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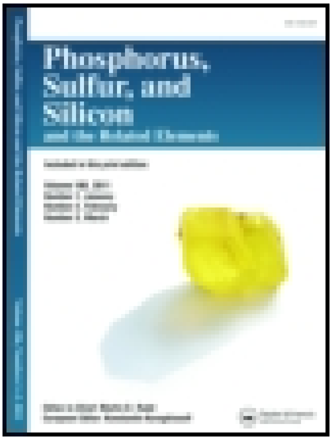

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A TETRAARYLDIPHOSPHORUS CATION AND A DIALKYLPHOSPHONIUM SALT

Stephen E. Johnson [a] & Carolyn B. Knobler [b]
[a] Department of Chemistry, The University of Iowa, Iowa City, IA, 52242-1294, USA
[b] Department of Chemistry and Biochemistry, The University of California at Los Angeles, Los Angeles, CA, 90024-1569, USA
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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A TETRAARYLDIPHOSPHORUS CATION AND A DIALKYLPHOSPHONIUM SALT

STEPHEN E. JOHNSON*
Department of Chemistry, The University of Iowa, Iowa City, IA 52242-1294, USA

and

CAROLYN B. KNOBLER
Department of Chemistry and Biochemistry, The University of California at Los Angeles, Los Angeles, CA 90024-1569, USA

Dedicated to Professor John G. Verkade on the occasion of his 60th birthday

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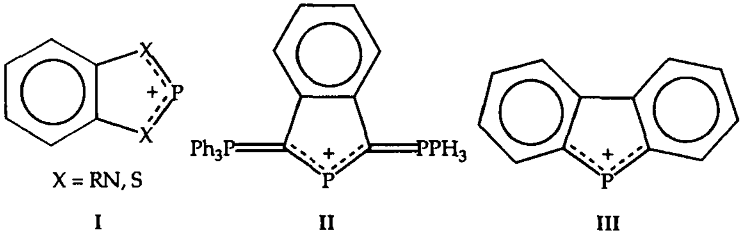
The compound 5-chorodibenzophosphole reacts with an equivalent amount or an excess of Al_2Cl_6 in methylene chloride solution to afford the respective tetraorganodiphosphorus cations $[R_2P(Cl)PR_2][AlCl_4]$ (R_2 = *o,o'*-dibenzophenylato), **1**. However, reaction of *t*-Bu_2PCl with an equivalent amount or an excess of Al_2Cl_6 in CH_2Cl_2 gives rise to a phosphonium ion, $[t\text{-}Bu_2PCl_2][AlCl_4]$ (**2**) as the major product, while reaction with 0.5 equivalent Al_2Cl_6 leads to a mixture of cationic organophosphorus species. In addition, the compound 5-chloro-*bis*-carboranylphosphole (**3**) was synthesized. Compound **3** fails to react with Al_2Cl_6 or $GaCl_3$, yet does afford 5-fluoro-*bis*-carboranylphosphole (**4**) upon treatment with $AgSbF_6$. The molecular structures of **1** and **2** have been determined from X-ray structural analysis. The former consists of a planar P(III) heterocyclic moiety joined to an essentially tetrahedral P(IV) heterocycle by a single P—P bond. The charge is balanced by the heptachlorodialuminate ion. Compound **1** crystallized in the triclinic space group $P\bar{1}$ with a = 10.5798(8) Å, b = 11.3656(9) Å, c = 13.8190(11) Å, α = 107.985(3)°, β = 100.9135(2)°, γ = 103.636(2)°, V = 1478 $Å^3$, Z = 2, R = 0.047. Compound **2** crystallized in the monoclinic space group, $P2_1$ with a = 7.2471(8) Å, b = 12.0235(12) Å, c = 9.9651(11) Å, β = 90.473(3)°, V = 868 $Å^3$, Z = 2, R = 0.109.

Key words: Synthesis, X-ray structures, diphosphorus cation, phosphonium cation, heptachloroaluminate ion, NMR.

INTRODUCTION

The Lewis acid-base interactions of amido-substituted phosphorus(III) halides and Lewis acids (e.g. Al_2Cl_6, PF_5) were elucidated in the pioneering work of Fleming and Parry.[1,2] It is now well established that low-coordinated phosphorus cations are generated by halide abstraction from precursor chlorophosphines and that the corresponding diphosphorus cations are derived from nucleophilic addition of phosphenium ions to organophosphine halides.[3] Examples of ions stabilized through N—P and S—P pπ-pπ interactions are also well documented.[4] Well characterized examples of phosphorus cations containing P—C bonds, such as phosphaalkenes and related methylene phosphonium ions, have been reported within the past few years.[5,6]

Scheme I



Schmidpeter and co-workers have provided the first example of a stable phosphole cation with phosphorus in a planar environment.[7] The existence of pπ-bonding at the phosphorus centers within phosphole and heterophosphole frameworks **I–III** (Scheme I), in the absence of steric constraints, is perhaps one of the most enlightening features of the heterocyclic derivatives. In view of these observations, we anticipated that an ion generated from the heterophosphole (**III**) would alter the character of the P—C bond and the subsequent stability of the phosphole cation formed. This was well documented in the case of diphosphonio isophosphindoles.[7] In addition, we wanted to examine the electronic effects of incorporating a *bis*-carboranyl substituent into a phosphole framework.[8] *Bis*-carborane has been reported to be a novel chelating agent with transition metal complexes.[9]

Here, we report the synthetic details, structural characterization data and solution-state studies of this investigation. The X-ray structures of **1** and **2** were determined. Functionalization of the phosphorus atom with alkyl versus carbocyclic-containing substituents appears to strongly influence the composition and structures of the organophosphorus cations observed. The solution-state behavior of the organophosphorus cations **1** and **2** was investigated by ^{1}H, ^{13}C, and ^{27}Al and ^{31}P NMR spectroscopy.

