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Structural Alternatives in $R_2(Cl)P{:}GaCl_3$ Systems (R = Alkyl, Phenyl), Including Examples of Intermolecular P → P Coordination

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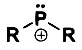
Systematic NMR studies of (dialkyl/diaryl)chlorophosphine−gallium chloride reaction mixtures reveal three structural alternatives, which are related by equilibria in solution, and their relative stability is dependent on the nature of the substituent (R = Me, Et, ^iPr, ^tBu, Ph) and the reaction stoichiometry. The coordination complex $R_2(Cl)P\rightarrow GaCl_3$ is observed in all cases, and a derivative (R = ^iPr) has been crystallographically characterized. Tetrachlorogallate salts of the diphosphorus cations $[R_2(Cl)P-PR_2]^+$ are observed for smaller R substituents (R = Me, Et, ^iPr, Ph), consistent with a previous report. Solid-state ^{31}P CP-MAS NMR spectra distinguish the methyl derivative from the novel salt $[Me_2(Cl)P-P(Me_2)-GaCl_3][GaCl_4]$, containing a phosphine−phosphenium−gallium chloride cation, which has been crystallographically characterized. Factors governing the relative stabilities of the structural alternatives are discussed, and comparisons are made between the isomeric forms for $R_2(Cl)P{:}GaCl_3$.

Introduction

Electron-rich pnictogen centers and electron-deficient sites in compounds of the group 13 elements form donor-acceptor bonds (e.g. $R_3N\rightarrow BX_3$), which represent the simplest models for coordination chemistry. Examples are well-defined in the chemistry of phosphorus (i.e. $R_3P\rightarrow EX_3$);[2] however, the predictably weak donor ability of halophosphines[3] and the heterolytic lability[4] of P−X bonds allow for interesting structural alternatives to P→E coordination. In the simplest case, $[EX_4]^-$ salts of phosphenium cations **1** are formed when phosphorus is bound to a nitrogen (amino) center or dicoordinate sulfur center.[5] Another option arises as a result of the molecular charge, coordinative unsaturation, and electron deficiency at phosphorus in derivatives of **1**, enabling the formation of a formal P→P coordinative bond, represented by **2a**, which can also be Lewis drawn as phosphinophosphonium cation **2b**. Derivatives of **2** have been identified by NMR spectroscopy in solution,[6−9] and intramolecular examples of such bonding arrangements have been crystallographically characterized.[10−12]



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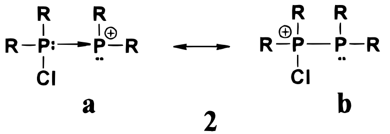

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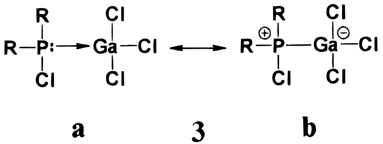
We now report systematic NMR studies of the (dialkyl/diaryl)chlorophosphine−gallium chloride reaction mixture, which reveal three structural alternatives related by equilibria in solution. Their relative stabilities are dependent upon the nature of the substituent (R) and the reaction stoichiometry. The familiar P→E complexes **3**, which were previously postulated for halophosphines[13] but not confirmed, are observed in all cases. Tetrachlorogallate salts of the diphosphorus cations **2** are observed for smaller R substituents, and the novel salt **4**[$GaCl_4$], containing a phosphine−phosphenium−gallium chloride cation, is present for R = Me



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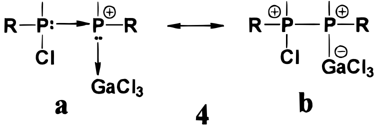

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Table 1. ^{31}P NMR Data and Assignments for Reaction Mixtures $R_2(Cl)P-GaCl_3$ of Varying Stoichiometry[a]

R	stoichiometry $R_2(Cl)P:GaCl_3$	$[R_2(Cl)P-PR_2]^+$ (**2**), two doublets	$R_2(Cl)P-GaCl_3$ (**3**), singlet	$[R_2(Cl)P-P(R_2)-GaCl_3]^+$ (**4**), two doublets	$[R_2(Cl)PH]^+$ (**5**), singlet	R_2PCl, singlet
Me	1:1	96 [311], −28 [311]	57 (<5)			
	1:2		56 (<5)	89 [219], −16 [219]		
	2:1	99 [340], −33 [340]	57 (<5)			
Et	1:1	101 [240], 0 [240]	79 (<10)			
	1:3	100 [237], 0 [240]	79 (<10)			
	2:1	101 [263], 0 [267]	79 (<10)			
^{i}Pr	1:1		91		86 (55)	
	1:3		91 (40)		87	
	2:1	115 [445], 14 [445] (<5)	92		86 (20)	
^{i}Bu	1:1		101		96 (45)	
	1:3		102		96 (15)	
	2:1		101		95 (25)	148
Ph	1:1	73 [393], 1 [391]	41 (<10)			
	1:3		41			
	2:1	73 [393], 0 [393]	41 (<10)			

[a] Data are given as chemical shifts in ppm, $^1J_{PP}$ values in Hz (in brackets), and relative integration with respect to the principal (without parentheses) signal in percent (in parentheses).

