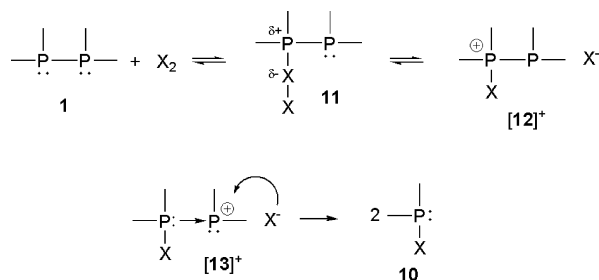
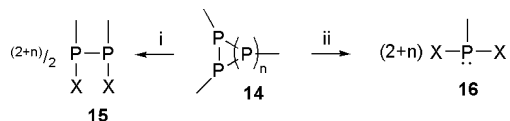
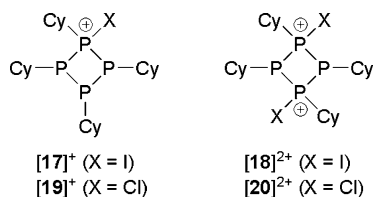


Scheme 3. Halogenation Reaction of Diphosphines via a Phosphinophosphonium Cation

Scheme 4. Halogenation Reaction of *cyclo*-Polyphosphines^a


^a (i) $(n+2)/2$ X_2 ; (ii) $(n+2)$ X_2 ($n = 1-4$).

Chart 1


the intermediate dihalodiphosphine **15** has been obtained from the reaction of Ph_5P_5 with 2.5 equiv of I_2 .¹⁵

Derivatives of the phosphino-halophosphonium cation $[12]^+$ have been previously isolated in conjunction with a weakly basic anion.^{1,16–20} In this context, the formation of phosphino-halophosphonium cations as intermediates in the halogenation reaction of polyphosphine has been exploited as a synthetic approach to *catena*-phosphinophosphonium cations by sequestering the product halide X^- into a complex anion. This is demonstrated by the reactions of tetracyclohexyl-*cyclo*-tetraphosphine (CyP)₄ with $PhICl_2$, PCl_5 or I_2 , in the presence of Me_3SiOTf or GaX_3 ($X = Cl, I$), which provide quantitative formation of salts containing the first *cyclo*-2-halo-1,3,4-triphosphino-2-phosphonium cations $[17]^+$ and $[19]^+$, and the first *cyclo*-2,4-dihalo-1,3-diphosphino-2,4-diphosphonium dication $[20]^{2+}$ (Chart 1). The new *cyclo*-phosphino-halophosphonium cation $[20]^{2+}$ can be considered as a phosphine–phosphenium donor–acceptor complex and undergoes ligand exchange reactions with PMe_3 or 1,2-bis(dimethylphosphino)ethane (dmpe) to effect dissociation

of the homocyclic framework and forming phosphinodiphosphonium cations and diphosphinodiphosphonium dications.

Experimental Section

General Considerations. All reactions were carried out in a dry box under an inert N_2 atmosphere. Dichloromethane and pentane were dried on an MBraun solvent purification system, degassed with three freeze–pump–thaw cycles, and stored under nitrogen and over molecular sieves prior to use. Acetonitrile (sure seal), phosphorus pentachloride, gallium(III) chloride, gallium(III) iodide, trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf), and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Sigma-Aldrich. Dichloriodobenzene ($PhICl_2$) and tetracyclohexyltetraphosphine (**2**) were prepared according to literature procedures.^{21,22} All new compounds (unless otherwise stated) were characterized by $^{31}P\{^1H\}$, including measurement of ^{31}P (non-decoupled) and $^{31}P-^{31}P$ DQF COSY. Measurements were performed at 25 °C. Bruker AVANCE 500 (^{31}P 202.46 MHz) and chemical shifts are referenced to $\delta_{H_3PO_4(85\%)} = 0.00$ and are reported in ppm; J values are reported in Hz. For compounds that give rise to higher order spin-systems in their $^{31}P\{^1H\}$ NMR spectra, the resolution-enhanced $^{31}P\{^1H\}$ spectra were transferred to the software program gNMR, version 5.0, by Cherwell Scientific.²³ After examining the line properties and noise, peak picking was performed. The full line-shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectra along with the assignment of all the peaks revealed in the resolution-enhanced spectra. The signs for the $^1J(^{31}P, ^{31}P)$ coupling constants were set negative and all other signs were obtained accordingly.^{24,25} Melting points were recorded on an electrochemical melting point apparatus in sealed capillary tubes under dinitrogen atmosphere and are uncorrected. Raman spectra were obtained for powdered and crystalline samples on a Bruker RFS 100 instrument equipped with a Nd:YAG laser (1064 nm). Chemical analyses were determined by Canadian Microanalytical Service LTD., Delta, BC, Canada.

Preparation of $[17][GaL_4] \cdot 1/2 CH_2Cl_2$. A solution of I_2 (5 mL, 0.05M, in CH_2Cl_2 ; 0.25 mmol) was added dropwise to a stirred solution of $(CyP)_4$ (114 mg, 0.25 mmol) and GaI_3 (113 mg, 0.25 mmol) in CH_2Cl_2 (8 mL). The reaction mixture was stirred at room temperature for 10 min, and the formation of the monocation was confirmed by ^{31}P NMR spectroscopy. The solvent was partially removed in vacuo (~ 5 mL), and the solution was filtered and layered with pentane (5 mL) and stored at -32 °C. Pale-yellow crystals of $[17][GaL_4] \cdot 1/2 CH_2Cl_2$ were obtained after 4 days. Data for $[17][GaL_4] \cdot 1/2 CH_2Cl_2$: Yield: 42% (122 mg, 0.11 mmol); m.p. 118–120 °C; Raman (300 mW, 25 °C, cm^{-1}): 2968 (18), 2933 (100), 2889 (39), 2867 (40), 2846 (57), 1439 (24), 1343 (17), 1297 (18), 1266 (16), 1187 (16), 1103 (12), 1076 (12), 1025 (27), 997 (15), 848 (18), 814 (21), 737 (20), 506 (17), 479 (18), 465 (17), 427 (20), 398 (28), 363 (16), 328 (15), 267 (37), 214 (36), 189 (34), 167 (31), 145 (87), 123 (34); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 300 K, [ppm]): -44.2 (2P, P_A), -31.1 (1P, P_M), 34.8 (1P, P_X , A_2MX spin system, $^1J_{AM} = -260$, $^1J_{MX} = -140$, $^2J_{AX} = -8$ Hz). Chemical analyses proved to be problematic for $[17][GaL_4] \cdot 1/2 CH_2Cl_2$ owing to the partial removal of solvents of crystallization upon isolation (Figure 1).

Reaction of **2 with $PhICl_2$ in the Presence of Me_3SiOTf .** A solution of freshly prepared $PhICl_2$ [(i) 75 mg, 0.275 mmol, in 5 mL CH_2Cl_2 ; (ii) 137 mg, 0.5 mmol, in 5 mL CH_2Cl_2] was added

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dropwise to a stirred solution of **2** (114 mg, 0.25 mmol) and Me₃SiOTf [(i) 45 μ L, 0.25 mmol; (ii) 90 μ L, 0.5 mmol] in CH₂Cl₂ (5 mL) at room temperature. The reaction was monitored by of ³¹P{¹H} NMR spectroscopy (Figure 2, i and ii).

Preparation of [23][GaCl₄]. A solution of GaCl₃ (88 mg, 0.5 mmol, in 8 mL CH₂Cl₂) was added dropwise to a stirred solution of PCl₅ (104 mg, 0.5 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred at room temperature for 10 min and stored at −32 °C. Clear, colorless needles of [23][GaCl₄] started to separate after 1 day. Data for [23][GaCl₄]: Yield: 95% (182 mg, 0.48 mmol); m.p. 308–310 °C; Raman (280 mW, 25 °C, cm^{−1}): 650 (16, ν_3 (F₂), PCl₄⁺), 455 (100, ν_1 (A₁), PCl₄⁺), 373 (2, ν_3 (F₂), GaCl₄[−]), 347 (61, ν_1 (A₁), GaCl₄[−]), 250 (74, ν_4 (F₂), PCl₄⁺), 178 (34, ν_2 (E), PCl₄⁺), 151 (35, ν_4 (F₂), GaCl₄[−]), 121 (39, ν_2 (E), GaCl₄[−]); ³¹P{¹H} NMR (CD₂Cl₂, 300 K, [ppm]): δ = 85.1 (s).

Reaction of **2 with PCl₅ in the Presence of GaCl₃.** A solution of freshly prepared PCl₅ (104 mg, 0.5 mmol, in 4 mL CH₂Cl₂) was added dropwise to a stirred solution of **2** (114 mg, 0.25 mmol) and GaCl₃ (176 mg, 1.0 mmol) in CH₂Cl₂ (5 mL) at room temperature. The reaction was monitored by ³¹P{¹H} NMR spectroscopy (Figure 3).

