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2-Phosphino-1,3-diphosphonium Ions

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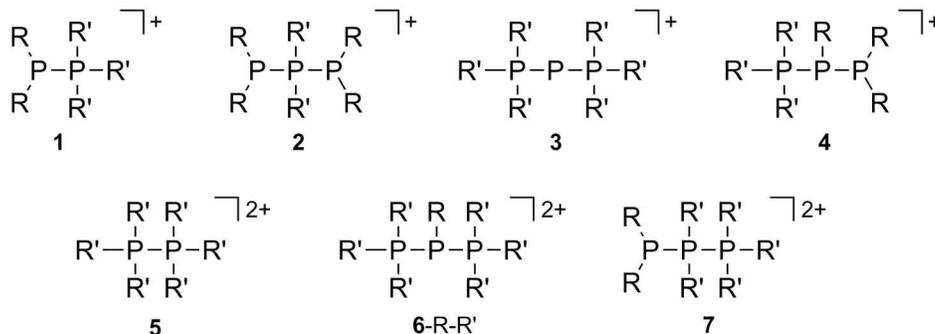
Abstract

A series of 2-phosphino-1,3-diphosphonium trifluoromethanesulfonate salts has been prepared and comprehensively characterized. The compounds represent rare examples of salts containing triphosphorus dications and establish important structural and spectroscopic parameters and trends for catenated phosphorus chains.

Introduction

A variety of analogies between the chemistry of carbon and phosphorus are often related to their diagonal relationship in the Periodic Table,¹ which also indicates the potential for phosphorus to adopt catenated frameworks that exhibit the extent and diversity established for hydrocarbons. However, development of hydrophosphorus frameworks is likely impeded by the relatively low P-P bond enthalpy (P-P = 201 kJ/mol, cf. C-C = 346 kJ/mol)² in neutral compounds, and the facile reactivity of P-H bonds, relative to C-H bonds. We have recently demonstrated that P-P bonded molecules possessing a cationic charge have a P-P bond enthalpy that is comparable to that of the C-C bond in neutral hydrocarbon frameworks.^{3,4} While a variety of cationic catenated phosphorus frameworks have been systematically synthesized and

comprehensively characterized,⁵ the extent and diversity of frameworks is still limited, even for short chain systems. Various derivatives of the prototypical diphosphorus cationic frameworks **1**,⁶ and diphosphorus dicationic frameworks **5**,^{7,8} are known, but examples of triphosphorus cations are rare. Preliminary reports for each of frameworks **2**,⁹ **3**,^{10,11} and **6**,¹² include one structurally characterized derivative, although cyclic derivatives of **3** and **6** involving a hydrocarbon backbone have been studied.^{13–16} We have now applied our versatile synthetic methods for *catena*-phosphorus cationic frameworks^{5,17–21} to prepare and comprehensively characterize a series of 2-phosphino-1,3-diphosphonium (**6**) trifluoromethanesulfonate (triflate) salts, including the solid state structures of four derivatives. The new compounds establish important structural and spectroscopic parameters and trends for catenated phosphorus chains.



Experimental

All reactions were carried out in an IT or MBraun glove box under an N₂ atmosphere. Solvents were dried on an MBraun solvent purification system and stored over 4 Å molecular sieves unless otherwise specified. MeCN was purchased anhydrous from Aldrich and dried over CaH₂ prior to use. Deuterated solvents were purchased from Aldrich or Cambridge Isotope Laboratories, and stored over molecular sieves for 24 hours prior to use. MePCl₂ was purchased from Strem and used as received. ¹PrPCl₂, ¹Pr₂NPCl₂, ^tBuPCl₂, Et₃P, CyPCl₂, Et₃P, and Me₃P (neat and 1.0 M solution in toluene) were purchased from either Aldrich or Strem Chemicals and

used as received. PhPCl_2 , EtPCl_2 , and $\text{Me}_3\text{SiO}_3\text{SCF}_3$ (TMSOTf) were purchased from Aldrich and purified by vacuum distillation prior to use.

