Inorg. Chem. **2007**, *46*, 4277−4285

Monocyclic Di- and Triphosphinophosphonium Cations: New Foundational Frameworks for *catena*-Phosphorus Chemistry

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Received November 25, 2006

The synthesis and characterization for trifluoromethanesulfonate (triflate) salts of the first definitive examples of cyclotriphosphinophosphonium and cyclodiphosphinophosphonium cations are described, representing new prototypical frameworks in the rational and systematic development of *catena*-phosphorus chemistry. Addition of methyl triflate (MeOTf) or triflic acid (HOTf) to cyclotetraphosphines (^{t}BuP)$_4$ (**1a**) or (CyP)$_4$ (**1b**) gives [(^{t}BuP)$_3$P^{t}BuMe][OTf] (**2a**[OTf]), [(CyP)$_3$PCyMe][OTf] (**2b**[OTf]), [(^{t}BuP)$_3$P^{t}BuH][OTf] (**3a**[OTf]), and [(CyP)$_3$PCyH][OTf] (**3b**[OTf]), respectively. Cyclotriphosphine (^{t}BuP)$_3$ (**4a**) reacts with HOTF or Me$_2$PCl/Me$_3$SiOTf to give the ring expanded cations **3a**[OTf] and [(^{t}BuP)$_3$PMe$_2$][OTf] (**5**[OTf]), respectively, but reactions with MeOTf and HCl give cyclic diphosphinophosphonium cation [(^{t}BuP)$_2$P^{t}BuMe][OTf] (**6a**[OTf]) and ring-opened triphosphine H^{t}BuP–P^{t}Bu–P^{t}BuCl (**7**), respectively. The analogous diphosphinophosphonium cation [(CyP)$_2$PCyMe][OTf] (**6b**[OTf]) is formed along with **2b**[OTf] in reactions of MeOTf with (CyP)$_3$ (**4b**). Compounds **2a**[OTf], **2b**[OTf], **3a**[OTf], **5**[OTf], and **6a**[OTf] have been crystallographically characterized. ^{1}H NMR spectra of **2a**[OTf], **2b**[OTf], **5**[OTf], and **6a**[OTf] demonstrate that $^3J_{PH}$ coupling is only observed for methyl protons if they are in a *cis* orientation to the lone pairs on the adjacent phosphine sites.

Introduction

The propensity for catenation is one of the prominent features that highlights the diagonal relationship between carbon and phosphorus.[1] *catena*-Phosphines[2−5] and *catena*-phosphorus anions[2−4,6] have been studied for some time and remain under active investigation,[7−15] representing a significant component of the fundamental chemistry for phosphorus. As *catena*-phosphorus anions (phosphinophosphide ions) are composed of phosphine (**I**) and phosphide (**II**) units, *catena*-phosphorus cations (phosphinophosphonium ions) are envisaged as a combination of phosphine (**I**) and phosphonium (**III**) units. Despite the ubiquitous nature of phosphonium salts, relatively few derivatives of *catena*-phosphorus cations have been reported,[16−37] yet the similar geometrical arrangement and isolobal nature of PH_4^+ and CH_4 highlight

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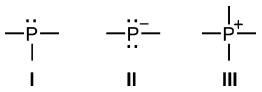
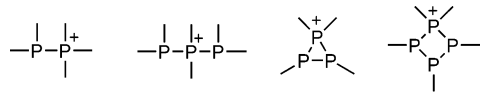
10.1021/ic0622499 CCC: $37.00
Published on Web 04/21/2007

a greater potential for parallels to *catena*-carbon chemistry (organic chemistry).



I II III

Versatile synthetic approaches to derivatives of phosphinophosphonium cations (**A**)[23] and acycylic diphosphinophosphonium cations (**B**)[38] have been developed from the realization of P−P homoatomic coordinate bonding. As the formation of cyclic phosphinophosphonium cations is not feasible through coordination chemistry, we have exploited the basicity of neutral *catena*-phosphines to synthesize and isolate salts of cyclodiphosphinophosphonium cations of type **C** and cyclotriphosphinophosphonium cations of type **D** (preliminary communication),[39] as first proposed on the basis of elemental analysis data for solids isolated from the reaction of $(EtP)_4$ with MeI.[40] The new cations represent key foundational frameworks for the rational and systematic development of *catena*-phosphorus chemistry.



A B C D

Experimental Section

General Procedures. Small scale reactions were carried out in an Innovative Technology, System One, glovebox with an inert N_2 atmosphere containing less than 10 ppm of oxygen and less than 5 ppm water. The reactions were done in 20 mL glass vials with Teflon-lined caps. Small amounts of liquid reagents were measured using an Ependorff pipet (10−100 μL). Solvents were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. $(^tBuP)_3$,[41] $(^tBuP)_4$,[42] and $(CyP)_4$[43] were prepared according to literature methods. HOTf (trifluoromethanesulfonic acid), MeOTf (methyltrifluoromethanesulfonate), HCl (2 M in Et_2O), and Me_3P (1 M solution in hexane) were purchased from Aldrich and used as received. Me_3SiOTf was purchased from Aldrich and was purified by vacuum distillation prior to use.

Solution ^1H, ^{13}C, and ^{31}P NMR spectra were collected at the indicated temperature on Bruker AC-250 and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm relative to an external reference standard [100% $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P)]. Deuterated $CDCl_3$ solvent was purchased from Aldrich and stored over molecular sieves for 24 h prior to use. NMR spectra of reaction mixtures were obtained by transferring an aliquot of the bulk solution to a 5 mm NMR tube. Tubes were then flame sealed or capped and tightly covered with Parafilm. All reported ^{31}P NMR parameters for second-order spin systems were derived by iterative simulation of experimental data at fields of 101.3 and 202.6 MHz by use of gNMR.[44] $[(^tBuP)_2P^tBuMe][OTf]$ (**6a**[OTf]) and $[(CyP)_3PCyH][OTf]$ (**3b**[OTf]) were only simulated at 101.3 MHz. Large $^1J_{PP}$ coupling constants are given a negative value.[45] The phase of ^{13}C signals from DEPTQ135 experiments is indicated with a "+" (for CH and CH_3) or "−" (for C and CH_2).

Infrared spectra were collected on samples prepared as Nujol mulls on CsI plates using a Bruker Vector FT-IR spectrometer. Peaks are reported in wavenumbers (cm^{-1}) with ranked intensities in parentheses, where a value of one corresponds to the most intense peak in the spectrum. Melting points were obtained on samples sealed in glass capillaries, under dry nitrogen, by use of an Electrothermal apparatus. Chemical analyses were performed by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada or by Desert Analytics, Tucson, AZ.