Table 2. ^{13}C and ^1H NMR Data Assignments for the Components of $R_2(Cl)P-GaCl_3$ Reaction Mixtures[a]

complex	$^{13}C\{^1H\}$ [$^nJ_{PC}$]	^1H [$^nJ_{PH}$,$^nJ_{HH}$]
2(Me)	17 [d of d: $^1J_{PC}$, 38; $^2J_{PC}$, 6], 8 [d of d: $^1J_{PC}$, 21; $^2J_{PC}$, 5]	2.50 [d of d: $^2J_{PH}$, 11.1; $^3J_{PH}$, 4.4],1.53 [d of d: $^2J_{PH}$, 24.2; $^3J_{PH}$, 4.6]
2(Et)	24 [$^1J_{PC}$, 27], 22 [$^1J_{PC}$, 17], 14, 9 [$^2J_{PC}$, 6], 8 [$^2J_{PC}$, 8], 7	3.05 [m], 2.59 [m], 1.59 [m]
2(Ph)	137, 136 [m], 133 [m], 131 [m]	7.65 [m]
3(^{i}Pr)	29 [d: $^1J_{PC}$, 11], 17 [d: $^2J_{PC}$, 2], 16 [d: $^2J_{PC}$, 3]	2.86 [d of q of q: $^3J_{HH}$, 7.0; $^3J_{HH}$, 7.1; $^2J_{PH}$, 2.6], 1.52 [d of d: $^3J_{HH}$, 7.0; $^3J_{PH}$, unresolved], 1.44 [d of d: $^3J_{HH}$, 7.0; $^3J_{PH}$, 3.4]
3(^{t}Bu)	42 [d: $^1J_{PC}$, 1], 28 [d: $^2J_{PC}$, 4]	1.59 [d: $^3J_{PH}$, 18.6]
3(Ph)	139, 134 [d: $^2J_{PC}$, 14], 132 [d: $^3J_{PC}$, 15], 115 [d: $^1J_{PC}$, 91]	7.95 [m]
4(Me)	16 [d of d: $^1J_{PC}$, 39; $^2J_{PC}$, 6], 9 [d of d: $^1J_{PC}$, 19; $^2J_{PC}$, 4]	2.90 [d of d: $^2J_{PH}$, 11.6; $^3J_{PH}$, 5.0], 2.15 [d of d: $^2J_{PH}$, 17.5; $^3J_{PH}$, 6.3]
5(^{i}Pr)	27 [d: $^1J_{PC}$, 34], 17 [d: $^2J_{PC}$, 2], 16 [d: $^2J_{PC}$, 4]	7.25 [d of t: $^1J_{PH}$, 516.4; $^3J_{HH}$, 4.7], 3.06 [d of d of q of q: $^3J_{HH}$, 7.0; $^2J_{PH}$, 1.5; $^3J_{PH}$, 4.3], 1.61 [d of d: $^3J_{HH}$, 7.0; $^3J_{PH}$, 11.0], 1.51 [d of d: $^3J_{HH}$, 7.0; $^3J_{PH}$, masked]
5(^{t}Bu)	40 [d: $^1J_{PC}$, 22], 27 [d: $^2J_{PC}$, 3]	6.92 [d: $^1J_{PH}$, 500.3], 1.62 [d: $^3J_{PH}$, 21.4]

[a] Data are given as chemical shifts in ppm and *J* values in Hz; m = unresolved multiplet.

only.[14] The factors governing the relative stability of each structural alternative and the empirically isomeric forms **1**[$GaCl_4$], **3**, and **4**[$GaCl_4$] are discussed. Throughout this paper, the R group associated with a complex is given in parentheses after the compound number.