Solution ^1H , ^{13}C , and ^{31}P NMR spectra were collected at room temperature on Bruker AC-250 (5.9 T), Bruker Avance 360 (8.4 T) and Bruker Avance 500 (11.7 T) NMR spectrometers. Chemical shifts are reported in ppm relative to trace protonated solvent (^1H), perdeuterated solvent (^{13}C), or an external reference standard (^{31}P , 85% H_3PO_4). NMR spectra of reaction mixtures were obtained by transferring an aliquot of the bulk solution to a 5 mm NMR tube, which was then capped and sealed with Teflon tape. All reported $^{31}\text{P}\{^1\text{H}\}$ NMR parameters for second-order spin systems were derived by iterative simulation of experimental data at 101.3 MHz using gNMR, version 5.0.6.0, and are listed in Table 1. The signs of the P–P coupling constants have been established by assigning the $^1J_{\text{PP}}$ coupling constants as negative.^{22,23} Infrared spectra were collected on samples prepared as nujol mulls between CsI plates using a Bruker Vector FT-IR spectrometer, or by ATR using a Perkin-Elmer Frontier FT-IR spectrometer. Peaks are reported in wavenumbers (cm^{-1}) with intensities (strong, medium, weak) in parentheses, relative to the most intense peak. Melting points were obtained on samples flame-sealed in glass capillaries under dry nitrogen using an Electrothermal apparatus. Elemental analyses were performed on selected compounds by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada.

Unless otherwise stated, crystals for single crystal X-ray diffraction studies were obtained by vapor diffusion at room temperature or from slow diffusion of a layered non-solvent into a saturated solution of the compound. Single crystal X-ray diffraction data were collected on a Bruker D8/APEX II CCD diffractometer at 173 K. All structures except $[\mathbf{6}\text{-}^t\text{Bu-Me}][\text{OTf}]_2$ were solved by direct methods and refined by full-matrix least squares on F^2 (*SHELXL-97* or

SHELXL-2013).²⁴ The compound [6-^tBu-Me][OTf]₂ was solved using the DIRDIF-2008 program suite.²⁵ All non-hydrogen atoms were refined anisotropically while hydrogen atoms were assigned positions based on the *sp*² or *sp*³ hybridization geometries of their attached carbons, and were given thermal parameters 20% greater than those of their parent atoms.

Synthesis of [Me₃P-P^tBu-PMe₃][OTf]₂, [6-^tBu-Me][OTf]₂: A solution of ^tBuPCl₂ (32 mg, 0.2 mmol) and TMSOTf (79.6 μL, 0.44 mmol) in 0.5 mL MeCN was stirred for 5 min in a glass vial. A solution of Me₃P in 0.5 mL MeCN (45.5 μL, 0.44 mmol) was added to the stirring solution by syringe. Once the reaction ceased to visibly fume (*ca.* 5 min), the reaction was capped and stirred for 1 h at room temperature. Vapor diffusion of Et₂O or CH₂Cl₂ into the reaction solution at room temperature after 24-48 h yielded long, needle-like colorless crystals.

Yield: 83mg (0.15 mmol, 77%); Melting Point: 114°C-117°C (decomp.); ¹H{³¹P} NMR (500.1 MHz, CD₃CN, 298K): δ (ppm) = 1.59 (s, 9H, -C(CH₃)₃), 2.32 ppm (s, 18H, -P(CH₃)₃); ¹³C NMR (125.8 MHz, CD₃CN, 298 K): δ = 13.7-14.3 (m, -P(CH₃)₃), 32.2 (dt [²J_{CP} = 14 Hz, ³J_{CP} = 5 Hz], -C(CH₃)₃), 41.5 ppm (dt [¹J_{CP} = 33 Hz, ²J_{CP} = *too broad to determine*], -C(CH₃)₃); FT-IR (ATR, cm⁻¹, [relative intensities]): 1308 (w), 1248 (s), 1224 (m), 1151 (s), 1028 (s), 977 (w), 951 (s), 765 (w), 756 (w), 634 (s), 572 (w), 516 (m). E.A. for C₁₂H₂₇F₆O₆P₃S₂ actual (calculated): C 26.65% (26.77%), H 5.44% (5.05%).

