

Figure 2. Crystallographic views of (a, left) **1**[GaCl$_4$] and (b, right) **2**[GaCl$_4$] showing the array of anions around each cation. Phosphorus atoms are black. P–Cl distances (Å): (a) P- - -Cl1 = 3.976(6), P- - -Cl3 = 3.867(6), P- - -Cl4 = 4.020(6); (b) P- - -Cl1 = 3.548(1), P- - -Cl2 = 3.982(2), P- - -Cl3 = 4.03(2), P- - -Cl4 = 4.04(2).

1[BPh$_4$] represents the first isolated example of a phosphenium salt containing such a weakly nucleophilic or weakly basic anion. It is interesting to note that the ^{31}P chemical shift of the phosphenium center is essentially identical in the two salts **1**[GaCl$_4$] and **1**[BPh$_4$], while the isopropyl hydrogen nuclei of the tetraphenylborate salt (3.92, 1.27 ppm) are significantly shielded with respect to those of the gallate salt (4.20, 1.52 ppm). As compound **5** represents a covalent alternative of **2**[BPh$_4$], we conclude that the ionic nature of **1**[BPh$_4$] relies on the steric shield provided by the isopropyl substituents, which prevent interaction between the B–C bond of the anion and the phosphenium site of the cation. Such a shield is not present in **2** allowing for rearrangement of the salt to the covalent alternative phosphine–borane **5**. Although we have not been able to determine the structure of **1**[BPh$_4$] in the solid state, we envisage the possibility of an arrangement similar to those observed for the metal salts, in which the electrophilic phosphenium site is either sandwiched between two of the phenyl substituents (η^{12}) of the tetraphenylborate anion **7**,[31] or is involved in η^6 coordination to one of the phenyl substituents.[14,29] We have recently demonstrated the potential for cationic phosphorus sites to engage in such π-arene complexation[32] but recognize that such interactions are very weak.

Reactivity of Phosphenium Cations. The chemistry of phosphenium cations is already extensive and has been shown to have characteristics consistent with coordinative unsaturation and electrophilicity, as well as the potential for Lewis base behavior.[10,11] Dichloromethane has been the solvent of choice for the study of these systems, offering sufficient polarity for solvation of the ions while apparently being inert toward the electrophilic phosphenium site. Indeed, we note that the tetrachlorogallate (and presumably aluminate) salts of cations **1** and **2** have essentially indefinite lifetimes in CH$_2$Cl$_2$ at room temperature (^{31}P NMR spectra are unchanged in excess of 1 year). In contrast, ^{31}P NMR studies on solutions of **1**[BPh$_4$] in CH$_2$Cl$_2$, CHCl$_3$, and CH$_2$Cl$_2$/CHCl$_3$ show reaction within hours at room temperature, and reaction with CHCl$_3$ occurs faster than that with CH$_2$Cl$_2$. Many products are formed, but a single signal at ~7 ppm in the ^{11}B NMR spectrum indicates that the tetraphenylborate anion is unchanged throughout these reactions. Although the ultimate mixtures was extremely complex, two species have been isolated by crystallization. In one instance the phosphonium salt [(^{i}Pr$_2$N)$_2$P(CH$_2$Cl)Cl][BPh$_4$] (**7**[BPh$_4$]) was isolated from a solution of **1**[BPh$_4$] in a 50:50 mixture of CH$_2$Cl$_2$ and CHCl$_3$, and [^{i}Pr$_2$NH$_2$][BPh$_4$] has been isolated on a number of occasions (both compounds characterized by X-ray crystallography; see Table 1 and ref 16, respectively). On the basis of these observations, it is clear that cation **1** reacts with the solvent and cation **8** can be viewed as the result of an oxidative addition of CH$_2$Cl$_2$ to the phosphenium center of **1**. The apparent faster reaction with CHCl$_3$ is likely due to the resultant CHCl$_2^+$ being a more stable carbocation than CH$_2$Cl$^+$. The corresponding reactions for **2**[BPh$_4$] are not observed, and this can be understood in terms of the rearrangement to the covalent phosphine-borane **5** being a more facile and substantially faster process.