RESULTS AND DISCUSSION

Synthesis

The compound 5-chlorodibenzophosphole reacts with an equivalent or excess aluminum chloride in methylene chloride solution to afford the tetraorganodiphosphorus cation **1** (Equation 1). The same products are observed when 0.5 equivalent of aluminum chloride is used, from ^{31}P NMR experiments. In contrast, di-*t*-butylchlorophosphine forms the phosphonium salt, **2**, as the major product from reaction with an equivalent or an excess of aluminum chloride (Equation 2). Reaction with 0.5 equivalents of aluminum choride affords a mixture of cationic phosphorus products from ^{31}P NMR experiments (*vide infra*).

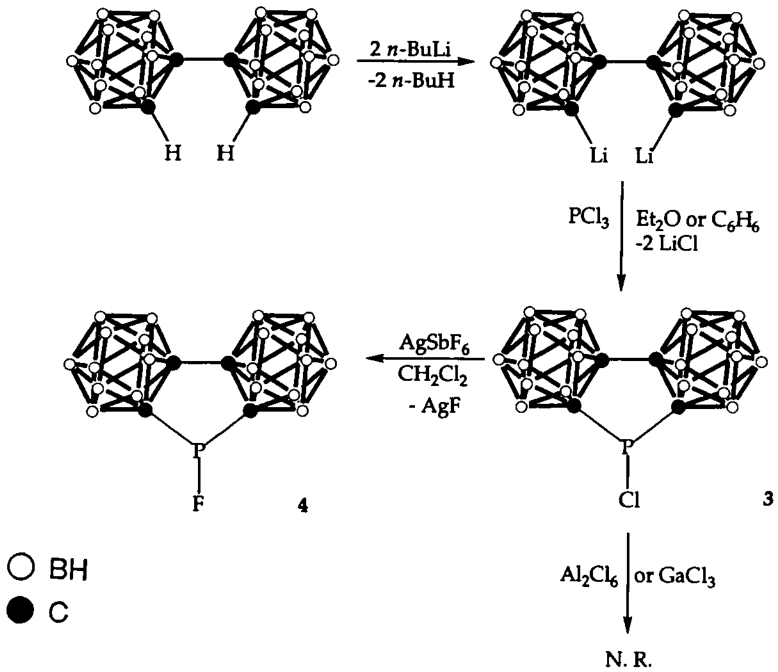
$$2\,R_2PCl + Al_2Cl_6 \xrightarrow{CH_2Cl_2} [R_2P(Cl){-}PR_2][Al_2Cl_7] \qquad (1)$$

$$\mathbf{1}\text{: } R_2 = o,o'\text{-dibenzophenylato}$$

$$2\,t{-}Bu_2PCl + Al_2Cl_6 \xrightarrow{CH_2Cl_2} [t{-}Bu_2PCl_2][AlCl_4] \qquad (2)$$

$$\mathbf{2}$$

Scheme II



The compound 5-chloro-*bis*-carboranylphosphole (**3**) was synthesized in high yield by first generating the C-substituted dilithio salt of *bis*-carborane *in-situ*, followed by the addition of PCl$_3$. It is the first example of a carborane-containing phosphole and is related to the heterocyclic phosphino-*o*-carboranes.[10] Interestingly, it does not react with stoichiometric or excess amounts of Al$_2$Cl$_6$ or GaCl$_3$. Reaction with AgSbF$_6$ only affords the compound 5-fluoro-*bis*-carboranylphosphole, **4**, as summarized in Scheme II. This result appears to be consistent with the observation of exceedingly stable transition metal-chelates of *bis*-carborane observed by Hawthorne.[9]

NMR Behavior

A complicated, non first-order splitting pattern of aromatic ring protons is observed for **1**, nevertheless the protons of the phosphole and phospholium moieties can be discerned. The ^{1}H NMR spectrum of **2** consists of a doublet, $^{3}J|^{1}H^{31}P|$ = 24 Hz. The ^{1}H NMR spectrum of both 5-chlor- (**3**) and 5-fluoro-*bis*-carboranylphosphole (**4**) exhibit broad resonances from 0.7–4.0 ppm, indicating B—H protons. No resonances attributable to the carborane C—H protons were observed, consistent with a heterophosphole framework.[9b] The ^{31}P{^{1}H} chemical shift data for compounds **1**, **2** and related compounds are summarized in Table I. The ^{31}P spectrum of **1** consists of a pair of doublets, characteristic of a mixed valence diphosphorus cation. The magnitude of $^{1}J|^{31}P^{31}P|$ for **1** is 407 Hz, consistent with ^{31}P NMR chemical shift data for other diphosphorus cations (e.g. R = Ph, 389 Hz, R = Me, 311 Hz).[11,12] It is interesting that both P(III) and P(IV) nuclei are significantly deshielded as compared

TABLE I

^{31}P and ^{27}Al NMR data for organophosphorus cations

Compound	$\delta^{31}P^{(III)}$(ppm)	$\delta^{31}P^{(IV)}$(ppm)	$J|^{31}P^{31}P|$(Hz)	$\delta^{27}Al$(ppm)	$\omega_{1/2}$(Hz)	Reference
1	-66.9	-23.3	389	102.5	846	this work
2	—	81.0	—	102.9	15	this work
5[a]	-1.5	72.0	407	—	—	11
6[b]	36.3	70.1	463	—	—	this work
7[c]	-18.8	109.5	375	—	—	11
8[d]	-118.2	-50	352	—	—	13a
9[e]	-33.0	99.0	340	—	—	12