Preparation of [19][GaCl₄] and [20][Ga₂Cl₇]₂. A solution of PCl₅ [(i) 52 mg, 0.25 mmol, in 5 mL CH₂Cl₂; (ii) 104 mg, 0.5 mmol, in 8 mL CH₂Cl₂] was added dropwise to a stirred solution of (CyP)₄ (114 mg, 0.25 mmol) and GaCl₃ [(i) 44 mg, 0.25 mmol; (ii) 176 mg, 1.0 mmol] in CH₂Cl₂ (8 mL). The reaction mixture was stirred at room temperature for 10 min, and the formation of (i) [19]⁺ or (ii) [20]²⁺ was confirmed by ³¹P-NMR spectroscopy. The solvent was partially removed in vacuo (~5 mL), and the solution was layered with pentane (5 mL) and stored at −32 °C. Colorless crystals of [19][GaCl₄] or [20][Ga₂Cl₇]₂ formed after a few days. Data for [19][GaCl₄]: Yield: 60% (106 mg, 0.15 mmol); m.p. 119–122 °C; Raman (300 mW, 25 °C, cm^{−1}): 2939 (100), 2890 (49), 2850 (80), 1495 (14), 1442 (32), 1344 (20), 1298 (19), 1267 (21), 1190 (16), 1080 (12), 1025 (26), 1000 (17), 849 (22), 816 (18), 734 (22), 572 (20), 461 (24), 423 (30), 367 (28), 344 (43), 291 (25), 166 (37), 150 (37), 121 (44); ³¹P{¹H} NMR (CD₂Cl₂, 300 K, [ppm]): −54.4 (P, P_A), −40.7 (2P, P_M), 95.1 (1P, P_X, AM₂X spin system, ¹J_{AM} = −285, ¹J_{MX} = −126, ²J_{AX} = 18 Hz); elemental analysis for C₂₄H₄₄Cl₅GaP₄ (703.49): calcd C 41.0, H 6.3; found: C 41.3, H 6.4. Data for [20][Ga₂Cl₇]₂: Yield: 90% (293 mg, 0.23 mmol); m.p. 106–109 °C; Raman (300 mW, 25 °C, cm^{−1}): 2944 (100), 2900 (360), 2859 (50), 1442 (18), 1342 (13), 1299 (9), 1290 (10), 1266 (12), 1192 (13), 1176 (12), 1106 (5), 1080 (7), 1022 (20), 993 (14), 843 (15), 800 (7), 743 (8), 720 (11), 592 (14), 471 (8), 420 (20), 369 (68), 357 (18), 287 (17), 262 (10), 234 (10), 212 (12), 191 (19), 166 (26), 138 (54); ³¹P{¹H} NMR (CD₂Cl₂, 300 K, [ppm]): 9.3 (2P, P_A), 83.2 (2P, P_X, A₂X₂ spin system, ¹J_{AX} = −288); elemental analysis for C₂₄H₄₄Cl₁₆Ga₄P₄ (1302.64): calcd C 22.1, H 3.4; found: C 22.1, H 3.6.

Preparation of [24][GaCl₄]. Method A: A solution of PCl₅ (104 mg, 0.50 mmol, in 8 mL CH₂Cl₂) was added dropwise to a stirred solution of [20][Ga₂Cl₇]₂ (130 mg, 0.10 mmol) in CH₂Cl₂ (4 mL). The reaction mixture was stirred at room temperature for 5 h. The solvent was partially removed in vacuo (~5 mL), the solution was layered with pentane (5 mL) and stored at −32 °C. Method B: To solution of **2** (91 mg, 0.20 mmol) and GaCl₃ (144 mg, 0.80 mmol) in CH₂Cl₂ (5 mL) was slowly added a solution PCl₅ (332 mg, 1.60 mmol) in CH₂Cl₂ (6 mL) at room temperature. The solvent was partially removed in vacuo (~5 mL), the solution was layered with pentane (5 mL) and stored at −32 °C. For both cases, colorless crystals of [24][GaCl₄] were formed within two days. Data for [24][GaCl₄]: Yield: 74% (160 mg, 0.37 mmol, method A); quantitative (method B); m.p. 96–98 °C; Raman (300 mW, 25 °C, cm^{−1}): 2959 (61), 2908 (25), 2872 (66), 2860 (65), 1515 (14), 1447 (48), 1351 (22), 1328 (17), 1296 (27), 1283 (20), 1268 (24), 1208 (17), 1179 (17), 1079 (17), 1027 (24), 1000 (21), 846 (22), 819 (27), 760 (24), 632 (29), 549 (52), 488 (55), 432 (41), 369 (31), 344 (100), 336 (83), 308 (44), 223 (54), 204 (61), 173 (37), 151

(55), 120 (84); ³¹P{¹H} NMR (CD₂Cl₂, 300 K, [ppm]): δ = 127.2 (s); elemental analysis for C₆H₁₁Cl₇GaP (432.02): calcd C 16.7, H 2.6; found: C 16.5, H 2.6.

Preparation of [27][GaCl₄]. To a cooled solution (0 °C) of PMe₃ (0.52 M in toluene, 1 mL, 0.52 mmol) in CH₂Cl₂ (5 mL) was added a solution of [20][Ga₂Cl₇]₂ (169 mg, 0.13 mmol) in CH₂Cl₂ (2 mL) within 2 min. After 15 min the reaction mixture was allowed to warm to room temperature and stirred for a further 24 h. The oily phase was separated and dissolved in MeCN (1.5 mL). The MeCN solution was under-layered with CH₂Cl₂ and stored at −20 °C. After four days, [27][GaCl₄]₂ was obtained as block shaped crystals. Data for [27][GaCl₄]₂: Yield: 35% (73 mg); ³¹P{¹H} NMR (CD₃CN, 300 K, [ppm]): only one diastereomer observed, broad signals, δ = −33.1 (AA') and 19.2 (XX'); elemental analysis for C₁₈H₄₀Cl₈Ga₂P₄ (803.48): calcd C 26.9, H 5.0; found: C 27.2, H 5.3.

Preparation of [29][GaCl₄]₂. A solution of dmpe (41.7 μ L, 37.5 mg, 0.25 mmol) in CH₂Cl₂ (3 mL) was added dropwise within 30 min to a cooled (0 °C) solution of [20][Ga₂Cl₇]₂ (163 mg, 0.125 mmol) in CH₂Cl₂ (10 mL). After warming to room temperature, the formed precipitate was separated and washed with hexane (2 $\times$ 6 mL). The precipitate was dissolved in MeCN (3 mL), carefully under-layered with CH₂Cl₂ (5 mL), and stored at −20 °C. Colorless crystals of [29][GaCl₄]₂ were formed within three days. Data for [29][GaCl₄]₂: Yield: 85% (146 mg, 0.21 mmol); m.p. 146–148 °C; Raman (300 mW, 25 °C, cm^{−1}): 2990 (34), 2943 (48), 2924 (49), 2908 (100), 2859 (25), 1444 (20), 1395 (21), 1342 (16), 1300 (17), 1261 (18), 1192 (17), 1022 (18), 997 (17), 845 (19), 804 (20), 770 (21), 743 (22), 729 (23), 651 (33), 453 (34), 421 (33), 369 (−44), 348 (66), 320 (31), 247 (39), 218 (39), 179 (37), 149 (45), 120 (42); ³¹P{¹H} NMR (CD₃CN, 300 K, [ppm]): −68.8 (1P, -P-P_A-P-), 50.0 (2P, -P_X-P-P_X-, AX₂ spin system, ¹J_{AX} = −293); elemental analysis for C₁₂H₂₇Cl₈Ga₂P₃ (687.33): calcd C 21.0, H 4.0; found: C 21.4, H 4.2.

Formation of a Mixture of [29][GaCl₄]₂ and [30][GaCl₄]₂. A solution of [20][Ga₂Cl₇]₂ (163 mg, 0.125 mmol) in CH₂Cl₂ (2 mL) was added all at once at room temperature to a solution of dmpe (41.7 μ L, 37.5 mg, 0.25 mmol) in CH₂Cl₂ (3 mL). The immediate formation of an oil was observed. The oily phase was separated and dissolved in MeCN (3 mL), and the formed precipitate (Cy₄P₄) separated. To the clear solution was added CH₂Cl₂ (5 mL) and an approximate 1:1 mixture (as shown by ³¹P{¹H} NMR) of compound [29][GaCl₄]₂ and [30][GaCl₄]₂ was obtained as a precipitate. Data for [29][GaCl₄]₂ and [30][GaCl₄]₂: Yield: 125 mg; ³¹P{¹H} NMR (CH₃CN, C₆D₆ Capillary, 300 K, [ppm]): [29][GaCl₄]₂: δ = −68.8 (1P, -P-P_A-P-), 50.0 (2P, -P_X-P-P_X-, AX₂ spin system, ¹J_{AX} = −293); [30][GaCl₄]₂: δ = −55.9 (2P, -P-P_A-P-), 18.8 (2P, -P_X-P-P-P_X-, AA'XX' spin system, ¹J_{AX} = ¹J_{AX'} = −315, ²J_{AA'} = 151, ²J_{AX'} = ²J_{AX} = 18, ³J_{XX'} = −9 Hz).