Unless otherwise stated, crystals for single-crystal X-ray diffraction studies were obtained by vapor diffusion at −25 °C (glovebox freezer) or room temperature by dissolving the sample (0.05−0.10 g) with a minimal amount of solvent A (1−2 mL) in a 5 mL vial which was placed within a capped 20 mL vial containing ~5 mL of solvent B. Solvents are reported for individual samples in the form A/B. After deposition of crystals, the solvent was carefully removed using a pipet, and the crystals were coated with paratone oil. Single-crystal X-ray diffraction data were collected using a Bruker AXS P4/SMART 1000 diffractometer. All measurements were made with graphite monochromated Mo-Kα radiation (0.71073 Å). The data were reduced (SAINT)[46] and corrected for absorption (SADABS)[47] and for Lorentz and polarization effects. The structures were solved by direct methods and expanded using Fourier techniques. Full matrix least-squares refinement was carried out on F^2 data using the program SHELX97.[48]

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Table 1. Crystallographic Data for **2a**[OTf], **2b**[OTf], **3a**[OTf], **5**[OTf], and **6a**[OTf]

compound	[(^{t}BuP)$_3$P^{t}BuMe][OTf]	[(CyP)$_3$PCyMe][OTf]	[(^{t}BuP)$_3$P^{t}BuH][OTf]	[(^{t}BuP)$_3$PMe$_2$][OTf]	[(^{t}BuP)$_2$P^{t}BuMe][OTf]
label	**2a**[OTf]	**2b**[OTf]	**3a**[OTf]	**5**[OTf]	**6a**[OTf]
CCDC no.	622978	271728	622977	271729	271727
formula	$C_{18}H_{39}F_3O_3P_4S$	$C_{26}H_{47}F_3O_3P_4S$	$C_{17}H_{37}F_3O_3P_4S$	$C_{15}H_{33}F_3O_3P_4S$	$C_{14}H_{30}F_3O_3P_3S$
mol wt (g/mol)	516.43	620.58	502.41	474.35	428.35
crystal system	orthorhombic	triclinic	monoclinic	tetragonal	monoclinic
space group	*Pna2$_1$*	*P-1*	*P2$_1$/n*	*I4$_1$/a*	*P2$_1$/n*
color, habit	colorless, plate	colorless, parallelepiped	colorless, irregular	colorless, parallelepiped	colorless, plate
cryst dim./mm	0.30 × 0.10 × 0.01	0.275 × 0.20 × 0.175	0.425 × 0.35 × 0.125	0.40 × 0.275 × 0.25	0.40 × 0.40 ×0.10
a/Å	17.498(9)	11.4946(7)	13.773(10)	25.6452(11)	13.6318(9)
b/Å	13.694(7)	11.5640(7)	12.781(9)	25.6452(11)	10.5918(7)
c/Å	11.349(6)	14.0822(9)	15.071(10)	14.7549(8)	15.487(1)
α/°	90	110.984(1)	90	90	90
β/°	90	102.476(1)	98.354(12)°	90	104.084(1)
γ/°	90	106.868(1)	90	90	90
V/Å^3	2719(2)	1561.6(2)	2625(3)	9703.9(8)	2168.9(2)
T/K	173(1)	173(1)	208(1)	173(1)	173(1)
Z	4	2	4	16	4
reflections	17506	10965	17562	33323	14573
independent reflcns	5729	6795	5889	5547	4869
parameters	275	522	401	367	337
R_1[a] ($I > 2\sigma(I)$, all data)	0.0446, 0.1024	0.0358, 0.0475	0.0406, 0.0760	0.0301, 0.0445	0.0368, 0.0487
wR_2[b] ($I > 2\sigma(I)$, all data)	0.0843, 0.0966	0.0899, 0.0964	0.0889, 0.0962	0.0731, 0.0809	0.0986, 0.1056
Δρ max and min/ e Å^{-3}	+0.502, −0.292	+0.491, −0.247	+0.361, −0.285	+0.414, −0.237	+0.646, −0.476

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[F_o^4])^{1/2}$.

Non-hydrogen atoms were refined anisotropically. For **2a**[OTf], hydrogen atoms were included in geometrically calculated positions and refined using a riding model. For all other crystals, the hydrogen atoms were found in the Fourier difference maps and refined isotropically. For **3a**[OTf], the crystal was a multiple twin, and the orientation matrix for the major component was determined (RLATT, GEMINI).[49,50] Crystal data are listed in Table 1.

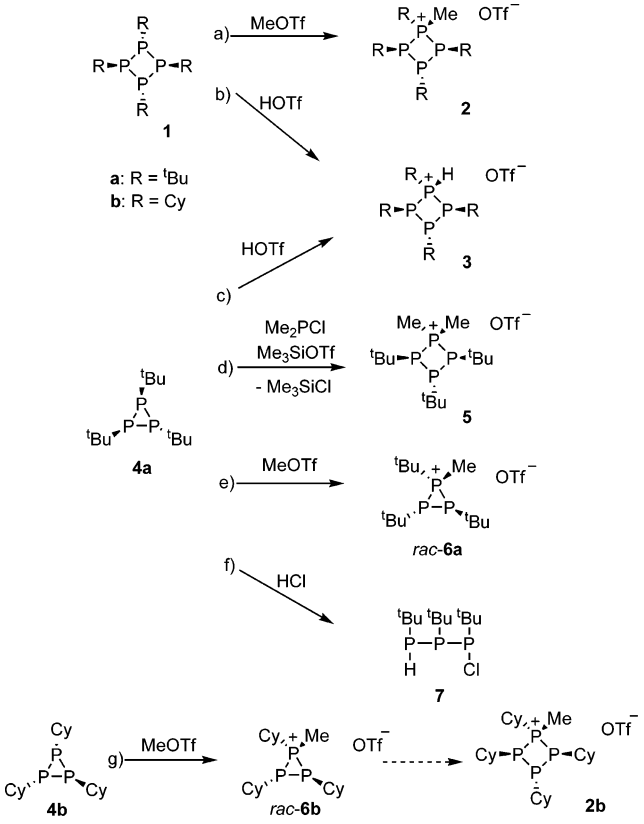
Preparation and Isolation Procedures. [(^{t}BuP)$_3$P^{t}BuMe][OTf], 2a[OTf]: MeOTf (0.090 mL, 0.79 mmol) was added to a solution of (^{t}BuP)$_4$ (0.14 g, 0.40 mmol) in 3 mL of fluorobenzene. Stirring was stopped after 1 h, and hexane was added dropwise, with periodic agitation, until the point where it seemed the precipitate would not likely go back into solution if more hexane was added. This saturated fluorobenzene/hexane solution was put in the freezer (−25 °C) for 40 days, giving colorless crystals suitable for X-ray diffraction. These crystals were isolated rapidly by decanting solvents, as they were found to redissolve upon warming. Crystals not submitted for X-ray analysis were washed with hexane (2 × 1 mL) and dried in vacuo. Yield: 0.10 g (0.20 mmol, 50%); mp 147−152 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K): AB_2X spin system, $\delta A = -43$ ppm, $\delta B = -39$ ppm, $\delta X = 18$ ppm, $^1J_{AB} = -152$ Hz, $^1J_{BX} = -275$ Hz, $^2J_{AX} = 9$ Hz; see also Table 2; ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta = 2.62$ ppm (d, $^2J_{PH} = 12$ Hz, 3H), 1.43 ppm (2 overlapping doublets, 18H), 1.32 ppm (d, $^3J_{PH} = 14$ Hz, 9H); ^{13}C NMR (125.8 MHz, DEPTQ135, $CDCl_3$, 298 K): $\delta = 30.3$ ppm (m, +), 28.8 ppm (m, +), 23.5 ppm (s, +), 5.6 ppm (d, $^1J_{PC} = 10$ Hz, +); low-intensity multiplets of negative phase, which likely correspond to quaternary ^{13}C signals, were observed at 36.1 and 31.7 ppm. FT-IR: 1282 (3), 1250 (4), 1225 (8), 1154 (5), 1030 (2), 844 (11), 801 (10), 756 (12), 637 (1), 572 (7), 517 (6), 394 (9) cm^{-1}.