[a] Compound **5** $[Ph_2P\text{-}P(Cl)Ph_2][Al_2Cl_7]$. [b] Compound **6** $[t\text{-}Bu_2P\text{-}P(Cl)t\text{-}Bu_2][AlCl_4]$. [c] Compound **7**: $[Et_2P\text{-}P(Cl)Et_2][AlCl_4]$. [d] Compound **8**: $[Me_2N(Cl)P\text{-}P(NMe_2)_3][AlCl_4]$. [e] Compound **9**: $[Me_3P\text{-}PMe_2GaCl_3][GaCl_4]$.

to corresponding amido-substituted diphosphorus cations.[13] Moreover, the ^{27}Al NMR spectrum of **1** ($\omega_{1/2}$ = 846 Hz) is worth noting. Both diphosphorus cations exhibit broad ^{27}Al signals, not characteristic of $AlCl_4^-$, but consistent with $Al_2Cl_7^-$ in solution.[14a] Compound **2** exhibits a single, sharp ^{27}Al signal, characteristic of $AlCl_4^-$ ($\omega_{1/2}$ = 15 Hz).[14b]

The $^{31}P\{^1H\}$ spectrum of **2** consists of a singlet centered at 81.0 ppm, which differs significantly from the chemical shift reported for $[t\text{-}Bu_2PCl_2][Cl]$, $\delta^{31}P$ = 158.0 ppm.[15] The phosphonium salt **2** is the major product of the reaction between equivalent amounts of $t\text{-}Bu_2PCl$ and Al_2Cl_6 or when the latter is in excess. Reaction of the chlorophosphine with half an equivalent of aluminum chloride, however, affords a mixture of products. In addition to **2**, the diphosphorus cation $[t\text{-}Bu_2P{-}P(Cl)t\text{-}Bu_2][AlCl_4]$ ($\delta^{31}P(IV)$ = 70.14 ppm, $\delta^{31}P(III)$ = 36.29 ppm, $^1J|^{31}P^{31}P|$ = 463 Hz), the phosphonium ion $(t\text{-}BuPCl_3][AlCl_4]$ ($\delta^{31}P(IV)$ = 133.0 ppm, br s),[13c] and the phosphonium ion $[t\text{-}Bu_3PCl][AlCl_4]$ ($\delta^{31}P(IV)$ = 119.5 ppm), the acid-base adduct $[t\text{-}Bu_2PCl\cdot AlCl_3]$ ($\delta^{31}P(IV)$ = 110 ppm)[19] and $[t\text{-}Bu_2PCl_2][Cl]$, $\delta^{31}P$ = 160.0 ppm could be identified. The $^{31}P\{^1H\}$ chemical shift of 5-chloro-*bis*-carboranylphosphole ($\delta^{31}P$ = 92.3 ppm) is somewhat deshielded as compared to 5-chlorodibenzophosphole (δ ^{31}P = 58.1 ppm). The 5-fluoro-*bis*-carboranylphosphole exhibits a doublet and the $^1J|^{31}P^{19}F|$ of 1148 Hz correlates well with values reported for R_2PF derivatives.[13b]

Description of the Molecular Structure of 1

The molecular structure of **1** is presented in Figure 1. Table II lists selected interatomic distances and angles and the atomic coordinates are summarized in Table III. For clarity, only the non-hydrogen atoms are shown, completely labelled. X-ray analysis of **1** confirms the conclusions drawn from spectroscopy by revealing a planar P(III) phosphole moiety joined to an essentially tetrahedral P(IV) heterocycle by a single P1—P2 bond length of 2.191(1) Å. The P1—Cl1 bond distance of 2.035(1)

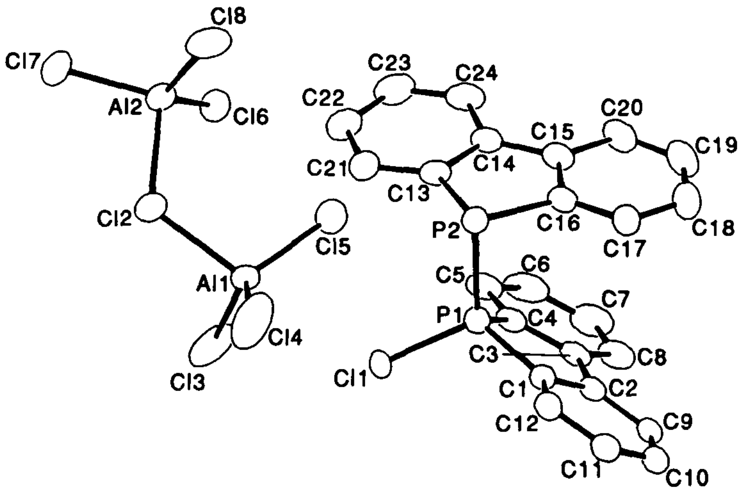


FIGURE 1 ORTEP representation of 1 showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at 0.30 probability level.