Experimental Procedures

General Considerations. Sample handling and reactions were performed under moisture-free conditions.[15] Di-*tert*-butylchlorophosphine (Aldrich), chlorodiisopropylphosphine (Aldrich), chlorodimethylphosphine (Strem), and chlorodiethylphosphine (Aldrich) were distilled under static vacuum. Chlorodiphenylphosphine (Aldrich) was used as received. Gallium trichloride (Aldrich) was sublimed under vacuum. Toluene was dried at reflux over sodium metal and benzophenone. *n*-Hexane and deuterated solvents were dried over calcium hydride. Dichloromethane was dried over CaH_2 and P_4O_{10}. Melting points were obtained on a Fisher-Jones apparatus and are uncorrected. FT-IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P spectrometer. Chemical analyses were performed by Beller Laboratories, Göttingen, Germany. Solution $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR data were recorded at room temperature on samples sealed in evacuated Pyrex tubes using a Bruker AC-250 spectrometer (250.13 MHz for ^1H, 62.89 MHz for ^{13}C, 101.26 MHz for ^{31}P). Chemical shifts are reported in ppm relative to external standards (85% aqueous H_3PO_4 for ^{31}P, TMS for ^1H and ^{13}C). Solid-state CP-MAS ^{31}P NMR experiments were carried out using a Bruker AMX-400 (B_0 = 9.4 T) spectrometer (161.98 MHz for ^{31}P), and each experiment was performed at several sample spinning frequencies (4−10 kHz). Chemical shifts are referenced with respect to external 85% aqueous H_3PO_4 by setting the peak of external solid $[NH_4][H_2PO_4]$ to 0.8 ppm.

NMR Studies of Reactions between R_2PCl and $GaCl_3$. In a typical experiment, a sample of R_2PCl was dissolved in 5 mL of CD_2Cl_2 and added to $GaCl_3$, and an aliquot of the resulting solution was transferred to a 5 mm NMR tube and flame-sealed. Spectra were obtained within 1 day of sample preparation, and the data are presented in Tables 1 and 2.

Precipitation of 2(Me)[$GaCl_4$]. Me_2PCl (0.32 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was added to $GaCl_3$ (0.29 g, 1.7 mmol) in CH_2Cl_2 (5 mL), and the solution was stirred for 15 min. Removal of the solvent *in vacuo* (static) gave a white solid characterized as 2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium tetrachlorogallate; crude yield 0.51 g, 84%. Recrystallization was unsuccessful, giving a powder. Mp: 236−246 °C. IR (cm^{-1}): 1410 (s), 1297 (s), 1169 (w), 1151 (w), 1104 (w), 960 (s), 929 (s), 888 (s), 871 (sh), 835 (w), 777 (m), 662 (w), 550 (s), 500 (w), 426 (m), 368 (s), 309 (w). ^{31}P solid-state CP-MAS NMR spectra: δ_{iso} 99 ppm ($^1J_{PP}$ = 331 Hz), 57 (s, 10%), −36 ppm ($^1J_{PP}$ = 331 Hz). NMR (CD_2Cl_2): $^{31}P\{^1H\}$,

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99 ppm (d, $^{1}J_{PP} = 340$ Hz), −32 ppm (d, $^{1}J_{PP} = 341$ Hz), 57 (s, <5%); $^{13}C\{^{1}H\}$, 17 ppm (d of d, $^{1}J_{PC} = 38$ Hz, $^{2}J_{PC} = 6$ Hz), 8 ppm (d of d, $^{1}J_{PC} = 21$ Hz, $^{2}J_{PC} = 5$ Hz); ^{1}H, 2.55 ppm (d of d, $^{2}J_{PH} = 11.3$ Hz, $^{3}J_{PH} = 4.4$ Hz), 1.65 ppm (d of d, $^{2}J_{PH} = 24.3$ Hz, $^{3}J_{PH} = 4.9$ Hz).

Isolation of 4(Me)[GaCl$_4$]. Me$_2$PCl (0.56 g, 5.8 mmol) in CH$_2$Cl$_2$ (10 mL) was added to GaCl$_3$ (1.02 g, 5.8 mmol) in CH$_2$Cl$_2$ (10 mL), and the solution was stirred for 15 min. Removal of the solvent *in vacuo* (static) gave a white crystalline solid, which was recrystallized from a mixture of *n*-hexane and benzene (1:2) and characterized as 1-(trichlorogallio)-2-chloro-1,1,2,2-tetramethyl-1-phosphino-2-phosphonium tetrachlorogallate; yield 0.48 g, 33%. Anal. Calcd: C, 8.8; H, 2.2. Found: C, 8.7; H, 2.2. Mp: 78−81 °C. IR (cm^{-1}): 1297 (s), 1167 (w), 1156 (w), 955 (s), 931 (m), 922 (m), 903 (s), 892 (s), 868 (w), 837 (w), 777 (w), 757 (w), 688 (w), 573 (s), 461 (w), 411 (s), 367 (s). ^{31}P solid-state CP-MAS NMR spectrum: δ_{iso} 84 ($^{1}J_{PP} = 154$ Hz), −16 ppm (broad and unresolved). NMR (CD$_2$Cl$_2$): $^{31}P\{^{1}H\}$, 98 ppm (d, $^{1}J_{PP} = 332$ Hz), 57 (s, <5%), −31 ppm (d, $^{1}J_{PP} = 332$ Hz); $^{13}C\{^{1}H\}$, 17 ppm (d of d, $^{1}J_{PC} = 39$ Hz, $^{2}J_{PC} = 6$ Hz), 7 ppm (d of d, $^{1}J_{PC} = 19$ Hz, $^{2}J_{PC} = 4$ Hz); ^{1}H, 2.54 ppm (d of d, $^{2}J_{PH} = 11.0$ Hz, $^{3}J_{PH} = 4.6$ Hz), 1.69 ppm (d of d, $^{2}J_{PH} = 23.9$ Hz, $^{3}J_{PH} = 4.0$ Hz).