General procedure for the synthesis of [R'₃P-PR-PR'₃][OTf]₂, [6-R-R']₂ (R = Me, Cy, ⁱPr, ⁱPr₂N, Ph; R' = Me, Et) : R'PCl₂ (0.4 mmol) and R'₃P (82.4 μL, 0.8 mmol) were sequentially added to a solution of TMSOTf (2 x 72.4 μL, 0.8 mmol) in 1.6 mL of CH₂Cl₂, with stirring, resulting in fuming and immediate generation of a white precipitate. After stirring for 1 h, the solvent was removed *in vacuo*. Isolated solids were redissolved in MeCN and crystallized by layering with CH₂Cl₂ or Et₂O. The isolated solids for R = NⁱPr₂, Cy, Me and R' = Me were

crystalline, and the solution was decanted from the crystals, which were subsequently dried *in vacuo* and washed with 5 mL hexanes, and 3 x 1 mL CH₂Cl₂. The solids for R' = Et were characterized by ³¹P{¹H} NMR spectroscopy and the relevant data for these compounds is presented in Table 1.

Characterization data for [Me₃P-P(NⁱPr)₂-PMe₃][OTf]₂, [6-NⁱPr-Me][OTf]₂: Yield: 156 mg (0.27 mmol, 67%); Melting Point: 189-190°C (decomp); ¹H{³¹P} NMR (500.1 MHz, CD₃CN, 298K): δ (ppm) = 1.24 (d, slightly broad, 6H, -N(CH(CH₃)₂)₂) and 1.28 (d, 6H, -N(CH(CH₃)₂)₂), 2.22 (s, 18H, -P(CH₃)₃), 3.49 ppm (septet, 1H, -N(CH(CH₃)₂)₂); ¹³C NMR (125.8 MHz, CD₃CN, 298 K): δ = 25.9 and 26.0 (s, -N(CH(CH₃)₂)₂), 48.3 (d (¹J_{CP} = 30 Hz), -P(CH₃)₃), 61.6 ppm (d (²J_{CP} = 11 Hz), -N(CH(CH₃)₂)₂); ¹⁹F NMR (376.50 MHz, CD₃CN, 300 K): δ (ppm) = -79.1 (s). FT-IR (nujol mull, cm⁻¹, [relative intensities]): 2288 (w), 1457 (bs), 1376 (m), 1351 (m), 1263 (bs), 1161 (bs), 1031 (s), 955 (m), 875 (m), 765 (w), 755 (m), 671 (m), 637 (m), 573 (m), 518 (m); E.A. for C₁₄H₃₂F₆NO₆P₃S₂ actual (calculated): C 28.60% (28.91%), H 5.51% (5.55%), N 2.93% (2.40%).

Characterization data for [Me₃P-PCy-PMe₃][OTf]₂, [6-Cy-Me]OTf]₂: Yield: 168 mg (0.298 mmol, 75%); Melting Point: 224-226°C (decomp); ¹H{³¹P} NMR (500.1 MHz, CD₃CN, 298K): δ (ppm) = 1.34 (qt, 1H, H_f), 1.49 (qt, 2H, H_d), 1.67 (qd/td, 2H, H_b), 1.71 (broad d, 1H, H_g), 1.85 (dt, 2H, H_e), 2.06 (broad d, 2H, H_c), 2.27 (s, 18H, -P(CH₃)₃), 2.82 ppm (tt, 1H, H_a); ¹³C NMR (125.8 MHz, CD₃CN, 298 K): δ = 13.0-13.5 (m, -P(CH₃)₃), 25.4 (s, CH₂), 27.8 (d, ³J_{CP} = 13 Hz, CH₂), 34.0-34.2 (m, CH₂), 35.6 ppm (d [¹J_{CP} = 29 Hz], CH_a); FT-IR (nujol mull, cm⁻¹, [relative intensities]): 1457 (bs), 1309 (w), 1260 (bs), 1226 (s), 1159 (s), 1028 (s), 954 (m), 757 (w), 634