TABLE II

Selected interatomic distances and angles for 1

Distances (Å)			
P1 - P2	2.191(1)	Al1 - Cl2	2.293(2)
P1 - Cl1	2.035(1)	Al2 - Cl2	2.277(2)
P1 - C1	1.775(4)	Al1 - Cl3	2.085(2)
P1 - C4	1.778(4)	Al1 - Cl4	2.093(2)
P2 - C13	1.824(4)	Al1 - Cl5	2.088(2)
P2 - C16	1.830(4)	Al2 - Cl6	2.095(2)
		Al2 - Cl7	2.123(2)
		Al2 - Cl8	2.104(2)

Angles (deg)			
C1 - P1 - C4	95.00(18)	Al1 - Cl2 - Al2	116.98(6)
C1 - P1 - Cl1	111.93(13)	Cl3 - Al1 - Cl5	115.39(10)
C1 - P1 - P2	111.64(13)	Cl3 - Al1 - Cl4	115.43(10)
C4 - P1 - Cl1	112.29(13)	Cl3 - Al1 - Cl2	101.05(7)
C4 - P1 - P2	116.75(19)	Cl5 - Al1 - Cl4	112.60(8)
Cl1 - P1 - P2	108.74(6)	Cl5 - Al1 - Cl2	108.72(6)
C13 - P2 - C16	90.19(18)	Cl4 - Al1 - Cl2	101.72(7)
C13 - P2 - P1	94.40(13)	Cl6 - Al2 - Cl8	118.08(8)
C16 - P2 - P1	90.25(12)	Cl6 - Al2 - Cl7	113.01(7)
		Cl6 - Al2 - Cl2	105.91(6)
		Cl8 - Al2 - Cl7	112.81(7)
		Cl8 - Al2 - Cl2	102.53(7)
		Cl7 - Al2 - Cl2	102.29(6)

TABLE III

Positional and equivalent isotropic thermal parameters for 1[a]

atom	x	y	z	$U_{eq}(\times 10^3)$
Cl6	0.3706(1)	0.1870(1)	0.9106(1)	38.8(9)
Cl1	–0.0298(1)	–0.5269(1)	0.2941(1)	29.5(8)
Cl2	0.0775(1)	–0.0806(1)	0.7994(1)	40.3(9)
P1	0.1436(1)	–0.5107(1)	0.2478(1)	27.1(8)
Cl7	0.2165(1)	0.0403(1)	1.0677(1)	39.3(9)
Cl5	0.2764(1)	–0.0120(1)	0.6293(1)	51.1(11)
P2	0.2681(1)	–0.6006(1)	0.3275(1)	27.1(8)
Cl8	0.3708(1)	–0.1354(1)	0.8940(1)	54.8(11)
Al1	0.0769(1)	–0.0673(1)	0.6371(1)	31.0(10)
Al2	0.2785(1)	0.0120(1)	0.9266(1)	31.8(10)
Cl4	–0.0319(2)	–0.2585(1)	0.5351(1)	88.0(15)
Cl3	–0.0241(2)	0.0697(2)	0.6376(1)	104.(2)
C10	0.0928(4)	–0.6447(5)	–0.1026(3)	37.(4)
C17	0.4331(4)	–0.5857(4)	0.1832(3)	35.(4)
C9	0.1629(4)	–0.5175(4)	–0.0340(3)	32.(4)
C2	0.1727(4)	–0.4839(4)	0.0730(3)	28.(3)
C21	0.2752(4)	–0.4349(4)	0.5361(3)	34.(4)
C3	0.2395(4)	–0.3542(4)	0.1585(3)	30.(3)
C11	0.0319(4)	–0.7395(4)	–0.0665(3)	34.(4)
C1	0.1105(4)	–0.5801(4)	0.1083(3)	26.(3)
C22	0.3448(5)	–0.3275(4)	0.6268(3)	39.(4)
C5	0.2748(4)	–0.2359(4)	0.3476(3)	37.(4)
C16	0.4099(4)	–0.5342(4)	0.2808(3)	29.(3)
C13	0.3338(4)	–0.4604(3)	0.4516(3)	28.(3)
C18	0.5442(5)	–0.5200(5)	0.1610(4)	45.(5)
C14	0.4596(4)	–0.3775(4)	0.4575(3)	29.(3)
C15	0.5005(4)	–0.4176(4)	0.3593(3)	33.(3)
C20	0.6141(4)	–0.3524(4)	0.3378(4)	41.(4)
C24	0.5293(4)	–0.2712(4)	0.5503(3)	37.(4)
C4	0.2233(4)	–0.3495(4)	0.2578(3)	28.(3)
C7	0.3661(4)	–0.1294(4)	0.2361(4)	47.(4)
C19	0.6330(5)	–0.4039(5)	0.2381(4)	51.(5)
C6	0.3476(4)	–0.1240(4)	0.3352(4)	46.(4)
C23	0.4721(5)	–0.2477(4)	0.6341(3)	43.(4)
C8	0.3118(4)	–0.2419(4)	0.1483(4)	40.(4)
C12	0.0413(4)	–0.7078(4)	0.0399(3)	30.(3)

[a] $U_{eq} = \left[1/\left(6\pi^2\right)\right]\sum\sum\beta_{ij}a_i a_j$. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Å is consistent with other P(IV)—Cl contacts. The mixed valence P(III)—P(IV) cation assignment is further supported by slightly longer P(III)—C bond lengths (1.824(4) Å and 1.830(4) Å) as compared to their respective P(IV)—C bond contacts of 1.775(4) Å and 1.778(4) Å. The bond angles C—P(III)—C of 90.19(18)° and C

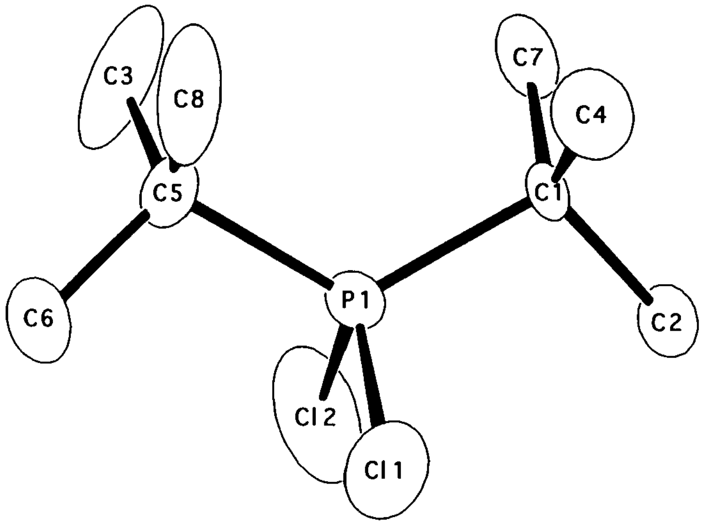


FIGURE 2 ORTEP representation of **2** showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.30 probability level.