Crystal Structures. Suitable single crystals for all compounds were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. X-ray diffraction data for **2**²⁶ and [29][GaCl₄]₂ were collected on a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) with a scan width of 0.3° and 7 s for **2**, and 5 s for [29][GaCl₄]₂ exposure times. In both cases generator settings were 50 kV and 180 mA. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction (SAINT)²⁷ and correction (SADABS)²⁸ was performed with the Bruker software. X-ray diffraction data for [17][GaCl₄] $\cdot$ 1/2CH₂Cl₂, [19][GaCl₄], [20][Ga₂Cl₇]₂, [23][GaCl₄], [24][GaCl₄], and [27][GaCl₄]₂ were collected on a Rigaku RAXIS RAPID diffractometer with a imaging plate area detector (graphite-monochromated Mo K α radiation, λ = 0.71073 Å). Crystals were mounted under fluorolube on the tip of 150 μ m micromounts. The data were

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Table 1. Crystallographic Data

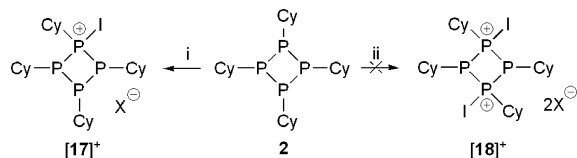
	2	[17][GaI ₄] · 1/2 CH ₂ Cl ₂	[19][GaCl ₄]	[20][Ga ₂ Cl ₇] ₂
formula	C ₂₄ H ₄₄ P ₄	C _{24.5} H ₄₅ ClP ₄ GaI ₅	C ₂₄ H ₄₄ Cl ₅ P ₄ Ga	C ₂₄ H ₄₄ Cl ₁₆ P ₄ Ga ₄
<i>M_r</i> [g mol ^{−1}]	456.47	1203.22	703.49	1302.63
dimension [mm ³]	0.16 × 0.13 × 0.13	0.27 × 0.19 × 0.16	0.29 × 0.27 × 0.21	0.27 × 0.14 × 0.06
color, habit	colorless block	yellow pinacoid	colorless block	colorless needle
crystal system	tetragonal	triclinic	monoclinic	orthorhombic
space group	<i>P</i> 4 ₂ <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> bca
<i>a</i> [Å]	10.1235(2)	10.5502(3)	18.491(9)	17.8070(4)
<i>b</i> [Å]	10.1235(2)	13.5437(5)	9.143(9)	17.9537(3)
<i>c</i> [Å]	12.4110(5)	13.9971(5)	19.970(5)	31.5222(8)
α [deg]	90	101.395(2)	90	90
β [deg]	90	93.704(1)	104.27(5)	90
γ [deg]	90	99.350(2)	90	90
<i>V</i> [Å ³]	1271.94(6)	1924.9(1)	3272(5)	10077.7(4)
<i>Z</i>	2	2	4	8
<i>T</i> [K]	153(1)	123(2)	123(2)	123(2)
ρ _c [g cm ^{−3}]	1.192	2.076	1.428	1.717
<i>F</i> (000)	496	1130	1456	5152
λ _{MoKα} [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm ^{−1}]	0.306	4.976	1.458	3.109
absorption correction	multi-scan	multi-scan	none	multi-scan
reflections collected	13577	96666	79803	86025
reflections unique	981	11152	6680	36726
<i>R</i> _{int}	0.0251	0.026	0.115	0.031
reflection obs. [<i>F</i> > 3σ(<i>F</i>)]	955	9830	5249	21819
residual density [e Å ^{−3}]	0.249, −0.123	2.33, −1.74	1.12, −0.66	1.42, −0.79
parameters	65	472	352	477
GOF	1.112	1.077	1.000	0.970
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0213	0.0258	0.0590	0.0478
w <i>R</i> ₂ (all data)	0.0583	0.0305	0.0589	0.0593
CCDC	745539	745543	745537	745538

	[23][GaCl ₄]	[24][GaCl ₄]	[27][GaCl ₄] ₂	[29][GaCl ₄] ₂
formula	Cl ₈ GaP	C ₆ H ₁₁ Cl ₁₇ GaP	C ₁₈ H ₄₀ Cl ₈ Ga ₂ P ₄	C ₁₂ H ₂₇ Cl ₈ Ga ₂ P ₃
<i>M_r</i> [g mol ^{−1}]	384.32	432.02	803.47	687.29
dimension [mm ³]	0.38 × 0.19 × 0.17	0.25 × 0.12 × 0.08	0.26 × .25 × 0.22	0.14 × .11 × 0.09
color, habit	colorless needle	colorless needle	colorless needle	colorless block
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> bcm	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> ca2 ₁
<i>a</i> [Å]	6.1146(3)	8.783(2)	9.740(2)	12.2913(3)
<i>b</i> [Å]	13.514(1)	13.740(3)	12.396(3)	14.9034(5)
<i>c</i> [Å]	13.792(1)	26.02(1)	28.660(7)	14.9881(6)
α [deg]	90	90	90	90
β [deg]	90	91.96(2)	90.19(1)	90
γ [deg]	90	90	90	90
<i>V</i> [Å ³]	1139.7(1)	3137(2)	3460.6(2)	2727.1(2)
<i>Z</i>	4	4	4	4
<i>T</i> [K]	123(2)	123(2)	123(2)	153(1)
ρ _c [g cm ^{−3}]	2.240	1.829	1.542	1.674
<i>F</i> (000)	728	1696	1624	1368
λ _{MoKα} [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm ^{−1}]	4.361	3.015	2.368	2.935
absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
reflections collected	8903	17765	48724	12814
reflections unique	1656	7802	7909	3810
<i>R</i> _{int}	0.030	0.040	0.101	0.0328
reflection obs. [<i>F</i> > 3σ(<i>F</i>)]	1397	6005	6752	3512
residual density [e Å ^{−3}]	0.72, −0.97	1.22, −0.78	1.75, −1.29	0.634, −0.533
parameters	52	294	290	231
GOF	1.098	1.114	1.089	1.026
<i>R</i> ₁ [<i>I</i> > 3σ(<i>I</i>)]	0.0338	0.0386	0.0662	0.0259
w <i>R</i> ₂ (all data)	0.0376	0.0427	0.1876	0.0579
CCDC	745544	745541	745540	745542

collected using sweeps of ω oscillations. After data reduction, equivalent reflections were merged. Intensity data were corrected for Lorentz, absorption and polarization effects. For further crystal and data collection details, see Table 1. The structures were solved by direct methods and expanded Fourier techniques. Full matrix least-squares refinement was carried out with the program

SHELXS97²⁹ against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were generated with idealized geometries and isotropically refined

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Scheme 5. Preparation of $[17][Ga_4]$ and Attempted Preparation of $[18][Ga_4]_2$ ($X = Ga_4$, OTf) Salts^a^a (i) I_2 , GaI_3 , or $AgOTf$ in CH_2Cl_2 ; (ii) $2I_2$, $2GaI_3$, or $2AgOTf$ in CH_2Cl_2 .**Table 2.** $^{31}P\{^1H\}$ NMR Parameters for Salts of Cations $[17]^+$, $[19]^+$, $[20]^{2+}$, $[27]^{2+}$, $[29]^{2+}$, and $[30]^{2+}$

	$[17]^+$	$[19]^+$	$[20]^{2+}$	$[27]^{2+}$	$[29]^{2+}$	$[30]^{2+}$
spin system ^{a,b}	A_2MX	AM_2X	A_2X_2	$AA'XX'$	AX_2	$AA'XX'$
δ_A^c	−44.2	−54.4	9.3	−33.1	−68.8	−55.9
δ_M	−31.1	−40.7				
δ_X	34.8	95.1	83.2	19.2	50.0	18.8
$^1J_{AM}^d$	−260	−285				
$^1J_{MX}$	−140	−126				
$^2J_{AX}$	−8	18				
$^1J_{AX}, ^1J_{AA'}$			−288	− ^e	−293	−315, −151
$^2J_{AX'}, ^3J_{XX'}$				− ^e		18, −9

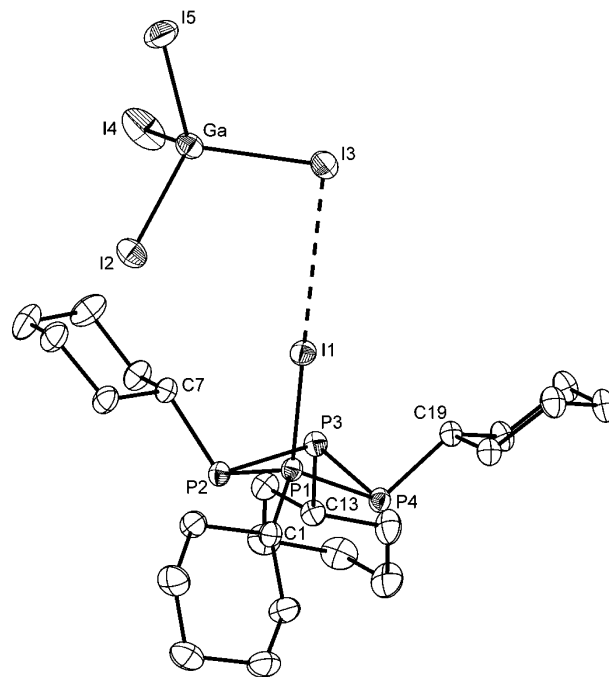
^a Furthest downfield resonance is denoted by the highest letter in the alphabet, and the furthest upfield by the lowest letter. By convention the letter in the spin system is determined by the ratio $\Delta\delta(P_iP_{ii})/J_{P_iP_{ii}} > 10$ (resonance considered to be pseudo-first order and the assigned letters are separated) < 10 (consecutive letters are assigned). ^b Parameters for spin systems of higher order are derived by iterative fitting of experimental data at 300 K. ^c Absolute signs of the $^1J_{PP(iso)}$ have been tentatively assigned to be negative. ^d Chemical shifts (δ) are given in [ppm] and coupling constants (J) in [Hz]. ^e Could not be simulated due to broad signals.