Isolation of 3(^{i}Pr). ^{i}Pr$_2$PCl (0.47 g, 3.1 mmol) in CH$_2$Cl$_2$ (5 mL) was added to a solution of GaCl$_3$ (0.54 g, 3.1 mmol) in CH$_2$Cl$_2$ (5 mL) and the solution was stirred for 12 h. Removal of the solvent *in vacuo* (static) gave a white crystalline solid, which was recrystallized twice from a mixture of CH$_2$Cl$_2$ and *n*-hexane (1:10) and characterized as diisopropylchlorophosphine−gallium trichloride; yield 0.26 g, 51%. Anal. Calcd: C, 21.9; H, 4.3; Cl, 43.1; Found: C, 21.7; H, 4.5; Cl, 42.9. Mp: 77−83 °C. IR (cm^{-1}): 1312 (w), 1291 (w), 1274 (w), 1244 (m), 1160 (m), 1100 (m), 1080 (m), 1065 (m), 1027 (m), 977 (sh), 966 (w), 932 (m), 899 (w), 877 (m), 773 (w), 679 (w), 651 (m), 567 (s), 506 (w), 463 (w), 389 (s), 373 (sh), 352 (s), 320 (w), 298 (w). NMR (CD$_2$Cl$_2$): $^{31}P\{^{1}H\}$, 91; $^{13}C\{^{1}H\}$, 29 ppm (d, $^{1}J_{PC} = 11$ Hz), 17 ppm (d, $^{2}J_{PC} = 3$ Hz); 16 ppm (d, $^{2}J_{PC} = 3$ Hz); ^{1}H, 2.77 ppm (d of d of q, $^{3}J_{HH} = 7.0$ Hz, $^{3}J_{HH} = 7.1$ Hz, $^{3}J_{PH} = 2.6$ Hz), 1.48 ppm (d of d, $^{3}J_{HH} = 7.1$ Hz, $^{3}J_{PH} = 8.3$ Hz), 1.41 ppm (d of d, $^{3}J_{HH} = 7.0$ Hz, $^{3}J_{PH} = 5.0$ Hz).

X-ray Crystallography. Crystals suitable for X-ray crystallographic analysis were obtained as described above and mounted in Pyrex capillaries in a drybox. X-ray data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.710\,69$ Å) at room temperature (23 ± 1 °C) using the $\omega-2\theta$ scan technique. Unit cell parameters were obtained from the setting angles of a minimum of 20 carefully centered reflections having $2\theta > 20°$. The choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures. The stability of the crystals was monitored by the remeasurement of 3 standard reflections every 150 reflections.

Structures were solved by direct methods[16] and expanded using successive Fourier syntheses. The function minimized by full-matrix least squares was $\Sigma w(F_o - F_c)^2$ (unit weights). Neutral atom scattering factors for non-hydrogen atoms were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_c;[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[20] Calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp.[21]

Table 3. Crystallographic Data

	3(^{i}Pr)	**4(Me)**[GaCl$_4$]
formula	C$_6$H$_{14}$PCl$_4$Ga	C$_4$H$_{12}$P$_2$Cl$_8$Ga$_2$
fw	328.69	545.15
λ(MoKα) (Å)	0.710 69	0.710 69
space group	*Cc*	*P*2$_1$/*c*
a (Å)	13.508(5)	10.227(2)
b (Å)	7.531(4)	13.504(3)
c (Å)	27.397(8)	13.868(4)
β (deg)	92.24(3)	91.39(2)
V (Å^3)	2784(1)	1928(1)
Z	8	4
T (°C)	23 ± 1	23 ± 1
D_c (Mg m^{-3})	1.568	1.878
μ (cm^{-1})	28.13	40.48
R^a	0.0579	0.0887
$R_w{}^b$	0.0667	0.1107

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg)