[(CyP)$_3$PCyMe][OTf], 2b[OTf]: First reported in a preliminary communication.[39] MeOTf (0.095 mL, 0.84 mmol) was added dropwise to a mixture of (CyP)$_4$ (0.25 g, 0.55 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was filtered after 90 min, and removal of the solvent in vacuo gave a white solid that was recrystallized at −25 °C by vapor diffusion with fluorobenzene/hexane over 3 days. Yield: 0.15 g (0.23 mmol, 43%); mp 175−177 °C; elemental analysis (%) calcd for $C_{26}H_{47}F_3O_3P_4S$: C 50.3, H 7.6; found: C 50.4, H 7.3; ^{31}P{^{1}H} NMR (202.6 MHz, $CDCl_3$, 298 K): A_2MX spin system, $\delta A = -70$ ppm, $\delta M = -56$ ppm, $\delta X = 10$ ppm, $^1J_{AM} = -122$ Hz, $^1J_{AX} = -230$ Hz, $^2J_{MX} = -17$ Hz; see also Table 2; ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta = 2.59$ ppm (m, 1H) 2.41 (m, 2H), 2.40 ppm (d, $^2J_{PH} = 12$ Hz, 3H), 2.05 ppm (m, 2H), 2.0−1.7 ppm (m, 19H), 1.5−1.1 ppm (m, 20H); ^{13}C NMR (125.8 MHz, DEPTQ135, $CDCl_3$, 298 K): 38.8 ppm (m, +), 37.3 ppm (m, +), 35.0 ppm (m, +), 32.3 ppm (m, −), 30.0 ppm (m, −), 28.4 ppm (m, −), 26.7 ppm (s, −), 26.6 ppm (m, −), 26.3 ppm (m, −), 25.9 (m, −), 25.6 ppm (s, −), 25.5 ppm (s, −), 25.4 ppm (s, −), 25.1 (s, −), 3.6 (d, $^1J_{PC}$ 15 Hz, +); FT-IR: 1284 (4), 1246 (1), 1158 (5), 1083 (3), 926 (9), 883 (8), 754 (10), 636 (2), 572 (7), 527 (6) cm^{-1}. Crystals suitable for X-ray diffraction were obtained by fluorobenzene/hexane vapor diffusion at room temperature.

[(^{t}BuP)$_3$P^{t}BuH][OTf], 3a[OTf]: HOTf (0.014 mL, 0.16 mmol) was added to a solution of (^{t}BuP)$_4$ (0.046 g, 0.14 mmol) in CH_2Cl_2 (2 mL). After having been stirred for 1 h, the reaction mixture was pumped to dryness, and the resulting precipitate was recrystallized over 10 days at room temperature by fluorobenzene/Et_2O vapor diffusion. Crystals not submitted for X-ray diffraction were washed with hexane (2 × 1 mL) and dried in vacuo. Yield: 0.045 g (0.090 mmol, 64%); mp 106−110 °C; ^{31}P{^{1}H} NMR (101.3 MHz, CH_2Cl_2, 200 K): A_2BX spin system; $\delta A = -57$ ppm, $\delta B = -55$ ppm, $\delta X = -32$ ppm, $^1J_{AB} = -156$ Hz, $^1J_{AX} = -260$ Hz, $^2J_{BX} = 12$ Hz; see also Table 2; ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, 298 K): −29 ppm (m), −52 (m); ^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K): 7.84 ppm (d, $^1J_{PH} = 452$ Hz), 1.40 (broad); peaks are broad and integrations are unreliable at room temperature; ^{13}C NMR (125.8 MHz, DEPTQ135, $CDCl_3$, 298 K): 28.5 ppm (broad s, +),

(49) *RLATT 2.72*; Bruker AXS, Inc.: Madison, WI, U.S.A., 1999.
(50) *GEMINI 1.0*; Bruker AXS, Inc.: Madison, WI, U.S.A., 1999.

Scheme 1. Synthetic Methods to Triflate Salts of Cyclophosphinophosphonium Cations **2**, **3**, **5**, and **6** and Triphosphine **7**



27.5 ppm (broad s, +), 24.0 ppm (broad s, +); FT-IR: 1282 (3), 1250 (4), 1225 (8), 1154 (5), 1030 (2), 844 (11), 801 (10), 756 (12), 637 (1), 572 (7), 517 (6), 394 (9) cm^{-1}.