using a riding model. For $[27][GaCl_4]_2$ the crystal was a twin (twin law 1 0 0, 0 −1 0, 0 0 −1) with not quite equal components (0.509:0.491). For compounds $[17][GaCl_4] \cdot 1/2CH_2Cl_2$, $[19][GaCl_4]$, $[20][Ga_2Cl_7]_2$, $[23][GaCl_4]$, $[24][GaCl_4]$, and $[27][GaCl_4]_2$ the calculations were performed using the CrystalStructure crystallographic software package.^{30,31}

Results and Discussion

The halonium addition reaction that occurs when a phosphine reacts with a dihalogen has been extrapolated to polyphosphines to provide a new synthetic approach to phosphinophosphonium cations. The $^{31}P\{^1H\}$ NMR spectra of reaction mixtures containing $(CyP)_4$ (**2**), I_2 and GaI_3 in CH_2Cl_2 solution (Scheme 5) show three resonances in a first order A_2MX spin pattern with relative intensities of 2:1:1. The data are summarized in Table 2 and are consistent with the formation of the monocation $[17]^+$ (Chart 1). Chemical shifts at higher field correspond to the phosphine centers ($\delta_A = -44.2$ and $\delta_M = -31.1$ ppm) and the low field shift ($\delta_A = 34.8$ ppm) corresponds to the phosphonium center, in accordance with those for previously reported phosphinophosphonium cations.^{1,17,32} Compound $[17][Ga_4]$ was isolated as extremely air- and moisture-sensitive yellow blocks in moderate yields (42 %) as a CH_2Cl_2 solvate.

The solid state structure of $[17][Ga_4] \cdot 1/2 CH_2Cl_2$ has been determined by X-ray crystallography and a view of the cation and anion in the solid state is shown in Figure 1. Selected

**Figure 1.** ORTEP plot of the molecular structure of the cation and anion in $[17][GaCl_4] \cdot 1/2CH_2Cl_2$. Thermal ellipsoids with 50% probability (hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths (Å) and angles (°) are included in Table 2.**Table 3.** Selected Structural Parameters for **2** and Cations $[17]^+$, $[19]^+$, and $[20]^{2+}$

	2	$[17]^+$ ($X = I$)	$[19]^+$ ($X = Cl$)	$[20]^{2+}$ ($X = Cl$)
Bond Lengths [Å]				
P1–P2 ^a	2.2224(5)	2.1872(8)	2.185(1)	2.1999(8)
P2–P3		2.2386(7)	2.2411(8)	2.2004(8)
P3–P4		2.2400(7)	2.2478(9)	2.2077(8)
P4–P1 ^a	2.2224(5)	2.1919(8)	2.1857(8)	2.2084(8)
P1–X		2.4041(5)	2.011(1)	1.9828(9)
P3–X				1.9832(8)
P1–C1	1.868(1)	1.838(2)	1.814(2)	1.820(2)
P2–C7		1.864(2)	1.864(2)	1.865(2)
P3–C13		1.872(2)	1.873(2)	1.791(2)
P4–C19		1.863(2)	1.863(2)	1.867(2)
Bond Angles [deg]				
P1–P2–P3 ^a	85.271(9)	84.03(2)	83.71(3)	80.55(2)
P2–P3–P4		86.97(2)	88.71(3)	94.60(3)
P3–P4–P1		83.89(2)	83.52(3)	80.21(2)
P4–P1–P2		89.46(3)	91.79(3)	94.59(3)
P2–P1–C1	102.55(5)	113.29(7)	115.3(1)	110.83(8)
P4–P1–C1		115.26(7)	115.32(8)	114.21(8)
P1–P2–C7	102.81(5)	105.78(7)	103.97(9)	105.15(8)
P1–P4–C19		104.73(8)	105.51(8)	106.27(9)
P2–P3–C13		100.70(7)	98.37(8)	111.47(8)
P4–P3–C13		100.86(7)	100.35(9)	112.68(8)
P2–P1–X		113.79(2)	113.74(4)	113.34(3)
P4–P1–X		114.57(2)	113.46(3)	112.41(3)
P2–P3–X				113.96(3)
P4–P3–X				112.91(3)
C1–P1–X		113.79(2)	107.44(9)	110.64(9)
C13–P3–X				110.45(9)

^a For **2** P1 = P3, P2 = Pⁱ, P4 = Pⁱⁱ, symmetry code: (i) $y - 1, -x + 1, -z + 2$; (ii) $-y + 1, x + 1, -z + 2$.

structural parameters are listed in Table 3 along with comparative parameters for the *cyclo*-tetraphosphine **2**. Consistent with the structural features of $[MeCy_4P_4]^+$,⁴ the cyclohexyl substituent at P1 in $[17]^+$ minimizes the steric interactions by twisting to enable a *gauche* conformation of the α -hydrogen atom of C1 and the iodine substituent.⁴ The P–P bonds at the four-

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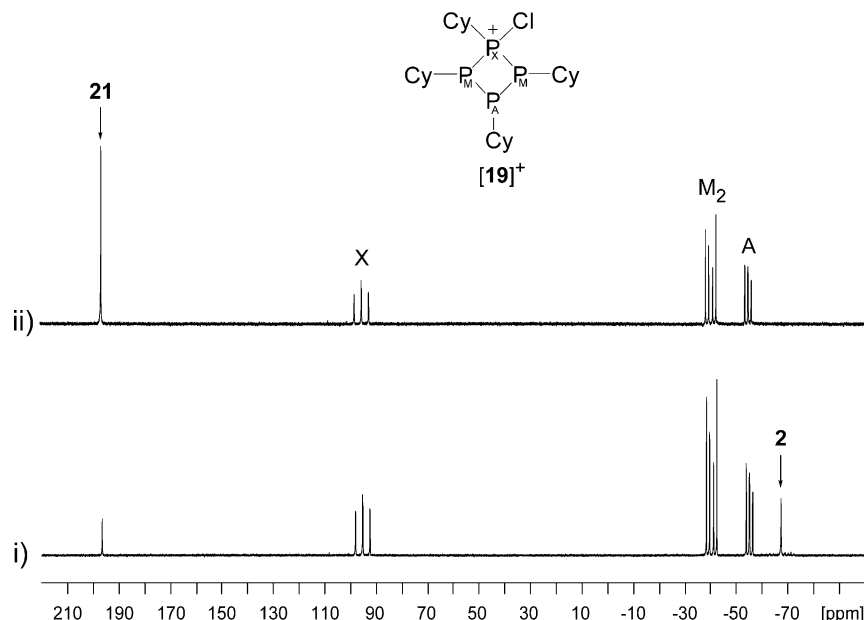
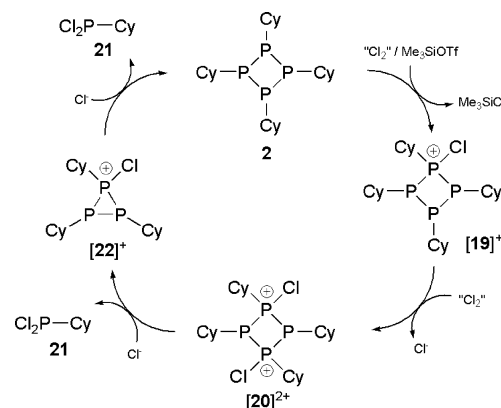


Figure 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of $(\text{CyP})_4$ with PhICl_2 in the presence of Me_3SiOTf at RT in CH_2Cl_2 ; (i) ~ 1.1 equiv of PhICl_2 ; (ii) 2 equiv of PhICl_2 .

coordinate phosphorus centers are slightly shorter than those involving the three-coordinate phosphorus centers. Moreover, the shortest P–C bond occurs at the phosphonium center. The P_4 ring is slightly more puckered than that in $[\text{MeCy}_4\text{P}_4]^+$, as indicated by greater P–P–P–P torsion angles ranging from $23.6\text{--}24.2^\circ$ (vs. $28.9\text{--}29.6^\circ$). The iodine atom at the phosphonium center has a weak interaction with an iodine of the gallate anion ($3.635(3)\text{ \AA}$), resulting in an almost linear P1–I1–I3 unit ($168.37(2)^\circ$). The P–I bond length ($2.4041(5)\text{ \AA}$) is typical ($2.40 \pm 0.01\text{ \AA}$),^{11,12,33} indicating that $[\mathbf{17}]\text{GaI}_4$ should be considered as an ionic compound. Attempts to prepare the dication $[\mathbf{18}]^{2+}$, by treatment of **2** with 2 equiv of I_2 and GaI_3 or AgOTf , leads to the formation of copious amounts of an orange precipitate, found to be completely insoluble in CH_2Cl_2 , CH_3CN , and $\text{C}_6\text{H}_5\text{F}$ (Scheme 5). We abstained from a detailed investigation of the precipitate.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction mixtures containing $(\text{CyP})_4$ (**2**), PhICl_2 and Me_3SiOTf in CH_2Cl_2 are summarized in Figure 2. Reaction mixtures involving an slight excess (1.1 equiv) of PhICl_2 exhibit an AM_2X spin system that is assigned to $[\mathbf{19}]^+$ (Table 2). The presence of $(\text{CyP})_4$ ($\delta = -67.0\text{ ppm}$)³⁴ and CyPCl_2 (**21**, $\delta = -192.0\text{ ppm}$)³⁵ in this reaction mixture is significant as the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a reaction of **2** with 2 equiv of PhICl_2 in the presence of 2 equiv of Me_3SiOTf (Figure 2(ii)) shows only the presence of $[\mathbf{19}]^+$ and CyPCl_2 (**21**). We interpret these observations according to Scheme 6, which shows the initial chloronium addition to **2** to give $[\mathbf{19}]^+$ followed by a second addition to give the dication $[\mathbf{20}]^{2+}$. The dication is not observed implying fast nucleophilic attacks by Cl^- at the phosphonium centers to first displace cation $[\mathbf{22}]^+$ and **21**. Under these reaction conditions, we speculate that cation $[\mathbf{22}]^+$ undergoes a further and rapid³⁶ nucleophilic attack by Cl^- to