3(^{i}Pr)		**4(Me)**[GaCl$_4$]	
P1−Ga1	2.40(1)	P1−Ga1	2.450(6)
P2−Ga2	2.38(1)	P1A−Ga1	2.474(9)
P1−Cl4	2.01(2)	P2−Cl1	1.977(7)
P2−Cl8	2.01(2)	P2A−Cl1	2.006(10)
		P1−P2	2.138(7)
		P1A−P2A	2.156(10)
Cl4−P1−Ga1	107.0(6)	P2−P1−Ga1	110.5(3)
Cl8−P2−Ga2	108.2(6)	P2A−P1A−Ga1	107.0(6)

Crystallographic details for **3(^{i}Pr)** and **4(Me)**[GaCl$_4$] are summarized in Table 3, and selected bond lengths and angles are presented in Table 4. For **3(^{i}Pr)**, there were two independent molecules in the asymmetric unit with slightly different orientations. The Ga, Cl, and P atoms were refined anisotropically, whereas the C atoms were refined isotropically. The P−C and C−C bond lengths were constrained to reasonable values. Hydrogen atoms were added at calculated positions but not refined; their isotropic displacement parameters (*B*'s) were set to 1.2 times the B_{eq} value of the atom to which they were bonded. The cation of **4(Me)**[GaCl$_4$] is disordered so that P(1), P(2), C(2), and C(4) occupy two positions, which were located from a Fourier difference map, and were refined with an occupation factor of 0.25 for the atoms labeled A. All atoms except C2 and C4 were refined anisotropically. The geometry of this part of the molecule was restrained so that chemically equivalent bonds are approximately equal. Because of the disorder, hydrogen atoms were not included in the model.

Results and Discussion

Identification and Characterization of Structural Alternatives for the R$_2$(Cl)P:GaCl$_3$ System. Various stoichiometric combinations of the (dialkyl/diaryl)chlorophosphine R$_2$PCl (R = Me, Et, ^{i}Pr, ^{t}Bu, Ph) with GaCl$_3$ in CD$_2$Cl$_2$ have been examined by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy and reveal the formation of one or two of three structural alternatives, depending

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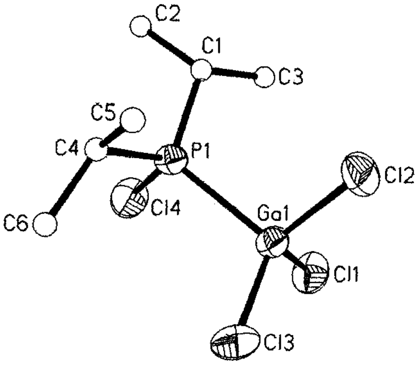

Figure 1. Crystallographic view of one of two molecules of **3(^{i}Pr)** in the asymmetric unit.

on the reaction stoichiometry and the substituent R. Table 1 lists the ^{31}P NMR data for each reaction mixture together with our assignment for each signal based on ^{13}C and ^{1}H NMR spectroscopic data (Table 2), comparative data available in the literature, and the solid-state characterization of three isolated compounds.

In contrast to previous studies (involving $AlCl_3$ as the Lewis acid reagent),[7] the classical 1:1 complex **3** is observed in all reactions and is assigned on the basis of the solid-state X-ray crystallographic characterization for **3(^{i}Pr)**, as well as a comparison with the previously reported ^{31}P NMR spectroscopic shift for $^tBu_2ClPAlCl_3$ (108 ppm).[22] Derivatives of **3** exhibit a consistent ^{31}P upfield shift of approximately 40 ppm with respect to the corresponding free phosphine R_2PCl (R = Me,[23] Et,[24] ^{i}Pr, ^{t}Bu,[25] Ph).[26] Complex **3** is the principal component for most stoichiometric combinations when R = ^{i}Pr and ^{t}Bu and is quantitatively formed when Ph_2PCl reacts with excess $GaCl_3$, but it is a minor component for 1:1 and 2:1 mixtures of Ph_2PCl with $GaCl_3$, and for all reactions when R = Me or Et.

All spectra for R = Me and Et are dominated by two related doublets (equal values of $^1J_{PP}$), which have previously been assigned to the structure **2** for R = Et, Ph, 4-ClC_6H_4.[7] The same doublet signals are also assigned to **2(^{i}Pr)** as a minor component of the 2:1 reaction of $^iPr_2PCl$ with $GaCl_3$. The phosphonium cation $[R_2(Cl)PH]^+$ (**5**) is observed as a significant component of all combinations when R = ^{i}Pr, ^{t}Bu and is the dominant species for the reaction of $^iPr_2PCl$ with excess $GaCl_3$. Free phosphine ($^tBu_2PCl$) is a principal component (concentration equivalent to that of **3(^{t}Bu)**) in the 2:1 reaction of $^tBu_2PCl$ with $GaCl_3$, but R_2PCl is not observed in the other reactions.