TABLE IV

Selected interatomic distances and angles for **2**

	Distances (Å)		
P1C - Cl1C	1.993(6)	Al1 - Cl1	2.133(6)
P1C - Cl2C	1.947(7)	Al1 - Cl2	2.152(5)
P1C - C1	1.843(11)	Al1 - Cl3	2.127(6)
P1C - C5	1.837(12)	Al1 - Cl4	2.130(6)
	Angles (deg)		
Cl1C - P1C - Cl2C	108.4(3)	Cl1 - Al1 - Cl2	109.3(2)
Cl1C - P1C - C01	106.4(4)	Cl1 - Al1 - Cl3	111.0(2)
Cl1C - P1C - C05	107.1(4)	Cl2 - Al1 - Cl3	109.6(2)
C01 - P1C - C05	121.8(5)	Cl2 - Al1 - Cl4	109.2(2)

—P(III)—P(IV) bond angles of 94.40(13)° and 90.25(12)° are acute compared to the respective bond angles, C—P(IV)—C (95.00(18)°) and C—P(IV)—P(III) (111.64(13)° and 116.75(13)°). Further evidence of the phosphole character of the P(III) heterocycle is reflected by the fact that the carbon and phosphorus atoms (P2, C13—C16) are planar to within 0.002(1) Å. The phospholium character of the P(IV) heterocycle is reflected by the roughly tetrahedral angles at P(1). Distortions from tetrahedral geometry may be reasonably accounted for by the constraints of the 5-membered ring and connection to the phosphole moiety. The heptachlorodialuminate anion adopts a staggered conformation with the two bridging Al—Cl bond lengths of 2.277(2) Å and 2.293(3) Å somewhat longer than the average terminal Al—Cl bond contact of 2.100(2) Å. The geometry at both Al centers remain essentially tetrahedral and the Al(1)—Cl(2)—Al(2) bond angle is 116.98(6)°.

TABLE V

Positional and equivalent isotropic thermal parameters for **2**[a]

atom	x	y	z	$U_{eq}(\times 10^3)$
P(1C)	0.0869(4)	0.2076	0.7386(3)	0.020(1)
Al(1)	0.4095(5)	−0.2179(4)	0.7640(4)	0.024(2)
Cl(1)	0.4554(5)	−0.1185(4)	0.9384(3)	0.050(2)
Cl(2)	0.1303(4)	−0.2789(4)	0.7640(4)	0.027(1)
Cl(3)	0.5961(5)	−0.3544(4)	0.7585(5)	0.038(2)
Cl(4)	0.4488(5)	−0.1151(4)	0.5925(3)	0.048(2)
Cl(1C)	0.2193(7)	0.1743(5)	0.5688(5)	0.079(3)
Cl(2C)	0.2403(8)	0.1585(5)	0.8886(7)	0.077(3)
C(01)	−0.1216(13)	0.1198(9)	0.7377(12)	0.017(4)
C(02)	−0.0515(18)	−0.0003(11)	0.7397(15)	0.029(6)
C(03)	0.0007(44)	0.3943(15)	0.8950(19)	0.185(26)
C(04)	−0.2391(23)	0.1480(17)	0.6097(18)	0.049(8)
C(05)	0.0738(19)	0.3596(10)	0.7535(13)	0.043(7)
C(06)	0.2688(21)	0.4072(13)	0.7314(17)	0.041(7)
C(07)	−0.2310(20)	0.1452(15)	0.8670(17)	0.039(7)
C(08)	−0.0483(38)	0.4054(15)	0.6459(28)	0.109(18)
H(2A)	0.028	0.013	0.660	0.06*
H(2B)	−0.149	−0.056	0.716	0.06*
H(2C)	0.026	−0.030	0.815	0.06*
H(3A)	0.100	0.369	0.958	0.08*
H(3B)	−0.123	0.373	0.931	0.08*
H(3C)	0.007	0.477	0.885	0.08*
H(4A)	−0.144	0.152	0.538	0.06*
H(4B)	−0.310	0.220	0.612	0.06*
H(4C)	−0.326	0.085	0.590	0.06*
H(6A)	0.344	0.374	0.806	0.06*
H(6B)	0.241	0.487	0.753	0.06*
H(6C)	0.340	0.404	0.646	0.06*
H(7A)	−0.274	0.224	0.871	0.07*
H(7B)	−0.149	0.130	0.946	0.07*
H(7C)	−0.340	0.094	0.869	0.07*
H(8A)	−0.186	0.408	0.642	0.09*
H(8B)	0.000	0.369	0.563	0.09*
H(8C)	0.001	0.483	0.652	0.09*

[a] Asterisk indicates an atom refined isotropically. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Description of the Molecular Structure of 2

The molecular structure of the phosphonium ion is presented in Figure 2, Table IV lists selected interatomic distances and angles, while the atomic coordinates are summarized in Table V. The compound crystallizes as a simple 1:1 cation-anion pair, with the anion not shown. The P—C bond lengths of 1.837(12) Å and 1.843(11) Å and the P—Cl bond distances of 1.993(6) Å and 1.947(7) Å bond length are consistent with those observed for phosphonium salts. The bond angles around phosphorus are essentially tetrahedral and exhibit only mirror distortions from idealized geometry. The tetrachloraluminate ion has Al—Cl distances ranging from 2.127(5) Å to 2.152(5) Å. The Cl—Al—Cl bond angles range from 107.9(2)° to 111.0(2)°. The chlorine atoms are "wagging" and are also probably disordered, as reflected by peaks on a final difference electron density map.