Scheme 6. Proposed Pathway for Reaction of **2** with PhICl_2 in the Presence of Me_3SiOTf



give **21** and $[\text{CyP}=\text{PCy}]$,³⁷ which dimerizes to give **2**. The characteristic A_2B pattern corresponding to $(\text{CyP})_3$ ³⁸ was not observed in the chlorination reactions in contrast to the ring contraction of $[\text{MeCy}_4\text{P}_4]^+$, which is observed on reaction with PMe_3 to yield $(\text{CyP})_3$ and the phosphinophosphonium cation $[\text{Me}_3\text{P}=\text{PCy}]^+$.⁴

Chloronium addition to $(\text{CyP})_4$ is also effected by reaction with PCl_5 and GaCl_3 in CH_2Cl_2 . Reaction mixtures of various stoichiometries have been monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at room temperature as summarized in Figure 3. In the absence of PCl_5 (Figure 3, $\text{X} = 0$ equiv), the two broad signals ($\delta = -43$ and -62 ppm) are indicative of a weak adduct between $(\text{CyP})_4$ and GaCl_3 which dissociates in solution. Introduction of a solution of PCl_5 in CH_2Cl_2 results in the formation of the tetrachlorophosphonium salt $[\mathbf{23}][\text{GaCl}_4]$, as shown in Scheme 7a, which reacts with $(\text{CyP})_4$ to give $[\mathbf{19}]^+$ (AM_2X spin system, Table 2) and PCl_3 ($\delta = -220.1\text{ ppm}$; X

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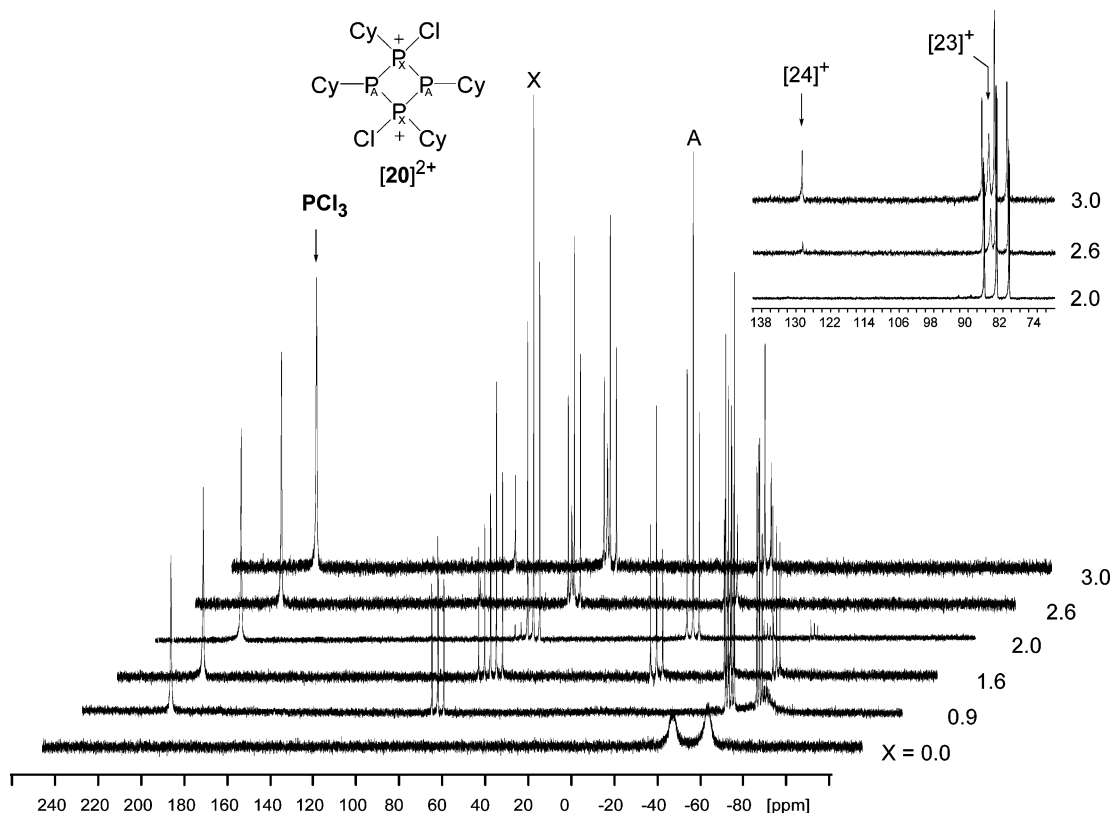
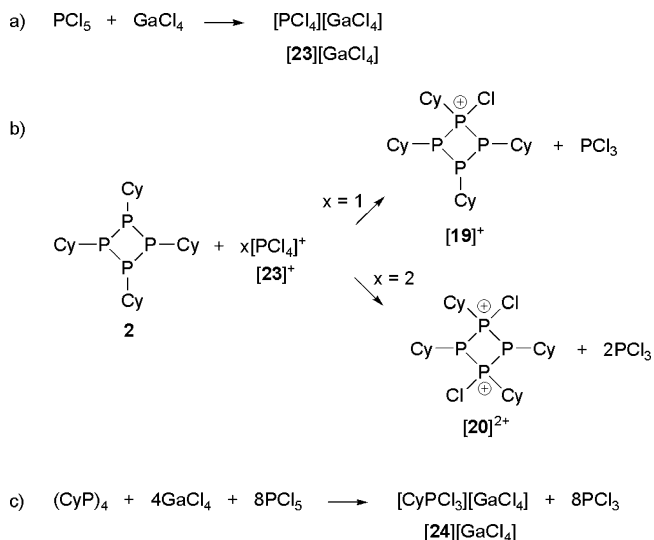


Figure 3. $^{31}\text{P}\{\text{H}\}$ NMR spectra (CH_2Cl_2 , C_6D_6 capillary, RT) of the stepwise chlorination reaction of **2** with PCl_5 in the presence of GaCl_3 according to Scheme 7; X = 0–3 equiv of PCl_5 .

Scheme 7. Successive Chlorination of (CyP)₄ with [PCl₄]⁺



= 1 equiv).³⁹ A high concentration of PCl_5 and GaCl_3 in solution leads to the crystallisation of $[\mathbf{23}][\text{GaCl}_4]$ as colorless needles.

The binary tetrachlorophosphonium cation $[23]^+$ has been known for some time and was characterized by vibrational⁴⁰ and ^{31}P NMR⁴¹ spectroscopic studies, as well as by crystal structure determinations with a large combination of several counter-anions.⁴² However, to the best of our knowledge, an X-ray determination of $[23]^+$ as the tetrachlorogallate salt has not been reported. Compound $[23][\text{GaCl}_4]$ crystallizes in the orthorhombic space group *Pbca* with four molecular units in the unit cell (Figure 4). The structure is isotypical with $[\text{PCl}_4][\text{FeCl}_4]$.⁴³ The cation displays an almost perfect tetrahedral

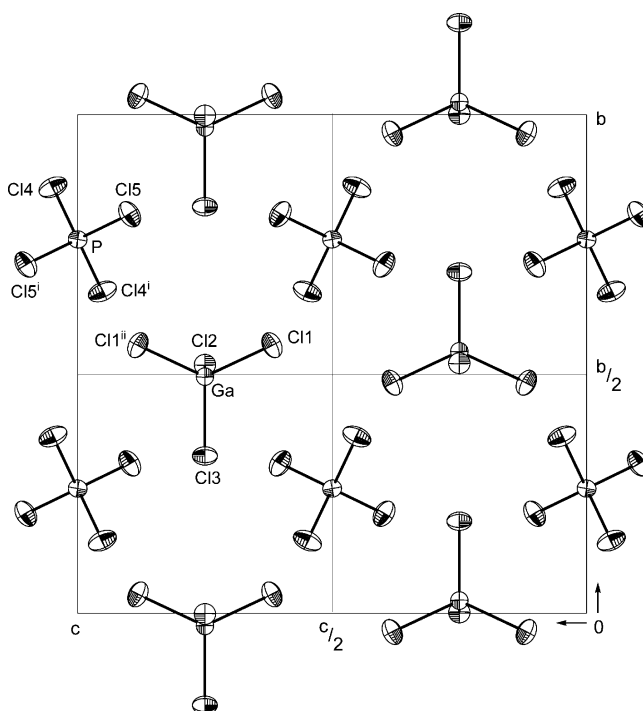


Figure 4. ORTEP plot of the perspective view of the unit cell of [23][GaCl₄] perpendicular to the *bc* plane. Thermal ellipsoids with 50% probability at 123(2) K [symmetry code: (i) *x*, 0.5 − *y*, −*z*; (ii) *x*, *y*, 0.5 − *z*].