Oily solids were obtained in most attempts at isolation and could not be characterized, but crystalline or microcrystalline materials were obtained in moderate yield in three cases, and spectroscopic characterization has confirmed them to correspond to the dominant species observed in each respective reaction mixture. Complex **3(^{i}Pr)** was isolated from the equimolar reaction mixture of $^iPr_2PCl$ with $GaCl_3$ and has been characterized by X-ray crystallography (Figure 1). The ionic compound **4(Me)**[$GaCl_4$] was obtained from the reaction of Me_2PCl with 1 equiv of $GaCl_3$ and has also been characterized by X-ray crystallography (Figure 2). A crude powder obtained from the 2:1 reaction of Me_2PCl with $GaCl_3$ has a significantly higher melting point (236−246 °C) than that of **4(Me)**[$GaCl_4$] (78−81 °C). Although recrystallization was unsuccessful, spectroscopic features allow for definitive identification of **2(Me)**[$GaCl_4$] as the major component of the powder.

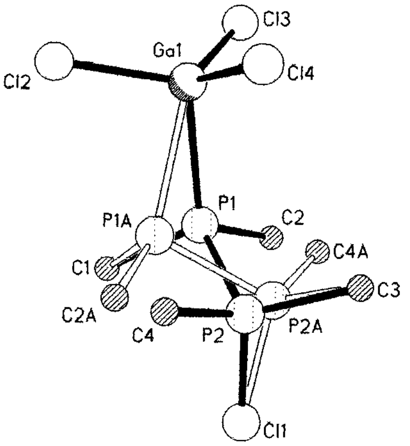

Figure 2. Crystallographic view of the disordered cation in **4(Me)**[$GaCl_4$].

Important comparisons can be made between the spectral properties of **2(Me)**[$GaCl_4$] and **4(Me)**[$GaCl_4$]. While the infrared spectra of the two compounds show some similarities, there are a number of significant fingerprint differences. Solution NMR spectra for redissolved samples of each compound are very similar and are consistent with those for 1:1 and 2:1 reaction mixtures of Me_2PCl and $GaCl_3$ (Tables 1 and 2). The solid-state ^{31}P CP-MAS NMR spectrum for **2(Me)**[$GaCl_4$] (δ_{iso} 99, −36 ppm, $^1J_{PP}$ = 331 Hz) is comparable with the solution ^{31}P spectra for both **2(Me)** and **4(Me)**. In contrast, the solid-state ^{31}P CP-MAS NMR spectrum for **4(Me)**[$GaCl_4$] exhibits significantly different chemical shifts for the two doublets (δ_{iso} 84, −16 ppm) and a coupling constant ($^1J_{PP}$ = 154 Hz) which is less than half of the value observed for **2(Me)**[$GaCl_4$] ($^1J_{PP}$ = 331 Hz). In solution, the chemical shift and coupling constant values only approach those observed in the solid state for **4(Me)**[$GaCl_4$] when an excess of $GaCl_3$ is present (δ 89, −16 ppm, $^1J_{PP}$ = 219 Hz), which effects an upfield shift of the high-frequency signal observed for **2(Me)**[$GaCl_4$] (corresponding to the tetracoordinate phosphonium-like environment) and a downfield shift of the low-frequency signal of **2(Me)**[$GaCl_4$] (corresponding to the tricoordinate phosphine-like environment). A downfield shift of the low-frequency signal was first recognized for **2**[$AlCl_4$] (R = Et, Ph) upon reaction with a europium shift reagent, implicating a similar interaction.[7] The phosphino center of **4(Me)**[$GaCl_4$] is further characterized by the broad and unresolved nature of the low-frequency signal (−16 ppm) in the ^{31}P NMR solid state spectrum, due to interaction of this phosphorus nucleus with the quadrupolar gallium nucleus.

Equilibria for the $R_2(Cl)P:GaCl_3$ System. Our NMR assignments of the four phosphinophosphonium cations **2(Me, Et, ^{i}Pr and Ph)** are consistent with the assignments originally made for R = Et and Ph derivatives (involving tetrachloroaluminate and heptachlorodialuminate anions) from ^{31}P, ^{1}H, and ^{13}C NMR