equivalents of TMSOTf in CH_2Cl_2 . The precipitates were identified spectroscopically and crystallographically as bis-triflate salts of 2-phosphino-1,3-diphosphonium cations **6**. In MeCN, ^{31}P NMR spectra of the reaction mixtures show the respective derivative of $[\mathbf{6}][\text{OTf}]_2$ as the only phosphorus containing species (Table 1). Broad $^{31}\text{P}\{^1\text{H}\}$ NMR signals are observed for the reaction mixture of MePCl_2 with TMSOTf and PMe_3 . Nevertheless, crystals of $[\mathbf{6}\text{-Me-Me}][\text{OTf}]_2$ redissolved in EtCN show sharp signals interpreted as an AXX' spin system (Figure 1c).

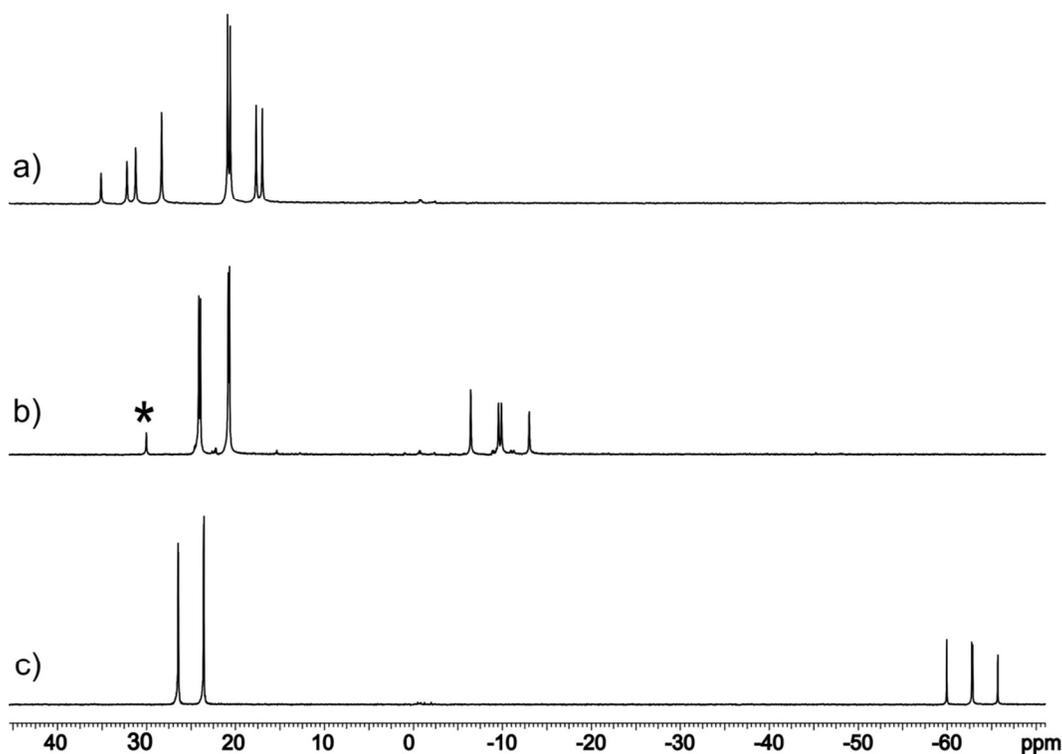


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for selected derivatives of $[\mathbf{6}\text{-R-Me}][\text{OTf}]_2$, showing the variations in spin system imposed by substitution at the central phosphorus atom: (a) $[\text{Me}_3\text{P-P}(\text{N}^i\text{Pr}_2)\text{-PMe}_3][\text{OTf}]_2$, $[\mathbf{6}\text{-N}^i\text{Pr}_2\text{-Me}][\text{OTf}]_2$, A_2B , (b) $[\text{Me}_3\text{P-P}^t\text{Bu-PMe}_3][\text{OTf}]_2$, $[\mathbf{6}\text{-}^t\text{Bu-Me}][\text{OTf}]_2$, AB_2 (asterisk indicates a minor impurity), and (c) $[\text{Me}_3\text{P-PMe-PMe}_3][\text{OTf}]_2$, $[\mathbf{6}\text{-Me-Me}][\text{OTf}]_2$, AXX' .

Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR parameters at 101.3 MHz for derivatives of 2-phosphino-1,3-diphosphonium triflates, $[\mathbf{6}][\text{OTf}]_2$. Derivatives of $[\mathbf{6}\text{-R-Ph}][\text{AlCl}_4]_2$ were previously reported.¹² Coupling constants are derived by iterative fitting of spectra at 298 K and 101.3 MHz.

Compound [R' ₃ P-PR-PR' ₃][A] ₂			Chemical Shift (ppm)		¹ J _{PP} (Hz) ^b	Spin system	Cation label
R'	R	A	δ _{PR'₃}	δ _{PR}			
Me	^t Bu	OTf	22.3	-9.5	-333	AB ₂	[6 - ^t Bu-Me]
	N ⁱ Pr ₂		19.3	31.2	-350	A ₂ B	[6 -N ⁱ Pr ₂ -Me]
	Cy		22.7	-30.8	-307 -326	AXX'	[6 -Cy-Me]
	Me		25.0	-62.6	-285 -295	AXX'	[6 -Me-Me]
	ⁱ Pr		23.0	-27.3	-305 -325	AXX'	[6 - ⁱ Pr-Me]
	Ph		24.7	-46.3	-286 -298	AXX'	[6 -Ph-Me]
Et	N ⁱ Pr ₂	OTf	39.6	22.0	-364	AB ₂	[6 -N ⁱ Pr ₂ -Et]
	Cy		42.4	-47.1	-326 -338	AXX'	[6 -Cy-Et]
	Me		41.7	-74.4	-300 -308	AXX'	[6 -Me-Et]
	ⁱ Pr		42.5	-42.9	-324 -337	AXX'	[6 - ⁱ Pr-Me]
	Ph		42	-60	--- ^a	AXX'	[6 -Ph-Me]
Ph	H	AlCl ₄	23	-120	-286	AX ₂	[6 -H-Ph] ^b
	Me		23	-48	-330		[6 -Me-Ph] ^b
	ⁱ Pr		21	-23	-354		[6 - ⁱ Pr-Ph] ^b

^a signal overlaps with those of diphosphinodiphosphonium ^b ¹J_{PP} previously reported as positive values.¹² Reported as negative values for convention.

The ^{31}P NMR chemical shifts assigned to the central phosphorus atom in derivatives of **6** span a broad range ($\delta_{\text{PR}} = -63$ to 31 ppm), likely due to the variation in the geometry at the central phosphorus atom.¹⁸ Derivatives of **6** can be considered as complexes of two phosphine ligands on a $[\text{PR}]^{2+}$ acceptor, analogous to the recently reported biscarbene derivatives $[(\text{NHC})_2\text{PR}]^{2+}$ and $[(\text{NHC})_2\text{PCI}]^{2+}$.^{26,27} In this context, the chemical shifts of the 4-coordinate (terminal) phosphorus centres ($\delta\text{-PR}'_3$) are essentially independent of the substituent at the central phosphine, with the exception of $\text{R} = \text{N}^i\text{Pr}_2$, in which $\text{N}=\text{P}$ π -bonding is envisaged to mediate the Lewis acidity of $[\text{PN}^i\text{Pr}_2]^{2+}$. Additionally, the σ -electron withdrawing amido-substituent effects a downfield ^{31}P NMR chemical shift, resulting in an A_2B spin system (Figure 1a).