[(CyP)$_3$PCyH][OTf], 3b[OTf]: HOTf (0.025 mL, 0.23 mmol) was added to mixture of $(CyP)_4$ (0.100 g, 0.22 mmol) in $CDCl_3$ (3 mL). Upon stirring for 2 min all $(CyP)_4$ was dissolved, and after another 20 min hexane (5 mL) was added. The resulting solution was then pumped to dryness. Yield: 0.107 g (0.176 mmol, 80%); D.p. 73−75 °C; $^{31}P\{^1H\}$ NMR (101.3 MHz, CH_2Cl_2, 200 K): A_2-MX spin system; $\delta A = -74$ ppm, $\delta M = -64$ ppm, $\delta X = -23$ ppm, $^1J_{AM} = -126$ Hz, $^1J_{AX} = -233$ Hz, $^2J_{MX} = 16$ Hz; see also Table 2; $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 298 K): A_2MX spin system; $\delta A = -71$ ppm, $\delta M = -64$ ppm, $\delta X = -27$ ppm; ^{31}P NMR (202.5 MHz, $CDCl_3$, 298 K): A_2MXZ spin system ($Z = {}^1H$); $\delta A = -71$ ppm, $\delta M = -64$ ppm, $\delta X = -27$ ppm, $^1J_{XZ} = {}^1J_{PH} = 461$ Hz; $^1J_{PH}$ was determined manually. ^1H NMR (500.1 MHz, $CDCl_3$, 298 K): 7.71 ppm (d, $^1J_{PH} = 464$ Hz), 2.63 ppm (m), 1.88 ppm (m), 1.37 (m); peaks are broad and integrations are unreliable at room temperature; ^{13}C NMR (125.8 MHz, DEPTQ135, $CDCl_3$, 298 K): 37.5 ppm (broad, +), 34.5 ppm (broad, +), 30.6 ppm (broad, −), 29.3 ppm (broad, −), 27.1 ppm (broad, −), 26.2 ppm (broad, −), 25.4 ppm (broad, −); FT-IR: 1264 (3), 1185 (1), 1020 (8), 996 (6), 849 (9), 814 (10), 631 (2), 551 (7), 511 (5), 440 (4) cm^{-1}. Attempts to grow single crystals of **3b**[OTf] repeatedly gave only $(CyP)_4$.

(CyP)$_3$, 4b: Previously prepared by Baudler et al. by an alternate method.[51] Here, a 1 M solution of Me_3P in hexane (0.202 mL, 0.202 mmol) was added to a solution of [$(CyP)_3$PCyMe][OTf] **2b**[OTf] (0.104 g, 0.168 mmol) in CH_2Cl_2 (3 mL). After having been stirred overnight, volatiles were removed in vacuo, and the resulting mixture was extracted into benzene (3 mL) and filtered through 1 in. of silica (packed into a pipet) to remove ionic materials. Washing the silica with another 1.5 mL of benzene and pumping to dryness afforded **4b** with less than 2% of $(CyP)_4$ as impurity. Yield: 0.025 g (0.073 mmol, 43%); $^{31}P\{^1H\}$ NMR (101.3 MHz, CH_2Cl_2, 298 K): A_2B spin system at −140 ppm.

[(tBuP)$_3$PMe$_2$][OTf], 5[OTf]: First reported in a preliminary communication.[39] A solution of PMe_2Cl (0.044 mL, 0.55 mmol) and Me_3SiOTf (0.10 mL, 0.67 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of $(^tBuP)_3$ (0.098 g, 0.37 mmol) in CH_2Cl_2 (3 mL). After having been stirred for 45 min, the solvent was removed in vacuo, and the white solid was washed with hexane (2 × 4 mL). The product was recrystallized over 5 days by vapor diffusion with fluorobenzene/hexane, giving X-ray quality crystals. Crystals not submitted for X-ray analysis were washed with hexane (2 × 1 mL) and dried in vacuo. Yield: 0.095 g (0.20 mmol, 54%); mp 112−114 °C; elemental analysis (%) calcd for $C_{15}H_{33}F_3O_3P_4S$: C 38.0, H 7.0; found: C 38.5, H 6.9; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): AB_2X spin system, $\delta A = -28$ ppm, $\delta B = -24$ ppm, $\delta X = -2$ ppm, $^1J_{AB} = -143$ Hz, $^1J_{BX} = -251$ Hz, $^2J_{AX} = 28$ Hz; see also Table 2; ^1H NMR (500.1 MHz, $CDCl_3$, 298 K): 2.66 ppm (d, $^2J_{PH} = 14$ Hz, 3H), 2.37 ppm (dt, $J_{PH} = 13$ Hz, $J_{PH} = 8$ Hz, 3H), 1.45 ppm (m, 18H), 1.34 ppm (d, $^3J_{PH} = 14$ Hz, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 298 K): 36.2 ppm (m), 30.8 ppm (m) 30.4 (m), 29.2 ppm (dt, $J_{PC} = 15$ Hz, $J_{PC} = 5$ Hz), 20.3 ppm (m), 11.2 ppm (d, $^1J_{PC}$ 15 Hz); FT-IR: 1304 (6), 1267 (2), 1224 (7), 1155 (3), 1032 (4), 957 (8), 914 (9), 638 (1), 573 (10), 517 (5) cm^{-1}.

[(tBuP)$_2$PtBuMe][OTf], 6a[OTf]: First reported in a preliminary communication.[39] MeOTf (0.080 mL, 0.71 mmol) was added dropwise to a solution of $(^tBuP)_3$ (0.096 g, 0.36 mmol) in fluorobenzene (4 mL). The reaction mixture was filtered after 15 min. Slow diffusion of hexane vapors into the filtrate at −25 °C gave colorless crystals suitable for X-ray diffraction. Crystals not submitted for X-ray analysis were washed with hexane (2 × 1 mL) and dried in vacuo. Yield: 0.14 g (0.32 mmol, 87%); mp 121−125 °C; elemental analysis (%) calcd for $C_{14}H_{30}F_3O_3P_3S$: C 39.3, H 7.1; found: C 39.5, H 7.0; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): AMX spin system, $\delta A = -110$ ppm, $\delta M = -51$ ppm, $\delta X = -20$ ppm, $^1J_{AM} = -123$ Hz, $^1J_{AX} = -334$ Hz, $^1J_{MX} = -317$ Hz; ^1H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta = 2.36$ ppm (dd, $J_{PH} = 13$ Hz, $J_{PH} = 8$ Hz, 3H), 1.62 ppm (d, $^3J_{PH} = 22$ Hz, 9H), 1.43 ppm (d, $^3J_{PH} = 17$ Hz, 9H), 1.35 ppm (d, $^3J_{PH} = 17$ Hz, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$, 298 K): $\delta = 39.6$ ppm (∼ddd, $J_{PC} = 3$ Hz, $J_{PC} = 9$ Hz, $J_{PC} = 13$ Hz), 35.0 ppm (∼ddd, $J_{PC} = 7$ Hz, $J_{PC} = 13$ Hz, $J_{PC} = 51$ Hz), 34.1 ppm (∼ddd, $J_{PC} = 5$ Hz, $J_{PC} = 13$ Hz, $J_{PC} = 45$ Hz), 31.8 ppm (∼ddd, $J_{PC} = 4$ Hz, $J_{PC} = 6$ Hz, $J_{PC} = 17$ Hz), 30.6 ppm (∼ddd, $J_{PC} = 3$ Hz, $J_{PC} = 5$ Hz, $J_{PC} = 17$ Hz), 28.8 ppm (m), 7.9 ppm (m); FT-IR: 1399 (9), 1260 (1), 1151 (2), 1030 (4), 904 (5), 800 (10), 751 (8), 638 (3), 572 (7), 516 (6) cm^{-1}. Larger quantities of spectroscopically pure, crystalline **6a**[OTf] have been prepared by the following method: MeOTf (0.42 mL) was added to a solution of $(^tBuP)_3$ (0.500 g) in 8 mL of CH_2Cl_2. After having been stirred for 10 min, hexane (15 mL) was added, and the resulting mixture was put in the freezer (−25 °C) overnight. Decanting solvents, washing the precipitate with hexane (2 × 1.5 mL), and drying in vacuo afforded 0.77 g (95%) of **6a**[OTf].