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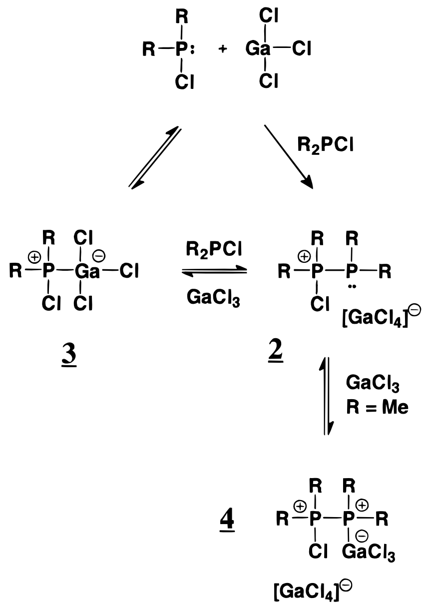
Scheme 1



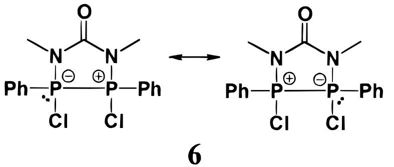
spectra obtained on an 80 MHz NMR spectrometer (therefore observed as AB patterns in the ^{31}P spectra).[7] In this previous study, inappropriate choice of stoichiometry and relatively low concentration likely prevented identification of **3**, which can be formed essentially quantitatively for R = Ph. Nevertheless, the spectra were interpreted in terms of equilibria involving the free phosphine. In addition, the chlorophosphonium cations **5** were generated by the introduction of HCl to effect cleavage of the P−P bond, as part of the structural confirmation for the phosphinophosphonium cations **2**.

The data presented here confirm the existence of derivatives of **2** and reveal two additional structural alternatives for the $R_2(Cl)P{:}GaCl_3$ system. The relative concentrations of **2**, **3**, **4**, and the free chlorophosphine are predictably dependent on the nature of R but, more importantly, are substantially affected by the reaction stoichiometry, implicating the equilibria summarized in Scheme 1. The identification of **4** is unique to R = Me, although other possible sources of similar complexes, such as $X_2(R)P{:}GaCl_3$ and $X_3P{:}GaCl_3$ (X = halide), have not been examined. The similar solution NMR spectra for redissolved samples of **4(Me)**[$GaCl_4$] and **2(Me)**[$GaCl_4$] reveal the dissociation of **4(Me)** to give **2(Me)** and $GaCl_3$. In the presence of excess $GaCl_3$, the equilibrium is forced in favor of **4(Me)**, as demonstrated by the solution NMR data for such samples being comparable to those in the solid-state spectra of crystalline **4(Me)**[$GaCl_4$].

The relative stabilities of the structural alternatives in the $R_2(Cl)P{:}GaCl_3$ system are likely influenced by various factors, including the σ-donor ability of the phosphine, the acidity of the phosphenium cation (R_2P^+) in relation to that of $GaCl_3$, and the consequences of steric interactions between the substituents bound to both the donor and the acceptor (for formation of **2**). The observation of **2** as a dominant component in the equilibria for R = Ph, Me, Et cannot be rationalized on the basis of the trend in σ-donor strength of the phosphine imposed by the inductive influence of the substituents (Ph < Me < Et < ^{i}Pr < ^{t}Bu). This is likely mediated by the steric presence (trend in substituent size: Me < Et < Ph < ^{i}Pr < ^{t}Bu) of the larger substituents, such that **2** is only a minor component when R = ^{i}Pr and is not observed when R = ^{t}Bu. Although the $^{1}J_{PP}$ values for derivatives of **2(Me)** and **4(Me)** indicate the trend in P−P bond strength **2(^{i}Pr)** (445 Hz) > **2(Me)** (331 Hz) > **4(Me)** (154 Hz), we have recently demonstrated that strong P−P interactions can have anomalously large $^{1}J_{PP}$ coupling constants.[27,28] It is also known that $^{1}J_{PP}$ is sensitive to molecular conformation about the P−P bond in these systems.[29]

There is no evidence of the formation of structure **4** for other derivatives (R = Et, ^{i}Pr, ^{t}Bu, Ph), and in the case of R = Et, the product distribution is independent of reaction stoichiometry. It seems that larger substituents (R = ^{i}Pr, ^{t}Bu) on phosphorus impede chloride ion abstraction. Instead, the P center interacts with $GaCl_3$ to give **3** or becomes protonated to give $[R_2(Cl)PH]^+$ (**5**). Protonation of the phosphine presumably occurs by reaction with the solvent, the acidity of which is enhanced by the presence of $GaCl_3$. The phosphonium derivative **5(^{i}Pr)** is not observed in solutions obtained by redissolving a crystalline sample of **3(^{i}Pr)** implying that the donor−acceptor interaction has a kinetic barrier large enough that deprotonation of the solvent is a competitive process. Reactions of the less sterically hindered methyl, ethyl, and phenyl derivatives show no evidence of **5**.