For all derivatives of **6**, the $^1\text{J}_{\text{PP}}$ coupling constants are within the range for phosphinophosponium cations. The largest $^1\text{J}_{\text{PP}}$ value is observed for $[\mathbf{6}\text{-N}^i\text{Pr}_2\text{-Me}][\text{OTf}]_2$, consistent with experimental and computational studies, which show a relationship between electronegativity of the substituent and $^1\text{J}_{\text{PP}}$,^{22,23} although electronic effects on $^1\text{J}_{\text{PP}}$ are expected to be small ($< ca. 5$ Hz).^{28,29} The steric influences on $^1\text{J}_{\text{PP}}$ are evidenced by the large $^1\text{J}_{\text{PP}}$ values observed for $\mathbf{6}\text{-}^t\text{Bu-Me}$, $\mathbf{6}\text{-}^i\text{Pr-Me}$ and $\mathbf{6}\text{-Cy-Me}$.

The solid state structures of $[\mathbf{6}\text{-Me-Me}][\text{OTf}]_2$, $[\mathbf{6}\text{-Cy-Me}][\text{OTf}]_2$, $[\mathbf{6}\text{-}^t\text{Bu-Me}][\text{OTf}]_2$ and $[\mathbf{6}\text{-N}^i\text{Pr}_2\text{-Me}][\text{OTf}]_2$ were determined by single-crystal X-ray diffraction and selected structural parameters are compared with those of $[\mathbf{6}\text{-H-Ph}][\text{AlCl}_4]_2$ in Table 2.¹² Figure 3 shows two perspectives of each dication in the solid state structures of $[\mathbf{6}\text{-Me-Me}][\text{OTf}]_2$, $[\mathbf{6}\text{-Cy-Me}][\text{OTf}]_2$, $[\mathbf{6}\text{-}^t\text{Bu-Me}][\text{OTf}]_2$ and $[\mathbf{6}\text{-N}^i\text{Pr}_2\text{-Me}][\text{OTf}]_2$. The images in the right column illustrate the conformation adopted by each compound that minimizes steric interactions between the alkyl groups on the terminal phosphorus atoms and that on the central phosphorus atom. It is apparent

that in all compounds except [6-Me-Me][OTf]₂, one of the methyl groups on the terminal phosphorus atoms is eclipsed with the plane defined by the three P atoms. The P-P bonds in derivatives of [6-R-Me][OTf]₂ are significantly longer than those in [3-Ph][AlCl₄] (avg 2.1311(12) Å),¹⁰ consistent with a single P-P bond in derivatives of **6** and a degree of multiple-bonding in [3-Ph][AlCl₄].

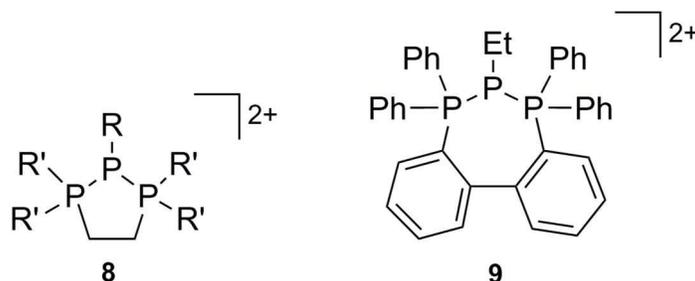


Figure 2. Representative examples of previously described cyclic 2-phosphino-1,3-diphosphonium ions

All four crystallographically characterized derivatives of [6-R-Me][OTf]₂ display a larger P-P-P angle than in the previously reported cyclic derivatives [8-R-R'] (R = Et, ^tPr; R' = Et, Ph; P-P-P avg = 89.0°)^{15,30} and **9** (P-P-P = 96.6°),³⁰ and also adopt a less pyramidal geometry at the central phosphorus atom ($\Sigma_{\text{angles}} = 310\text{-}318^\circ$).¹⁵ The C-P-C angles in ^tBu₃P (107°-108°, $\Sigma_{\text{angles}} = 322^\circ$)³¹ are comparable to the C-P-P and P-P-P angles in derivatives of **6** ($\Sigma_{\text{angles}} = 323^\circ\text{-}325^\circ$).

Table 2. Selected bond lengths and angles in the solid state structures of [6-R-Me][OTf]₂, in comparison with parameters for [Ph₃P-PH-PPh₃][AlCl₄]₂, [6-H-Ph][AlCl₄]₂.