[(CyP)$_2$PCyMe][OTf], 6b[OTf]: MeOTf (0.009 mL, 0.079) was added to $(CyP)_3$ (0.025 g, 0.073 mmol) in CH_2Cl_2 (1.5 mL). After having been stirred for 1.5 h, $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K) of the colorless solution shows **6b**[OTf] (AMX spin system, $\delta A = -156$ ppm, dM = −129 ppm, $\delta X = -46$ ppm, $^1J_{AM} =$

(51) Baudler, M.; Pinner, C.; Gruner, C.; Hellmann, J.; Schwamborn, M.; Kloth, B. *Z. Naturforsch., B: Chem. Sci*. **1977**, *32b*, 1244−1251.

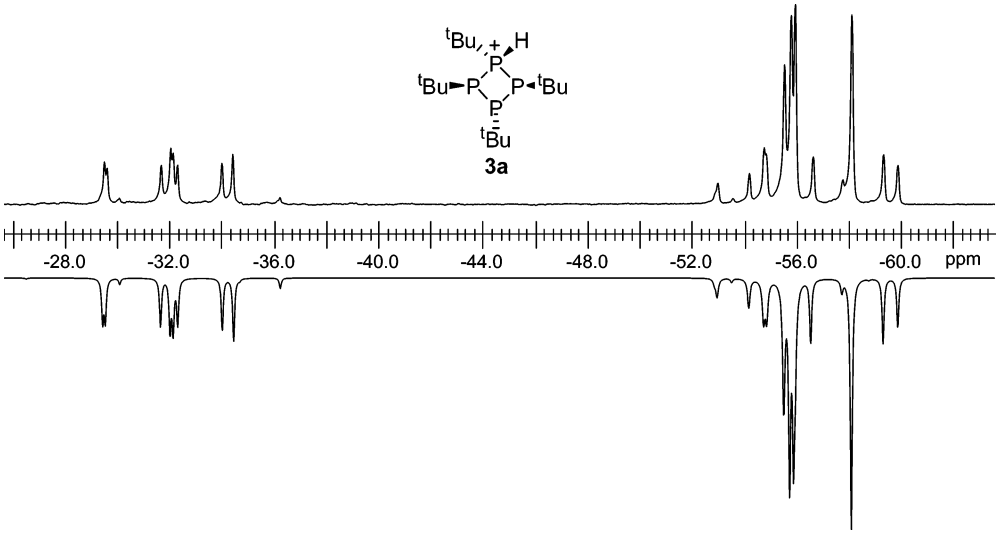


Figure 1. Experimental (top) and simulated (inverted) A_2BX spin system in the $^{31}P\{^1H\}$ NMR spectrum of **3a**[OTf] at 101.3 MHz.

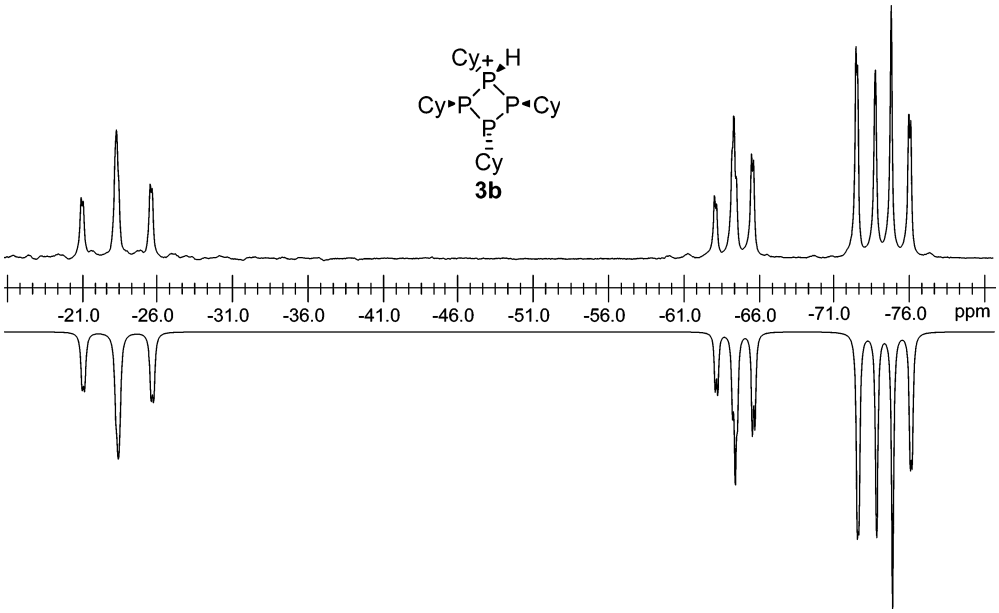


Figure 2. Experimental (top) and simulated (inverted) A_2MX spin system in the $^{31}P\{^1H\}$ NMR spectrum of **3b**[OTf] at 101.3 MHz.

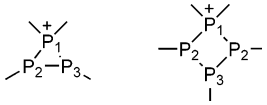
−97 Hz, $^1J_{AX}$ = −292 Hz, $^1J_{MX}$ = −292 Hz), along with approximately equal amounts of **2b**[OTf], and some minor unassigned multiplets at −10 and 55 ppm.