Anionic Protection.[18] The inert nature (relative to **1**[BPh$_4$]) of the tetrachlorogallate (and presumably aluminate) salts of both **1** and **2** in chlorinated solvents must be attributed to the relationship between cation and anion in solution. We conclude that the Lewis acidity (and possibly electrophilicity and general reactivity) of the cations is mediated by the presence of electron-rich anions, such as polyhalogenated anions. The localized nonbonding electron pairs available on these anions offer sites for effective electrostatic interaction with the cation and allow for ion pairing or clustering which inhibits the reactivity or "*protects*" the phosphenium center. This may also involve chloride ion exchange (equilibria) resulting in the presence of the chlorophosphine.[12] The tetraphenylborate anion is expected to form weaker interactions rendering the Lewis acidity of cation **1** sufficiently high to engage the solvent molecules that are small enough to penetrate the steric shield of the cation. However, both the cation and the anion are sufficiently bulky to prevent an electrophilic attack of the phosphenium center on the B–phenyl bond. Nevertheless, the well-documented cycloaddition reaction of phosphenium cations with 1,3-dienes to give phospholenium cations[20] occurs readily for both BPh$_4^-$ and GaCl$_4^-$ salts of **1** (^{31}P NMR studies).

Solid-state structural features of the salts involving polyhalogenated anions confirm the intimacy of the cation–anion relationship. Figure 2 illustrates the packing of anions around the cation in the structures of **1**[GaCl$_4$] (a) and **2**[GaCl$_4$] (b). In spite of the different space groups, the different size and shape of the cations, and the different degrees of steric shielding present on the cations, the structures consist of cationic units surrounded by three anions above, below, and in the N–P–N plane. The closest interion distances occur between the chlorine atoms and the phosphorus center, although the distances {**1**[GaCl$_4$], P- - -Cl1 = 3.976(6) Å, P- - -Cl3 = 3.867(6) Å, P- - -Cl4 = 4.020(6) Å; **2**[GaCl$_4$], P- - -Cl1 = 3.548(1) Å, P- - -Cl2 = 3.982(2) Å, P- - -Cl3 = 4.03(2) Å, P- - -Cl4 4.04(2) Å} are in excess of the sum of the van der Waals radii (P- - Cl = 3.7 Å).[33] Cation–anion distances slightly less than the sum of the van der Waals

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radii are common for non-metal salts[34] and other phosphenium salts.[6,12,35,36] Although such interactions are considered as donations from the anion to the cation,[37] they generally have little or no effect on the structural features within the cation or the anion.[38] Nevertheless, the electrostatic factor represents a substantial component of the crystal lattice energy, and we envisage the acidity and ultimately the reactivity of the cation to be reliant on the degree of similar interactions in solution.

The neutral zwitterionic system **9**, which contains a phosphenium site,[10,11,39,40] offers an obvious comparison. We have noted that the compound reacts slowly with $CHCl_3$ (first signs of unidentified products occur after 1 day). While **9** cannot benefit from the cation–anion interaction in solution, the solid-state structure[40] reveals a number of intermolecular phosphorus–chlorine contacts (Figure 3) that are comparable if not shorter than the cation–anion interactions in the salts **1**[$GaCl_4$] and **2**[$GaCl_4$] (Figure 2). We conclude that the strength of the interion interactions (apparently weak or longer than van der Waals) in these salts is less significant than the fact that they may electrostatically associate in solution.

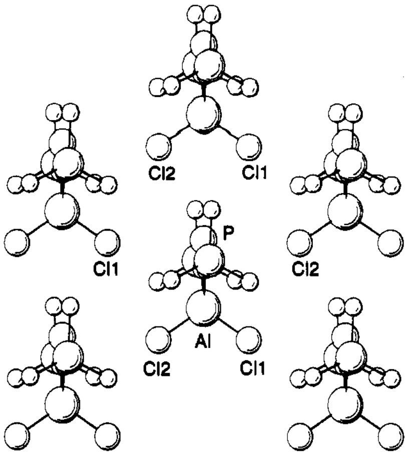

Figure 3. Crystallographic view of compound **8** generated from the data presented in ref 40. P–Cl distances (Å): P- - -Cl1 = 3.73, P- - -Cl2 = 3.89.

The coordinative unsaturation of the phosphenium center renders it particularly susceptible to effective electrostatic interaction with the anion allowing for recognition of "*anionic protection*" of the cation. However, it is likely that the effect is a general feature for complex ionic non-metal systems and it is possible that the thermodynamic consequences of the cation–anion interaction in solution are overlooked.

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Supplementary Material Available: Crystal data, anisotropic thermal parameters, and bond lengths and angles for $[(^i\text{Pr}_2\text{N})_2\text{P}][\text{GaCl}_4]$, $[\text{MeNCH}_2\text{CH}_2\text{N(Me)P}][\text{GaCl}_4]$, $\text{MeNCH}_2\text{CH}_2\text{N(Me)PPh–BPh}_3$ (**5**), and $[(^i\text{Pr}_2\text{N})_2\text{P(Cl)CH}_2\text{Cl}][\text{BPh}_4]$ (11 pages). Ordering information is given on any current masthead page.

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