Structural Comparisons

Very little structural data has been reported for mixed valence phosphorus cations. The P—P bond distance of 2.191(1)Å for **1** can be compared with the methyl derivative reported by Burford (2.138(7) and 2.156(10) Å).[12] The P—P bond length of **1** is similar to the range of P—P distances, 2.165 Å–2.25 Å, reported.[16] The heptachlorodialuminate anion in **1** has been observed in a binuclear sandwich compound of palladium,[17] a π-complex of a cationic zirconium chloride cluster,[18] and as a gegen ion with a zintl ion of tellurium.[19] There is good agreement in the terminal and bridging Al—Cl bond distances with the aluminum anion in **1**. The Cl—Al—Cl bond angle of the palladium complex (115.6°) more closely resembles that observed for **1** than that of the Te_4^{2+} zintl ion (110.8°), although the chlorine atoms in the former anion are eclipsed, in contrast to the latter anion and those in **1**, which adopt staggered conformations. The principal coordination environment for the heptachlorodialuminate anion may be indirectly responsible for the discrepancy in the bond parameters. There appears to be little variation in the P—C and P—Cl bond lengths for the phosphonium ion in **2** compared with other structurally characterized organophosphonium ions.

CONCLUSIONS

The structural analyses of **1** and **2** confirm the conclusions drawn from the spectroscopic data, namely, that the tetraorganodiphosphorus cation **1** is formed from the initial generation of a transient phosphole cation, which undergoes rapid nucleophilic addition with a second equivalent of the chlorophosphole, whereas the phosphonium salt appears to result from an oxidation pathway. The latter reaction is unusual in that dialkylphosphonium salts are normally prepared by the action of strong Lewis acids (e.g. BCl_3, $SbCl_5$, PCl_5) on trichlorodiorganophosphoranes.[20] Schumann and coworkers have reported that t-Bu_2PCl and Al_2Cl_6 react in a 1:1 stoichiometry in methylene chloride and benzene to afford the adduct [t-$Bu_2PCl \cdot AlCl_3$], from a $^{31}P\{^1H\}$ NMR study.[21] We have observed this adduct also. However, it is one of several cationic phosphorus species in solution when half an equivalent of aluminum chloride reacts with the chlorophosphine. It is not unreasonable to suggest that **2** is formed from the addition of Cl^+ to t-Bu_2PCl via solvent or a solvent aluminum chloride adduct. The evidence is circumstantial, however, and the formation of **2** is an observation that warrants further study. The apparent lack of reactivity of **3** with Lewis acids can be reasonably understood in view of the strong electron withdrawing effect of the *bis*-carboranyl substituents. Future work will focus on phosphole cations stabilized by organometallic species.

EXPERIMENTAL

General Considerations

Standard glovebox, Schlenk and vacuum line techniques were employed for all manipulation of air and moisture-sensitive compounds. Reaction solvents were reagent grade and were distilled from appropriate drying agents under argon before use. Methylene chloride and hexane were dried over CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories or Aldrich. Aluminum chloride (99.99%), di-*t*-butylchlorophosphine, diphenylchlorophosphine were purchased from Aldrich and were used as received. The compound 5-chlorodibenzophosphole was prepared by literature methods.[22]

Physical Measurements

NMR spectra were obtained on Bruker AF 200, AM 360 and 500 MHz spectrometers. ^1H and ^{13}C chemical shifts for ^1H and ^{13}C NMR spectra were referenced to deuterated solvents as internal standards. Chemical shift values for ^{31}P spectra were referenced relative to external H_3PO_4 (0.00 ppm). Resonances observed upfield of the references were assigned negative chemical shift values in all cases. Chemical shift values for ^{27}Al spectra were referenced relative to external Al(*acac*)$_3$ (0.00 ppm). Electron impact (EI) mass spectra were obtained on an AEI Ltd. Model MS-902 sector filled double-focusing spectrometer, while xenon FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer.