H^{t}BuP−P^{t}Bu−P^{t}BuCl, 7: Previously observed by Baudler et al.[42] A 2 M solution of HCl in Et_2O (0.38 mL, 0.72 mmol) was added to a solution of (^{t}BuP)$_3$ (0.20 g, 0.76 mmol) in CH_2Cl_2 (5 mL) at −80 °C. The mixture was allowed to warm slowly to room temperature and was analyzed by $^{31}P\{^1H\}$ and ^{31}P NMR spectroscopy, demonstrating virtually quantitative formation of **7**.[42]

Results and Discussion

Reactions of cyclotetraphosphines **1** with MeOTf or HOTf result in methylation or protonation and quantitative formation of cyclotriphosphinophosphonium cations **2** and **3**, as illustrated in Scheme 1a,b. The reactions are conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, and the products are identified by their AB_2X (**2a**), A_2MX (**2b**, **3b**), and A_2-BX (**3a**) spin systems, respectively (Table 2), implying C_s molecular symmetry in each case. Representative examples

Table 2. Iteratively Simulated ^{31}P NMR Parameters for Cyclotriphosphinophosphonium and Cyclodiphosphinophosphonium Cations[a]



cation	P_1 (ppm)	P_2 (ppm)	P_3 (ppm)	$^1J_{12}$ (Hz)	$^1J_{23}$ (Hz)	J_{13} (Hz)
2a	18	−39	−43	−275	−152	+9
2b	10	−70	−56	−230	−122	−17
3a[b,c]	−32	−57	−55	−260	−156	+12
3b[b,c]	−23	−74	−64	−233	−126	+16
5	−2	−24	−28	−251	−143	+28
6a	−20	−51	−110	−334	−123	−317
6b[b]	−46	−129	−156	−292	−97	−292

[a] Unless otherwise indicated, data were obtained in $CDCl_3$ solution at 298 K. [b] In CH_2Cl_2 solution. [c] Measured at 200 K.

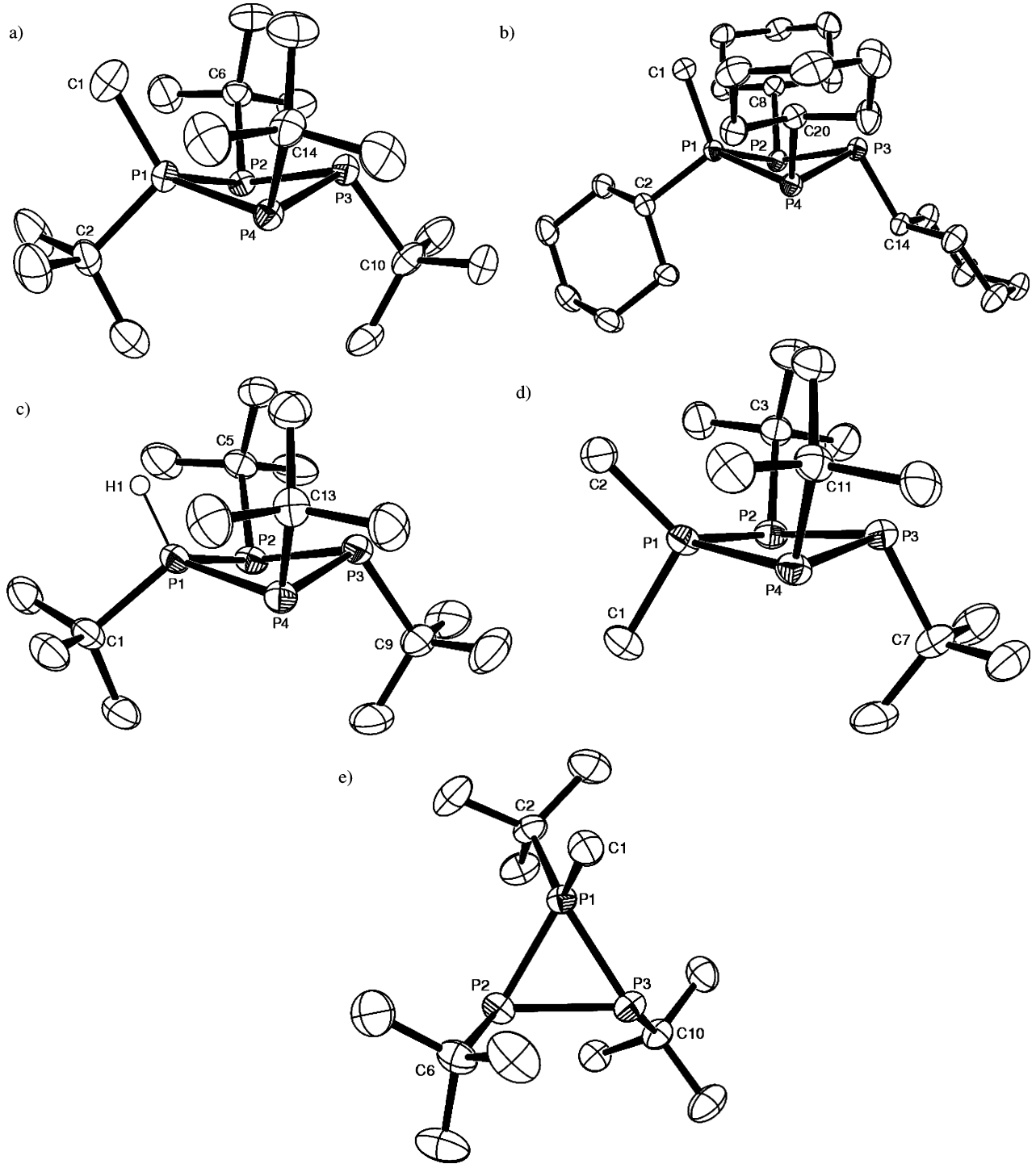


Figure 3. Solid-state structure of the cations in (a) **2a**[OTf], (b) **2b**[OTf], (c) **3a**[OTf], (d) **5**[OTf], and (e) **6a**[OTf], drawn with 50% probability ellipsoids, and hydrogen atoms (except H1 in **3a**) omitted.

of the simulated spectra are shown in Figures 1 and 2. Although the $^{31}P\{^{1}H\}$ NMR spectra for derivatives of **2** are well-resolved at room temperature, the spectra for the protonated cations (**3**) show broad peaks at room-temperature that resolve at 200 K (spectra obtained at 200 K were used in the NMR simulations). Featureless broad signals are observed in the spectra for the ^{t}Bu derivative (**3a**) at room temperature, but peaks for **3b** maintain the basic form of the spectra at low temperature. This dynamic behavior at room temperature is interpreted in terms of labile P−H bonds and rapid exchange in solution. Attempts to slowly grow single crystals of **3b**[OTf] gave only **1b**. In the ^{1}H coupled ^{31}P NMR spectrum of **3a** (200 K), the low field triplet is split into an overlapping, five line, doublet of triplets, with $^{1}J_{PH} = 461$ Hz. This coupling is also observed in the ^{1}H NMR spectrum [7.71 ppm, d (broad peaks), $^{1}J_{PH} = 464$ Hz]. A complicated second-order ^{31}P NMR spin system is observed for **3b** that precludes the determination of the P−H coupling constant, nevertheless, the ^{1}H NMR data reveal $^{1}J_{PH} = 452$ Hz [7.84 ppm, d (broad peaks)].