geometry, whereas the anion is significantly distorted, exhibiting Cl–E–Cl angles between 108.69(2) and 113.47(2)° ([GaCl₄][−]) and between 108.43(5) and 110.38(3)° ([PCl₄]⁺). This trend is

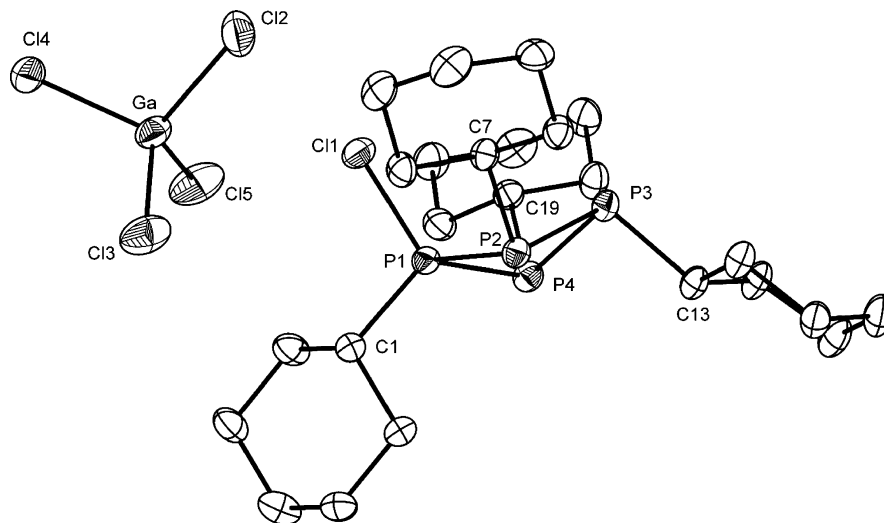


Figure 5. ORTEP plot of the molecular structure of $[19][\text{GaCl}_4]$. Thermal ellipsoids with 50% probability at 123(2) K (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) are included in Table 2.

also reflected by the Ga–Cl distances varying from 2.1704(7) to 2.1867(9) Å, whereas the P–Cl bond lengths are within the limits and are almost identical (1.9285(8) and 1.9302(9) Å). The molecular structure of $[23][\text{GaCl}_4]$ shows short interatomic $\text{Cl}\cdots\text{Cl}$ distances in the range of 3.338(2) to 3.470(2) Å between the $[\text{PCl}_4]^+$ and $[\text{GaCl}_4]^-$ units, which are shorter than the sum of the van der Waals radii (3.50 Å),⁴⁴ indicating weak cation $\cdots$ anion interactions.

Two triplets, assigned to $[20]^{2+}$, are observed when the stoichiometry of PCl_4^+ exceeds that of $(\text{CyP})_4$ (Table 2; Scheme 7b, Figure 3, X = 2 equiv). The cations $[19]^+$ and $[20]^{2+}$ are resilient in this reaction mixture due to the absence of chloride anion. Addition of excess PCl_5 leads to appearance of two singlets attributed to $[23]^{+41}$ ($\delta = 85.1$ ppm) and $[24]^+$ ($\delta = 127.2$ ppm). Cation $[24]^+$ represents the final chlorination product of **2** when 8 equiv of PCl_5 are added (Scheme 7c). Equimolar reaction mixtures of $(\text{CyP})_4$, GaCl_3 , and PCl_3 in CH_2Cl_2 at room temperature have enabled isolation of $[19][\text{GaCl}_4]$. Similarly, $[20][\text{Ga}_2\text{Cl}_7]_2$ has been isolated from the 1:4:2 reaction of $(\text{CyP})_4$, GaCl_3 , and PCl_3 in CH_2Cl_2 (Scheme 7b). Both compounds were obtained as colorless needles. A view of the molecular units of $[19][\text{GaCl}_4]$ and $[20][\text{Ga}_2\text{Cl}_7]_2$ is shown in Figures 5 and 6, respectively, and structural parameters are listed in Table 3.

The structural features of $[19][\text{GaCl}_4]$ are comparable with those discussed for $[17]\text{GaI}_4 \cdot 1/2 \text{CH}_2\text{Cl}_2$. The solid state structure of $[20][\text{Ga}_2\text{Cl}_7]_2$ contains a symmetric (approximate C_{2v}) cation $[20]^{2+}$ consistent with the A_2X_2 spin system observed in the solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The P–P bond lengths in $[20]^{2+}$ are essentially identical [2.1999(8) to 2.2084(8) Å]

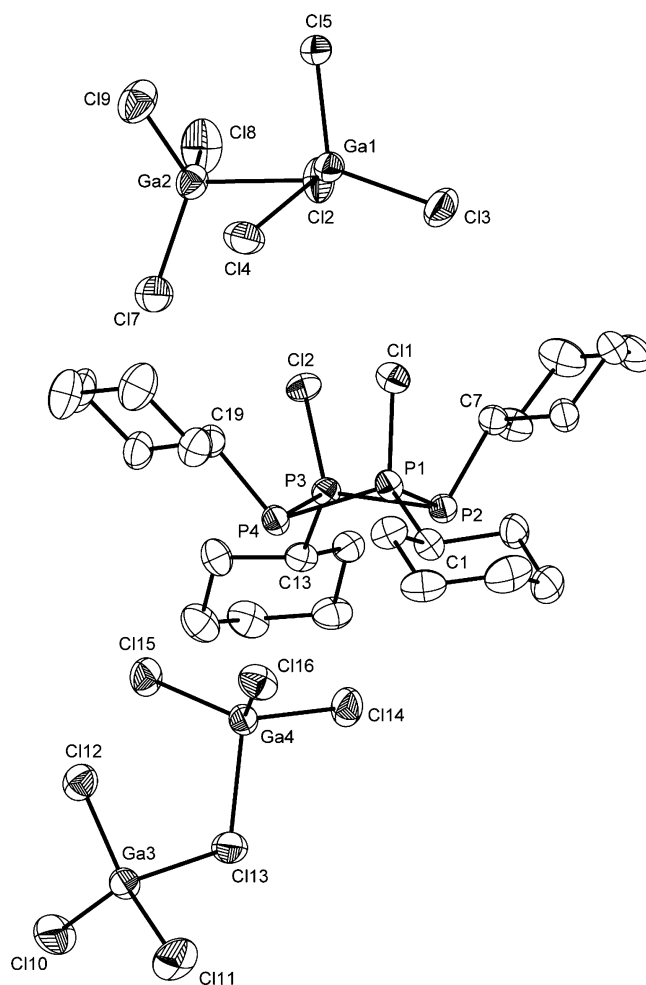


Figure 6. ORTEP plot of the molecular structure of $[20][\text{GaCl}_4]$. Thermal ellipsoids with 50% probability at 123(2) K (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg) are included in Table 2.

and are only slightly shorter than those in $(\text{CyP})_4$ [2.2224(5) Å] and in $[19]^+$ [2.1872(8) to 2.2478(9) Å]. The P–Cl bonds [1.9828(9) and 1.9832(8) Å] in $[20]^{2+}$ are shorter than that in $[19]^+$ [2.011(1) Å] as expected due to the higher charge in the

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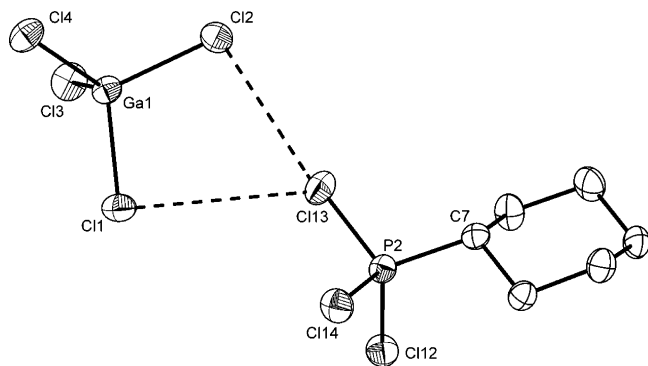
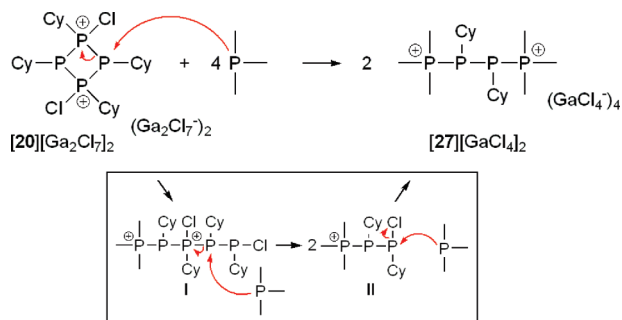


Figure 7. ORTEP plot of $[24][\text{GaCl}_4]_2$. Thermal ellipsoids with 50% probability (hydrogen atoms and counterions are omitted for clarity) Only one cation of the asymmetric unit and the interaction of the counteranion is shown. Selected bond lengths (Å) and angles (deg): P2–Cl12 1.954(1), P2–Cl13 1.953(1), P2–Cl14 1.954(1), P2–C7 1.792(2), Ga1–Cl1 2.1834(7), Ga1–C2 2.1932(8), Ga1–Cl3 2.1753(8), Ga1–Cl4 2.1578(8), Cl12–P2–Cl13 108.36(4), Cl12–P2–Cl14 107.94(5), Cl12–P2–C7 110.57(9), Cl13–P2–Cl14 107.66(4), Cl13–P2–C7 110.7(1), Cl14–P2–C7 111.52(9).