Preparation of **1**

The compound 5-chlorodibenzophosphole was prepared by reaction of *o,o'*-dilithium biphenylate with PCl_3 excess in THF (69% yield). New characterization data: m.p. 58–60°C (lit.56°C).[22] ^1H NMR (359.9 MHz, CD_2Cl_2, 21°C): 6.00–8.00 (m, 8 H, Ar-H). $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2, 21°C): δ 58.1. MS (EI, 70 eV): m/e 218 (M^+, 47%), 183 (—Cl, 100%). Equivalent amounts of 5-chlorodibenzophosphole (0.99 g, 4.52 mmol) and aluminum chloride (0.08 g, 4.52 mmol) in CH_2Cl_2 (30 mL) at −78°C for several hours and slowly warmed to ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 3.02 g of **1** in 96% yield: m.p. 148–150°C (dec). The same product was observed when an excess amount of aluminum chloride was used. This compound is hygroscopic and should be stored in moisture-free environment. ^1H NMR (359.9 MHz, CD_2Cl_2, 21°C): δ 7.00–8.43 (m, 16 H, Ar-H). $^{13}C\{^1H\}$ NMR (90.56 MHz, CD_2Cl_2, 21°C) δ 115.6 (d, J = 97.8 Hz); 119.0 (d, J = 74.5 Hz), 123.3 (d, J = 12.4 Hz), 124.4 (d, J = 14.0 Hz), 126.2 (dd, J = 3.90 Hz), 130.2 (dd, J = 4.00 Hz), 131.4 (dd, J = 8.58 Hz), 131.6 (dd, J = 8.60 Hz), 132.1 (dd, J = 31.0 Hz, J = 15.5 Hz), 133.2 (dd, J = 12.4 Hz, J = 29.5 Hz), 133.5 (d, J = 7.80 Hz), 138.5 (d, J = 1.55 Hz), 139.1 (dd, J = 2.60 Hz, J = 16.3 Hz), 142.8 (d, J = 20.2 Hz), 144.8 (d, J = 28.0 Hz), 147.5 (d, J = 3.10 Hz). $^{27}Al\{^1H\}$ NMR (130.3 MHz, CD_2Cl_2, 21°C): δ 102.5 ($\omega_{1/2}$ = 846 Hz). $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2, 21°C): δ −23.3 (d, P(IV), $^1J|^{31}P^{31}P|$ = 389 Hz), −66.9 (d, P(III), $^1J|^{31}P^{31}P|$ = 389 Hz). MS (EI, 70 eV): m/e 704 (M^+, 4%), 402 ($-Al_2Cl_7$, 34%), 366 ($-Al_2Cl_8$, 100%). Correct C and H Analysis.

Preparation of **2**

Equivalent amounts of *t*-Bu_2PCl (2.50 g, 26.5 mmol) and Al_2Cl_6 (3.53 g, 13.3 mmol) in CH_2Cl_2 (50 mL) at −78°C for several hours and slowly warmed to ambient temperature with stirring. The mixture was allowed to stir overnight. After stirring for 24 h, the solvent was removed *in vacuo* to afford a colorless crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 3.60 g of **2** in 70% yield: mp 118–120°C. The same product was observed when an excess amount of aluminum chloride was used. A mixture of products was observed when 0.5 equivalent of Al_2Cl_6 was used, as determined from a ^{31}P NMR spectrum of the reaction mixture. This compound is hygroscopic and should be stored in moisture-free environment. ^1H NMR (359.9 MHz, CD_2Cl_2, 21°C): δ 1.64 (d, 18 H, *t*-Bu, $^1J|^1H^{31}P|$ = 24 Hz). $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2, 21°C); δ 26.87 (s, $\underline{C}H_3^-$); 49.15 (d, qC, $^1J|^{13}C^{31}P|$ = 24 Hz). $^{27}Al\{^1H\}$ NMR (130.3 MHz, CD_2Cl_2, 21°C): δ 102.9. $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2, 21°C): δ 81.0. MS (EI, 70 eV): m/e 384 (M^+, 12%), 281 ($-AlCl_3$, 56%), ($-AlCl_4$, 5%), ($-AlCl_5$, 100%). Correct C and H Analysis.

Preparation of **3**

A solution of *bis*-carborane (5.14 g, 17.9 mmol) in 150 mL of Et_2O was prepared and cooled to 0°C, with vigorous stirring. Two equivalents of a 2.5 M solution of *n*-BuLi (14.4 mL, 35.9 mmol) were slowly added (0.5 h). After the addition was complete, the reaction was stirred at 0°C for 4 h and the ether was removed *in vacuo* and replaced with 100 mL of dry benzene. The suspension was added to 10 equivalents of PCl_3 (31.3 mL, 359 mmol). The addition was completed in 1 h. The mixture was heated to reflux temperature and stirred overnight. Excess PCl_3 was removed by distillation at atmospheric pressure. The mixture was cooled and was then filtered to remove LiCl. The benzene filtrate was concentrated *in vacuo* to afford 5.91 g of **3** in a 94% yield. Compound **3** (2.90 g, 8.27 mmol) and Al_2Cl_6 (3.30 g, 12.3 mmol) were combined in CH_2Cl_2 (75 mL) at −78°C for 3 h, then slowly warmed to ambient temperature with stirring. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture indicated only the starting material. This compound is hygroscopic and should be stored in moisture-free environment. ^1H NMR (360.1 MHz, $CDCl_3$, 21°C): δ 0.70–3.80 (m, 20 H, B—H). ^{11}B (160.5 MHz, $CDCl_3$, 21°C): δ 0.48 (d, 2B, $^1J|^{11}B^1H|$ = 155 Hz), −4.00 (d, 2B, $^1J|^{11}B^1H|$ = 163 Hz), −6.90 (d, 4B, $^1J|^{11}B^1H|$ = 150 Hz), −9.86 (d, 2B, ^1J $|^{11}B^1H|$ = 172 Hz). $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$, 21°C); δ 92.25. MS (FAB): m/e 351 (M^+, 100%), 315 (−Cl, 5%). Correct C and H Analysis.

Preparation of **4**

Equivalent amounts of **3** (2.90 g, 8.27 mmol) and $AgSbF_6$ (2.84 g, 8.27 mmol) were combined in CH_2Cl_2 (60 mL) at −78°C for 3 h, then slowly warmed to ambient temperature with stirring. A precipitate of AgF was observed and was filtered. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture indicated the fluorinated product **4**. The filtrate was then concentrated *in vacuo* to afford 1.66 g of **4** in a 60% yield. This compound is corrosive and hygroscopic and should be stored in moisture-free environment. ^1H NMR (359.9 MHz, $CDCl_3$, 21°C): δ 0.80–4.00 (m, 20 H, B—H). $^{31}P\{^1H\}$ NMR (146 MHz, $CDCl_3$, 21°C): δ 23.76 (d, $^1J|^{31}P^{19}F|$ = 1148 Hz). MS (FAB): m/e 334 (M^+, 100%), 315 (−F, 38%). Correct C and H Analysis.