Table 3. Selected Interatomic Distances and Angles for Cyclodiphosphinophosphonium and Cyclotriphosphinophosphonium Cations[a]

cation	P−C (Å)	P−P (Å)	C−P−P (°)	C−P−C (°)	P−P−P (°)	P−P−P−P (τ, °)
2a	1.848(4) [1,2]	2.204(2) [1,2]	118.6 (2) [1,1,2]		92.04(6) [4,1,2]	
	1.813(4) [1,1]	2.203(2) [1,4]	119.1(2) [1,1,4]		85.10(5) [1,2,3]	
	1.903(4) [2,6]	2.244 (2) [2,3]	109.8(2) [2,1,2]	106.5(2) [1,1,2]	89.85(6) [2,3,4]	21.09
	1.903(4) [3,10]	2.246(2) [3,4]	110.1(2) [2,1,4]		85.08(6) [1,4,3]	
	1.894(3) [4,14]					
2b	1.822(2) [1,2]	2.1952(6) [1,2]	114.45(7) [1,1,2]		91.05(2) [4,1,2]	
	1.797(2) [1,1]	2.1896(6) [1,4]	115.54(7) [1,1,4]		84.92(2) [1,2,3]	
	1.867(2) [2,8]	2.2387(6) [2,3]	113.68(6) [2,1,2]	108.44(8) [1,1,2]	88.68(2) [4,3,2]	23.92
	1.871(2) [3,14]	2.2378(6) [3,4]	113.03(6) [2,1,4]		85.07(2) [1,4,3]	
	1.858(2) [4,20]					
3a	1.850(2) [1,1]	2.191(1) [1,2]	115.29(9) [1,1,2]		92.68(5) [4,1,2]	
	1.32(2) [1,H1]	2.180(1) [1,4]	113.58(8) [1,1,4]		85.17(4) [1,2,3]	
	1.892(2) [2,5]	2.237(2) [2,3]	115.0(9) [H1,1,2]	105.3(9) [1,1,H1]	89.83(4) [2,3,4]	19.86
	1.890(3) [3,9]	2.242(1) [3,4]	115(1) [H1,1,4]		85.30(4) [1,4,3]	
	1.881(3) [4,13]					
5	1.800(2) [1,2]	2.2032(5) [1,2]	106.33(6) [1,1,2]		94.33(2) [4,1,2]	
	1.802(2) [1,1]	2.1983(6) [1,4]	105.12(6) [1,1,4]		85.50(2) [1,2,3]	
	1.890(2) [2,3]	2.2385(6) [2,3]	122.72(6) [2,1,2]	105.99(9) [2,1,1]	92.47(2) [4,3,2]	10.43
	1.890(2) [3,7]	2.2307(6) [3,4]	120.56(6) [2,1,4]		85.80(2) [1,4,3]	
	1.885(2) [4,11]					
6a	1.858(2) [1,2]	2.1465(6) [1,2]	123.15(7) [1,1,2]		62.31(2) [2,1,3]	
	1.806(2) [1,1]	2.1652(6) [1,3]	108.62(7) [1,1,3]	110.41(9) [1,1,2]	59.26(2) [1,2,3]	
	1.886(2) [2,6]	2.2306(6) [2,3]	112.97(6) [2,1,2]		58.43(2) [1,3,2]	
	1.894(2) [3,10]		133.21(6) [2,1,3]			

[a] Numbers in square brackets denote atom labels as shown in Figure 3.

Reaction mixtures of Me_2PCl and Me_3SiOTf with $(^tBuP)_3$ (**4a**) give $^{31}P\{^1H\}$ NMR spectra showing a major product (>95%) that has been simulated (Table 2) as an AB_2X spin system. This product has been isolated and characterized as *meso*-**5**[OTf]. Formation of **5** represents a ring expansion via the selective insertion of Me_2P^+ into the P−P bond between the two identical phosphorus atoms of **4a** (Scheme 1d). Other diastereomeric forms of **5** are not observed. The *cis* configuration of two ^{t}Bu substituents in **4a** presumably provides access to only one P−P bond via the face of the molecule opposite to two substituents. An analogous insertion of "PX" (X = Cl, Br) has been observed for **4a**.[52]

The cyclodiphosphinophosphonium cation **6a** is formed quantitatively in the reaction of **4a** with MeOTf (Scheme 1e) as shown by an AMX spin system in the $^{31}P\{^1H\}$ NMR spectrum (Table 2). Although some second-order effects are indicated by the nonuniform peak intensities (at 101.3 MHz), each signal occurs as a doublet of doublets, with the signals corresponding to the tetracoordinate phosphonium center occurring at low field (X of AMX). The methylation of **4a** is stereoselective at either of the *cis* substituted phosphorus centers to give racemic **6a** (Scheme 1e), and the *meso* isomer is not observed.

The cyclohexyl derivative **6b**[OTf] is observed by $^{31}P\{^1H\}$ NMR spectroscopy (AMX spin system, Table 2) in the reaction mixture of $(CyP)_3$ (**4b**) with MeOTf. The cyclotriphosphinophosphonium salt **2b**[OTf] is a prominent component of the product mixture (Scheme 1g), and over time the concentration of **2b** increases relative to that of **6b**; however, the observation of other unidentified byproducts

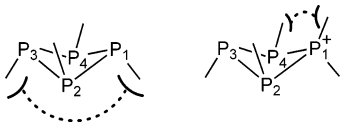


Figure 4. Schematic demonstrating some principle steric interactions in cyclotetraphosphines (left) and cyclotriphosphinophosphonium cations (right).

prevents the definitive identification of a conversion of **2b** → **6b**. An analogous ring expansion has been observed involving $(PhP)_4$ and MeOTf, which gives the corresponding cyclotetraphosphinophosphonium cation quantitatively.[38]

In a related process, the reaction of **4a** with HOTf gives the ring expansion product **3a**[OTf] (Scheme 1c), rapidly and quantitatively, as indicated by $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (Figure 1). Interestingly, addition of equimolar amounts of hydrochloric acid (2.0 M in Et_2O) to **4a** at −80 °C afforded the ring-opened product **7**, almost quantitatively (Scheme 1f). Compound **7** is identified by its characteristic $^{31}P\{^1H\}$ and ^{31}P NMR spectra.[42]

These results illustrate that the nature of the product of a given reaction can be dependent on the substituents, the ring size of the starting cyclopolyphosphine, the electrophile, and the counterion, making predictions difficult. Previous reports of cyclopolyphosphinophosphonium cations involve the assignment of products of type **D** based only on elemental analysis[53−55] or NMR data;[56] therefore, we undertook a crystallographic analysis of **2a**[OTf], **2b**[OTf], **3a**[OTf],

(52) Riegel, B.; Pfitzner, A.; Heckmann, G.; Binder, H.; Fluck, E. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1365−1372.