Scheme 8. Formation of *acyclic*-2,3-Diphosphino-1,4-diphosphonium Dication $[27]^{2+}$ via Displacement Reaction of $[20]^{2+}$ with PMe_3 and Proposed Mechanism



dication. The P–C bond lengths at the phosphonium centers in $[19]^+$ and $[20]^{2+}$ [1.791(2) to 1.820(2) Å] are significantly shorter than those at the phosphine centers [1.863(2) to 1.873(2) Å]. The $[\text{GaCl}_4]^-$ anions in $[19][\text{GaCl}_4]$ adopt a slightly distorted tetrahedral geometry with Cl–Ga–Cl bond angles between 107.36(3) and 111.94(4)°. The anion in $[20][\text{Ga}_2\text{Cl}_7]_2$, which is isosteric with Cl_2O_7 ,⁴⁵ contains two distorted tetrahedral gallium centers associated via a chloride bridge with a mean Ga–Cl–Ga bond angle of 110.88(4)°. The *gauche* conformation of the $[\text{Ga}_2\text{Cl}_7]^-$ anion can be explained by the minimization of Cl–Cl interactions.⁴⁶ The molecular structures of $[19][\text{GaCl}_4]$ and $[20][\text{Ga}_2\text{Cl}_7]_2$ show no interion $\text{Cl}\cdots\text{Cl}$ interactions.

In the presence of excess PCl_5 and GaCl_3 in CH_2Cl_2 , $(\text{CyP})_4$ dissociates to give $[24][\text{GaCl}_4]$ quantitatively (Scheme 7c), which crystallizes with two independent, but essentially identical formula units of $[24][\text{Ga}_2\text{Cl}_7]_2$ in the unit cell. A view of one of the molecular units is depicted in Figure 7. The mean P–Cl bond lengths (1.954 Å) in the cations are slightly shorter than those in the monocation $[19]^+$ (2.011(1) Å) and the dication $[20]^{2+}$ (1.983(1) Å) due to the inductive effect of the chloro substituents in $[24]^+$. The Cl–P–Cl and Cl–P–C angles range from 107.86(4) to 111.60(9)° consistent with the tetrahedral arrangement of the cation. The $\text{Cl}\cdots\text{Cl}$ contact (3.281(2) Å)

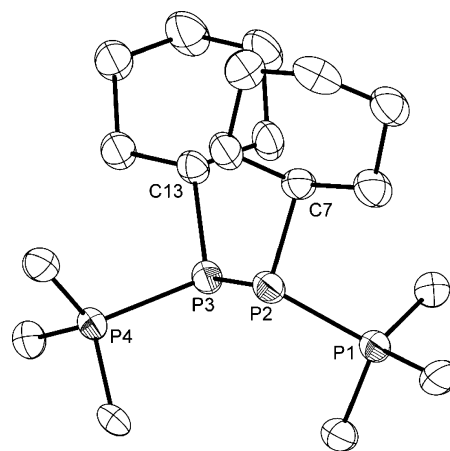


Figure 8. ORTEP plot of the molecular structure of the cation $[27]^{2+}$ in $[27][\text{GaCl}_4]_2$. Thermal ellipsoids with 50% probability (hydrogen atoms and counteranions are omitted for clarity). Selected bond lengths (Å), angles (deg) and dihedral angles: P1–P2 2.186(2), P2–P3 2.227(2), P3–P4 2.198(2), P2–C7 1.874(6), P2–C7 1.879(5); P1–P2–P3 94.98(8), P2–P3–P4 95.10(8), P1–P2–C7 107.6(2), P3–P2–C7 107.9(2), P2–P3–C13 107.1(2), P4–P3–C13 107.3(2), Cl12–P2–C7 110.57(9), Cl13–P2–Cl14 107.66(4), Cl13–P2–C7 110.7(1), Cl14–P2–C7 111.52(9); P1–P2–P3–P4 132.13(8), C7–P2–P3–C13 –7.6(2), C7–P2–P3–P4 –117.5(2), C13–P3–P2–P1 –118.0(2).

between Cl13 of $[24]^+$ and Cl2 of $[\text{GaCl}_4]^-$ is within the sum of the van der Waals radii ($r_{\text{Cl}} = 1.75$ Å, $2r_{\text{Cl}} = 3.50$ Å),⁴⁴ classifying this as a weak donor–acceptor interaction.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the slow addition of 1 equiv $[20][\text{Ga}_2\text{Cl}_7]_2$ to 4 equiv of PMe_3 show mainly two broad signals ($\delta_{\text{A}} = -33.1$, $\delta_{\text{X}} = 19.2$ ppm; Table 2) due to fluxional behavior that in accordance to other observation are assigned to the 2,3-diphosphino-1,4-diphosphonium dication $[27]^{2+}$ (Scheme 8). As shown in Scheme 8, nucleophilic attack of dication $[20]^{2+}$ by PMe_3 is proposed to give the five-membered monocation **I**, which is subsequently attacked by a second equivalent PMe_3 to yield monocation **II**.⁴⁷ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a test reaction obtained from the slow addition of 2 equiv PMe_3 to dication $[27]^{2+}$ is complicated, however, an AMX spin system with resonances at –40.5 (1P_A, dd, $^1J_{\text{AM}} = 293$, $^1J_{\text{AX}} = 312$ Hz), 17.3 (1P_M, dd, $^1J_{\text{AM}} = 293$, $^2J_{\text{MX}} = 47$ Hz), and 95.7 (1P_X, dd, $^1J_{\text{AX}} = 312$, $^2J_{\text{MX}} = 47$ Hz) ppm indicates the formation of cation $[\text{Me}_3\text{P}_M\text{P}_A\text{CyP}_X\text{CyCl}]^+$ (**II**) as an intermediate. We envisage that cation **II** subsequently undergoes conversion to dication $[20]^{2+}$ with addition of PMe_3 . Colorless crystals of $[27][\text{GaCl}_4]_2$ were obtained in low yield (35%), but spectroscopic characterization was hampered by dynamic behavior in solution. The solid state structure of the cation $[27]^{2+}$ (Figure 8) is consistent with those of other derivatives^{48,49,47} prepared by reductive coupling of chlorophosphinophosphonium ions $[12]^+$ (Scheme 9), and the eclipsed conformation of the central C–P–P–C framework [torsion angle of 7.7(3)°] is due to a combination of steric interactions in the terminal and internal positions.⁴⁷

The reaction of $[20][\text{Ga}_2\text{Cl}_7]_2$ with PMe_3 can be considered as a ligand-induced cyclodissociation, highlighting $[27]^{2+}$ as a

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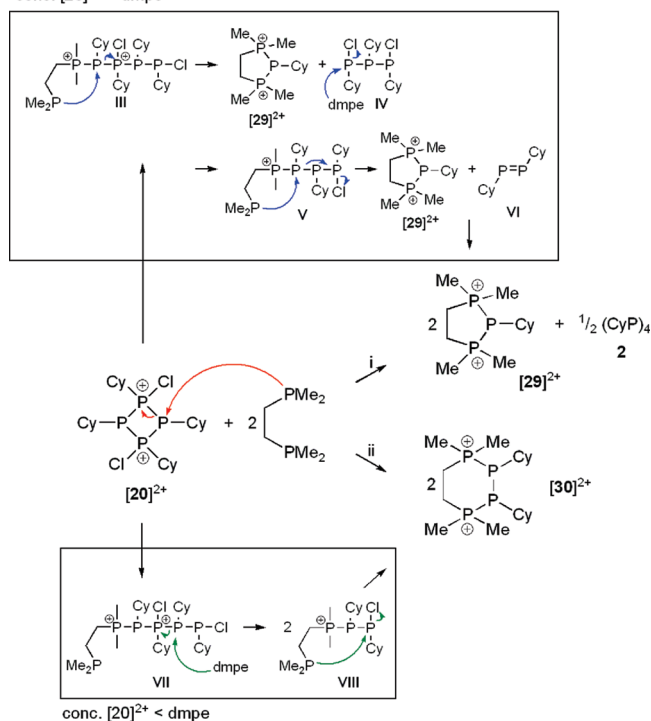
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$$2 \begin{array}{c} | \\ \oplus \\ \text{P} - \text{P} - \\ | \\ \text{X} \end{array} + \begin{array}{c} | \\ \text{P} - \\ | \end{array} \longrightarrow \begin{array}{c} | \\ \oplus \\ \text{P} - \text{P} - \text{P} - \text{P} - \\ | \quad | \quad | \quad | \end{array} + \begin{array}{c} | \\ \oplus \\ \text{Cl} - \text{P} - \\ | \\ -\text{Cl} \end{array}$$