Phosphinophosphonium Cations. Phosphines are perhaps the most familiar moieties to be employed as ligands in coordination chemistry for both metals[30] and nonmetals.[2] The ability and potential for phosphorus (in phosphines) to behave as an acceptor is perhaps less obvious. Nevertheless, complexes involving amines bound to trihalophosphines have been demonstrated with vapor pressure measurements,[31] amine complexes of a diaminophosphine have been crystallographically characterized,[32] phosphines with different substitutions have been shown to form adducts with each other,[33] and an intramolecular P-P bond in **6** can be interpreted as



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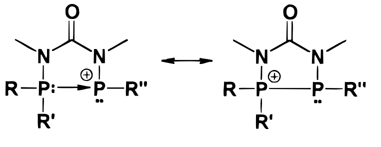

a **7** **b**

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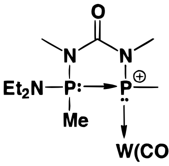
a donor-acceptor interaction.[34] A positively charged phosphorus center naturally demands a more effective coordinative interaction, and recent structural reports of amine,[10] imine,[35] phosphine,[28,36] and arene[37] complexes of phosphorus cations highlight new directions in phosphorus chemistry.

Crystal structures for derivatives of **7**[11,12] provide confirmed intramolecular examples of phosphine−phosphenium (**7a**) or phosphinophosphonium (**7b**) complexes, but compound **4(Me)**[$GaCl_4$] represents the first structural characterization of an intermolecular P→P complex. It is composed of discrete ions, with the cation (shown in Figure 2) involving Me_2PCl as a ligand on **1(Me)**, which is itself a donor toward $GaCl_3$. Such “in series” or two-step coordination is evident in the tungsten complex **8**[12] and has been invoked in a number of cases for low-oxidation-state group 14 elements.[38] The labile or dissociative nature of both the P−P and P−Ga bonds in solution is consistent with such a model. Alternatively, one can envisage **4(Me)** in terms of cation **2(Me)** behaving as a phosphine ligand on $GaCl_3$ or as the phosphenium unit **1(Me)** inserted in the P−Ga coordinative bond of **3(Me)**.



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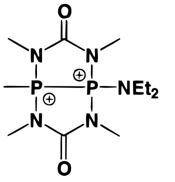

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The structural features of the cation are also consistent with the diphosphonium model **4(Me)b**, with P−P bond lengths (2.138(7) and 2.156(10) Å) comparable to that of the novel diphosphonium cation **9** (2.189 Å)[39] and to other P^V-P^V bonds (e.g. $Me_2P(S)-P(S)Me_2$, 2.245(6) Å;[40] $Me_2P(BH_3)-P(BH_3)Me_2$, 2.189(5) Å[41]). Moreover, the environments for both phosphorus centers are essentially tetrahedral. The P−Ga bond length (2.450(6) and 2.474(6) Å) within the cation is typical of phosphino−gallane complexes (range 2.35 Å−2.68 Å),[2] and is comparable to those of symmetrically alkylated complexes such as $Me_3P \rightarrow GaCl_3$ (2.353(2) Å)[42] and $Me_3P \rightarrow GaMe_3$ (2.455(4) Å),[43] as well as **3(^{i}Pr)** (2.40(1), 2.38(1) Å).

Isomeric Forms in the $R_2(Cl)P{:}GaCl_3$ System. Halide ion lability for the phosphorus−halogen bond in the presence of a strong Lewis acid was first recognized for aminophosphines,[6,44,45] and cations of type **1** and **2** have been demonstrated as ionic structural alternatives to coordination complexes of general structure **3**. Reaction of **2(NR′$_2$)** with excess Lewis acid ($AlCl_3$) results in quantitative chloride ion abstraction and formation of 2 equiv of **1(NR′$_2$)**[$AlCl_4$],[6] and the corresponding $[GaCl_4]^-$ salts are readily accessible.[46] However, the corresponding reactions do not occur for (dialkylchlorophosphino)dialkylphosphonium salts **2**.[7] Instead, isolation of **4(Me)**[$GaCl_4$] presents an unexpected empirical isomer of both **3(Me)** and the hypothetical **1(Me)**[$GaCl_4$]. We rationalize these observations in terms of the relative stabilization imparted on the aminophosphenium cation **1(NR′$_2$)** by π-delocalization of the molecular charge through effective phosphorus−nitrogen π-overlap, which is precluded in **1(Me)**, other than in the form of hyperconjugation.

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Supporting Information Available: Tables giving crystallographic data, positional parameters, bond lengths and angles, and anisotropic thermal parameters for **3(^{i}Pr)** and **4(Me)**[$GaCl_4$] and figures giving additional views of the two structures (8 pages). Ordering information is given on any current masthead page.

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