(53) Issleib, K.; Hoffmann, M. *Chem. Ber.* **1966**, *99*, 1320−1324.
(54) Issleib, K.; Rockstroh, C.; Duchek, I.; Fluck, E. *Z. Anorg. Allg. Chem.* **1968**, *360*, 77−87.
(55) Appel, R.; Milker, R. *Z. Anorg. Allg. Chem.* **1975**, *417*, 161−170.
(56) Laali, K. K.; Geissler, B.; Regitz, M. *J. Org. Chem.* **1995**, *60*, 3149−3154.

Table 4. ^{1}H NMR Data for the Methyl Groups of Cyclotriphosphinophosphonium Cations **2a**[OTf], **2b**[OTf], **5**[OTf], and **6a**[OTf]

compound	δ (ppm)	multiplicity	$^2J_{PH}$ (Hz)	$^3J_{PH}$ (Hz)
2a[OTf]	2.62	d	12	0
2b[OTf]	2.40	d	12	0
5[OTf]	2.66	d	14	0
	2.37	dt	13	8
6a[OTf]	2.36	dd	13	8

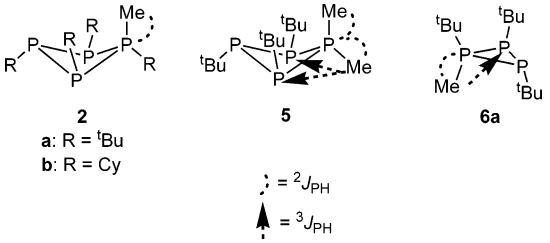


Figure 5. Schematic showing the P−H couplings of the methyl groups of **2a**, **2b**, **5**, and **6a** as observed by ^{1}H NMR spectroscopy.

5[OTf], and **6a**[OTf] in order to rule out potential ring-opened or phosphinophosphorane products. The solid-state structures for these derivatives are shown in Figure 3. All compounds show ionic formulations in the solid state, with the closest anion−cation interactions involving hydrogen atoms of the cations, confirming their identity as examples of cyclic phosphinophosphonium monocations rather than neutral phosphinophosphoranes.

The bond distances and angles of *catena*-phosphorus systems show minimal dependence on the molecular charge. Although the shortest bonds in all crystallographically characterized tri- and tetraphosphorus monocations involve the tetracoordinate phosphonium center (Table 3), the observed P−P (2.15−2.23 Å) bond lengths are consistent with typical P−P single bonds found in neutral [2.24(3) Å for aryl and alkyl tetrasubstituted diphosphines according to a CCDC analysis using Mogul][57] and anionic *catena*-phosphorus systems. Similarly the shortest P−C bond lengths involve the phosphonium center (Table 3).

Cyclotetraphosphines adopt puckered P_4 frameworks in part to minimize the steric interaction between substituents on nonadjacent phosphorus atoms (Figure 4). The addition of a fifth substituent, as in the cyclotriphosphinophosphonium cations, creates a steric imposition between the fifth substituent and substituents on both adjacent phosphorus atoms (Figure 4), which is alleviated by a flattening of the ring, and therefore the averaged P−P−P−P torsional angles (Table 3) in cations **2a**, **2b**, and **3a** are substantially smaller ($\tau = 10-24°$) than those in the neutral cyclotetraphosphines **1a** ($\tau = 24.5°$)[58] and **1b** ($\tau = 31.4°$).[59]

The P_4 framework of **2b**[OTf] exhibits the greatest fold due to the relatively small Me(P1)-Cy(P2,P4) steric repulsions, reflected in the wide C1−P1−C2 angle [108.44(8)°], and narrow range of C−P−P angles [113.03(6)°−115.54-(7)°]. The methylated **2a** exhibits greater ring puckering than the less sterically restricted protonated cation **3a** likely due to packing effects in the crystal and the limited flexibility imposed by the four ^{t}Bu groups. The τ values are approximately equal in **2a** and **3a**, and the planarity of both rings are very similar to that in $(^t\text{BuP})_4$. Finally, the cyclo-P_4 unit of **5** is closer to planarity than both **2a** and **3a**. Thus the reduced Me1(P1)-^{t}Bu(P3) steric interaction allows for the relief of the Me2(P1)-^{t}Bu(P2,P4) interactions by flattening the P_4 ring. As indicated in Table 3, these interactions are also manifested in the narrow C2−P1-C1 angle [105.99(9)°], large C2−P−P angles [120.56(6)°, 122.72(6)°] ,and relatively small C1−P−P angles [105.12-(6)°−106.33(6)°].

Compound **6a**[OTf] crystallizes as a racemic compound in the centrosymmetric space group $P2_1/n$. The steric strain in **6a** resulting from unfavorable *cis* interactions between ^{t}Bu (at C6) and Me (C1) substituents on one face of the molecule and two ^{t}Bu (*C*2 and C10) groups on the other is evidenced by the angle of 72.5° between the plane defined by C1, P1, and C2 and the plane containing the three phosphorus atoms, which is substantially distorted from the ideal angle of 90°. Thus, although the endocyclic angles in **4a**[60] and **6a** are similar, the four-coordinate P1 atom of **6a** is highly distorted with C−P1−P angles ranging from 108.62(7)° to 133.21(6)°.

The ^{1}H NMR data for the methyl groups in derivatives of **2**, **5**, and **6** are presented in Table 4. All tetraphosphorus cations have one signal with doublet multiplicity, while in **5** one methyl group is observed as a six-line doublet of triplets. The signal for the methyl group of **6a** is a doublet of doublets. The observed multiplicities can be rationalized by considering the configurational arrangements for these cations. The methyl protons show coupling to the phosphorus atom to which they are bound ($^2J_{PH}$) and to adjacent phosphorus atoms ($^3J_{PH}$) only if the lone pair is on the same face of the ring (Figure 5). This suggests a dominant through-space mechanism for long-range P−H coupling in these systems.

Conclusions

Triflate salts of cyclotriphosphinophosphonium cations **2a**, **2b**, **3a**, and **3b**, and the cyclodiphosphinophosphonium cation **6a** have been prepared by methylation or protonation of the corresponding neutral cyclo-tri- or -tetraphosphines. The cyclotriphosphinophosphonium triflate **5**[OTf] was also prepared via phosphenium ion insertion into cyclotriphosphine **4a**. The crystal structures of **2a**[OTf], **2b**[OTf], **3a**[OTf], **5**[OTf], and **6a**[OTf] confirm these compounds as the first unequivocal examples of monocyclic *catena*-tri- and -tetraphosphorus monocations. ProtonNMR spectra show that $^3J_{PH}$ is only observed for the

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methyl protons if the lone pair of the phosphine sites are in the *cis* position.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and the Walter C. Sumner Foundation for funding.

Supporting Information Available: Crystallographic information files (CIF) for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0622499