$[12]^+$ $[25]^{2+}$ $[26]|\text{Cl}|$

$$(H_2C)_n \begin{array}{c} \text{PR}_2 \\ | \\ \text{PR}_2 \end{array} + 2R'PCl_2 + SnCl_2 \longrightarrow (H_2C)_n \begin{array}{c} \text{R} \\ | \\ \text{P}^{\oplus} \\ | \\ \text{R}' \end{array} - \begin{array}{c} \text{R}' \\ | \\ \text{P} \\ | \\ \text{P}^{\oplus} \\ | \\ \text{R} \end{array} \begin{array}{c} \text{R}' \\ | \\ \text{P} \\ | \\ \text{R}' \end{array} (SnCl_6)^{2-}$$

conc. $[20]^{2+} > \text{dmpe}$



ligand-stabilized diphosphenium dication. In this context, Dillon and co-workers reported the reductive cycloaddition reaction of dichlorophosphines with a bidentate diphosphine to form *cyclo*-2,3-diphosphino-1,4-diphosponium dications [28]²⁺ with an organic backbone (Scheme 10).⁵⁰ By analogy, when a solution of [20][Ga₂Cl₇]₂ in CH₂Cl₂ is added rapidly to a CH₂Cl₂ solution containing 2 equiv of dmpe, a oily phase is formed which has been characterized as an equimolar mixture of the new salts [29][GaCl₄]₂ and [30][GaCl₄]₂ and **2**, as illustrated in Scheme 11. The oil dissolves in acetonitrile accompanied by precipitation of **2**. The clear solution exhibits the ³¹P{¹H} NMR spectrum depicted in Figure 9, displaying AX₂ and AA'XX'

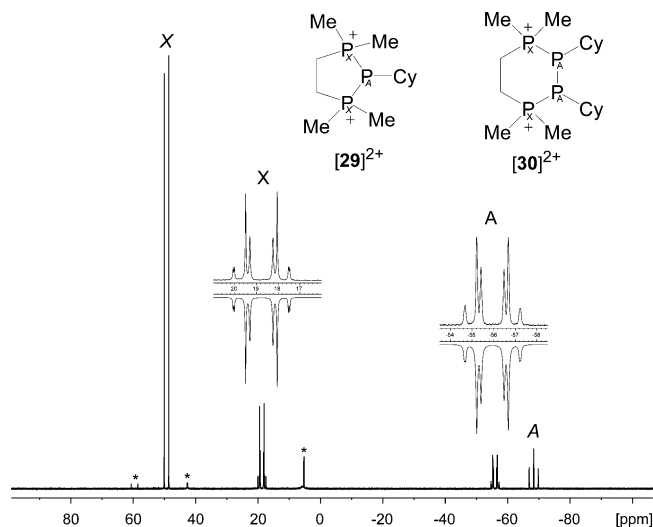


Figure 9. $^{31}\text{P}\{\text{H}\}$ NMR spectra (CH_3CN , C_6D_6 capillary, RT) of the redissolved precipitate of the reaction mixture of $[\mathbf{20}][\text{Ga}_2\text{Cl}_7]_2$ with dmpe according to Scheme 11 (a.ii). Signals assigned to unknown side-products are labeled with asterisks (inset) show the experimental (up) and fitted²³ (down) spectra for cation $[\mathbf{20}]^{2+}$.

The reaction of dmpe with dication $[20]^{2+}$ to form cations $[29]^{2+}$ and $[30]^{2+}$ can be interpreted according to the proposed mechanisms in Scheme 11. The initial step for both cases is the ring-opening of $[20]^{2+}$ by nucleophilic attack of dmpe to form dication **III**. The subsequent reaction can now proceed in one of two ways. The dication **III** is not observed implying either fast intermolecular nucleophilic attack by a second dmpe molecule (conc. $[20]^{2+} < \text{dmpe}$) to form cation **VII** or by an intramolecular attack (conc. $[20]^{2+} > \text{dmpe}$) to form cation $[29]^{2+}$ and triphosphine **IV**. Intramolecular ring-closure of cation **VII** results in the formation of dication $[30]^{2+}$. Triphosphines of type **IV** are known to be highly reactive and we speculate that the reaction of a second equivalent of dmpe leads to the formation of cation **V**. Subsequent intramolecular attack according to Scheme 11 results in the formation of the second equivalent of $[29]^{2+}$ and $[\text{CyP}=\text{PCy}]$,³⁷ which dimerizes to give **2**. Attempts to identify the intermediates **III–VII** in various stoichiometric combinations of dication $[20]^{2+}$ and dmpe and under various reaction conditions were unsuccessful. However, when 2 equiv of dmpe are added slowly to a cooled (0 °C) solution of $[20][\text{GaCl}_2\text{I}_7]$ in CH_2Cl_2 , the $^{31}\text{P}\{\text{H}\}$ NMR spectrum of the reaction mixture reveals the stoichiometric formation of only $[29][\text{GaCl}_4\text{I}_2]$ and **2** (Scheme 11). The salt was isolated in high yield (85 %) as air- and moisture-sensitive colorless blocks. The solid state structure of $[29]^{2+}$, shown in Figure 10, exhibits structural features that are consistent with those of derivatives previously prepared by the alkylation⁵¹ of cyclic triphosphenium ions to form triphosphenium salts.^{52,53} The formation of the mixture of cations $[29]^{2+}$ and $[30]^{2+}$ might be explained by these two competitive reactions, however, dication $[29]^{2+}$ is the thermodynamically favored product. The formation of the kinetically favored dication $[30]^{2+}$ results from the local

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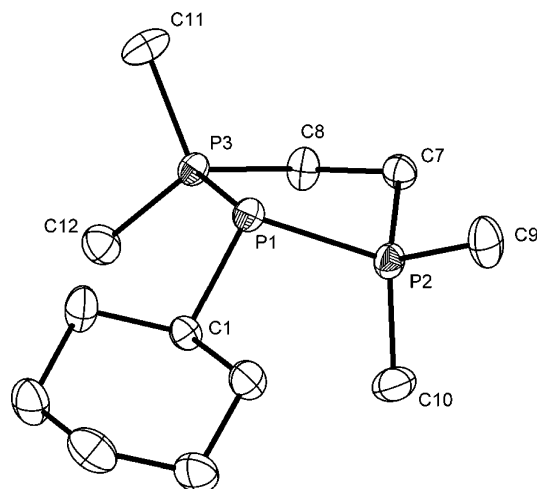


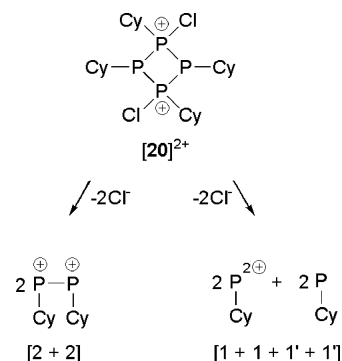
Figure 10. ORTEP plot of the molecular structure of the cation $[29]^{2+}$ in $[29][GaCl_4]_2$. Thermal ellipsoids with 50% probability (hydrogen atoms and counteranions are omitted for clarity). Selected bond lengths (Å) and angles (deg): P1–P2 2.191(1), P1–P3 2.214(1), P1–C1 1.873(3), P2–C7 1.806(3), P2–C9 1.792(4), P2–C10 1.795(4), P3–C8 1.815(3), P3–C11 1.787(3), P3–C12 1.783(4), C7–C8 1.535(5), P2–P1–P3 90.18(4), P2–P1–C1 104.4(1), P3–P1–C1 108.1(1), C9–P2–C10 110.6(8), C9–P2–C7 110.1(2), P1–P2–C10 116.4(1), P1–P2–C7 100.2(1), C11–P3–C12 108.6(2), C8–P3–C11 110.3(2), P1–P3–C12 117.3(1), P1–P3–C11 107.2(1), P1–P3–C8 104.4(1).

overconcentration of dmpe, since the dication $[20]^{2+}$ was slowly added to the dmpe solution.

Conclusion

Reactions of tetracyclohexyl-*cyclo*-tetrphosphine $(CyP)_4$ with a source of halonium cations in the presence of GaX_3 ($X = Cl, I$) allows for the isolation of first *cyclo*-2-halo-1,3,4-triphosphino-2-phosphonium cations and *cyclo*-2,4-dihalo-1,3-diphosphino-2,4-diphosphonium dications as their corresponding met-

Scheme 12. Formal Retro $[2 + 2]$ or $[1 + 1 + 1' + 1']$ Reaction Channels for the Degradation of Dication $[20]^{2+}$



allates. Isolation of the new cations is made possible by the presence of GaX_3 , which engages the halide anion and inhibits the P–P bond cleavage. In contrast to the analogous dications $[28]^{2+}$ reported by Dillon and co-workers, the formation of $[30]^{2+}$ represents a new approach for the generation of ligand-stabilized diphosphonium dications. Dication $[20]^{2+}$ reacts with Me_3P or dmpe and dissociates formally via a retro $[2 + 2]$ or $[1 + 1 + 1' + 1']$ process (Scheme 12) releasing $[RP]^{2+}$ and $[R_2P_2]^{2+}$ fragments.

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Supporting Information Available: Crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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