Collection and Reduction of X-Ray Data for **1**

A colorless parallelepiped, obtained from a methylene chloride/hexane solution, was sealed in a capillary and mounted on a Picker FACS-1 diffractometer constructed by Professor C. E. Strouse of UCLA. Unit cell parameters were determined from a least-squares fit of 49 accurately centered reflections ($9.49 < 2\theta < 20.49°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table VI. Data were collected at 128 K in the θ-2θ scan mode. Three intense reflections (0 1 −4, 0 2 2, 4 2 −4) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and fluctuated less than 1.1% during the course of the experiment (96.9 h). Of the 5211 unique reflections measured, 4401 were considered observed ($F^2 > 3\ \sigma\ (F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction. Programs used in this work include locally modified versions of crystallographic programs listed in Reference 23.

Solution and Refinement of the Structure of **1**

Atoms were located by use of direct methods. All calculations were performed on a VAX 3100 computer. All non-hydrogen atoms were refined with anisotropic parameters. All phenyl hydrogen atoms were in located positions as members of rigid groups, C—H = 1.0 Å, H—C—H = 120°. H atoms were assigned u values of 0.07 Å.[2] Scattering factors for H were obtained from Stewart, *et al.*[24] and for other atoms were taken from the International Tables for X-Ray Crystallography.[25] Anomalous dispersion terms were applied to the scattering of Cl and P. The maximum and minimum peaks on a final difference electron density map were 0.30 e $Å^{-3}$. Final positional and thermal parameters for non-hydrogen atoms are given in Table III.

Collection and Reduction of X-Ray Data for **2**

A colorless crystal, obtained from a hexane/methylene chloride solution, was sealed in a capillary and placed on a Picker FACS-1 diffractometer constructed by Professor C. E. Strouse of UCLA. Unit cell parameters were determined from a least-squares fit of 52 accurately centered reflections ($9.9 < 2\theta < 19.9°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table VI. Data were collected at 128 K in the θ-2θ scan mode. Three intense reflections (−1 2 −1, 0 −1 3, 2 − 1 0) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay and fluctuated less than 3% during the course of the experiment (52.9 h). Of the 2809 unique reflections measured, 2243 were considered observed ($F^2 > 2\sigma\ (F^2)$) and were used in the sub-

TABLE VI

Details of the crystallographic data collection for **1** and **2**

	1	**2**
T, °K	128	128
cryst size, mm	0.25 x 0.55 x 0.20	0.12 x 0.24 x 0.17
normal to faces	001, 100, 010	100, 01$\bar{1}$, 011
appearance	colorless parallelepiped	colorless parallelepiped
radiation (graphite monochromator)	MoKα	MoKα
wavelength, Å	0.7107	0.7107
space group	$P\bar{1}$	$P2_1$
a, Å	10.5798 (8)	7.2471 (8)
b, Å	11.3656 (9)	12.023 (2)
c, Å	13.8190 (11)	9.965 (1)
α, deg	107.985 (3)	—
β, deg	100.315 (2)	90.473 (3)
γ, deg	103.636 (2)	—
V, Å^3	1478	868
Z	2	2
ρ (calcd), g cm^{-3}	0.791	1.47
μ, cm^{-1}	.47	11.1
scan width		
below Kα_1	1.3	1.3
above Kα_2	1.6	1.6
scan rate deg min^{-1}	3.0	3.0
no. of unique rflns	5211	2809
no of observed $\left(F^2 > 3\sigma\left(F^2\right)\right)$ rflns	4401	2243
2Θ (max), deg	60	60
data collected	$+h, \pm k, \pm l$	$+h, +k, \pm l$
no. of parameters refined	205	163
R, R_w, GOF [a]	0.047, 0.069, 1.99	0.109, 0.121, 2.34

[a] $\mathrm{GOF} = \left[\sum w\left(|F_o| - |F_c|\right)^2 / (N_o - N_v)\right]^{1/2}$ where $w = 1/\left(\sigma^2|F_o|\right)$. $R = \sum\left||F_o| - |F_c|\right| / |F_c|$. $R_w = \left[\sum w\left(|F_o| - |F_c|\right)^2 / \sum w|F_o|^2\right]^{1/2}$.

sequent structure analysis. Data were corrected for Lorentz and polarization effects and extinction, but not for absorption. Other conditions for collection and reduction were the same as those that were applied to **1**.

Solution and Refinement of the Structure of **2**

Atoms were located by use of direct methods (SHELX86). All calculations were performed on a VAX 3100 computer. All non-hydrogen atoms were refined with anisotropic parameters. No hydrogen atoms were included for the butyl group. All hydrogen atoms were included in calculated positions as members of rigid groups, C—H = 1.0 Å, H—C—H = 109.5°. H atoms were assigned u values based approximately on the u value of the attached atom. Scattering factors for H were obtained from Stewart, *et al.*,[24] and for other atoms were taken from the International Tables for X-Ray Crystallography.[25] Anomalous dispersion terms were applied to the scattering of Al, Cl and P. The largest peak on a final difference electron density map was 0.9 e$\mathring{A}^{-3}$, located near Cl atoms of the anion. Final positional and thermal parameters for non-hydrogen atoms are given in Table V.

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Supplementary Material Available. Tables of positional and thermal parameters and complex interatomic distances and angles (10 pages); listings of observed and calculated structure factors (43 pages) will be deposited in the Cambridge Crystallographic Database.

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