	[6-R-Me][OTf] ₂				[6-H-Ph][AlCl ₄] ₂ ¹²
	R = Me	R = Cy	R = ^t Bu	R = N ⁱ Pr ₂ ^a	
P-P (Å)	2.2262(5) 2.2273(5)	2.1979(5) 2.1976(6)	2.2391(15) 2.2354(16)	2.2181(9) <i>to</i> 2.2271(9)	2.205(1) 2.224(1)
P-P-P (°)	109.49(2)	103.11(2)	100.97(5)	104.26(3) <i>to</i> 105.48(3)	106.39(4)
P2-E (Å) E = H, C, N	1.842(1)	1.858(1)	1.925(3)	1.655(2) <i>to</i> 1.660(2)	1.13(2)
Σ_{angles} (at P2)	310	318	317	318 <i>to</i> 319	287

^a Asymmetric unit contains three crystallographically independent molecules of [6-ⁱNPr₂-Me][OTf]₂. Range and standard deviation (σ) of the mean value are given. ^b Only one of the three independent cations in the asymmetric unit displays a close contact with an associate triflate anion.

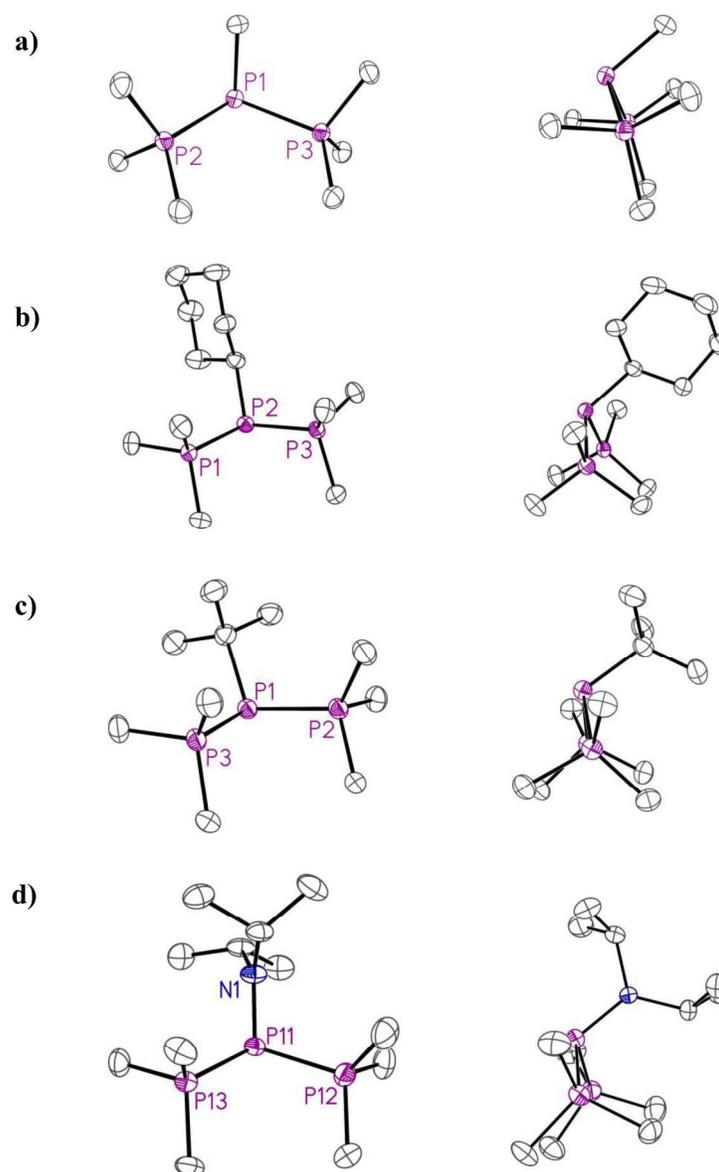
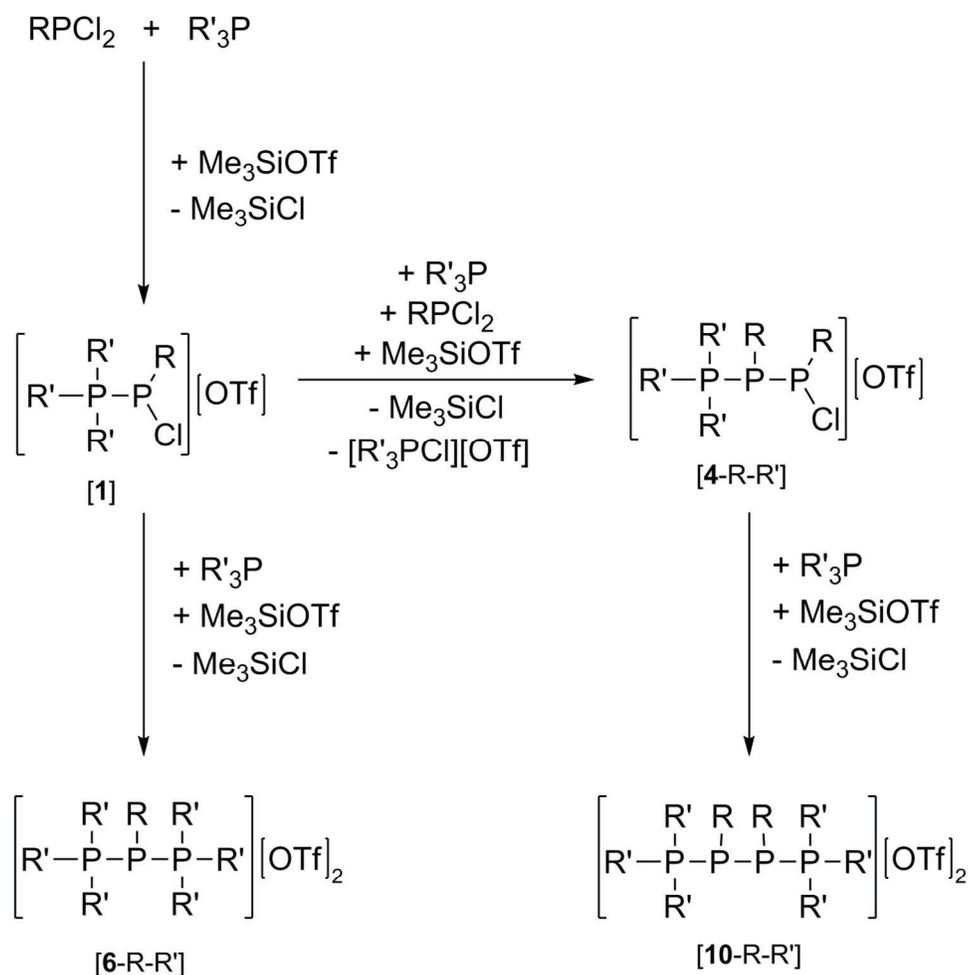


Figure 3. Two perspectives of each dication in the solid state structures of (a) [6-Me-Me][OTf]₂, (b) [6-Cy-Me][OTf]₂, (c) [6-t-Bu-Me][OTf]₂ and (d) [6-iNPr₂-Me][OTf]₂. Hydrogen atoms are omitted for clarity and thermal ellipsoids shown at the 50% probability level.

The reaction of a dichlorophosphine with a trialkylphosphine and TMSOTf has multiple potential outcomes depending on the stoichiometric association of dichlorophosphine and trialkylphosphine, which are illustrated in Scheme 2. We have previously reported that derivatives of [1][OTf] are readily isolated from equimolar reaction mixtures. In the presence of

excess Ph_3P , NMR spectra indicate the intermediate formation of the triphosphorus cations $[\mathbf{4}\text{-R-Ph}]^+$, from which the tetraphosphorus dication $[\mathbf{10}\text{-R-Ph}]^{2+}$ are formed, and a variety of derivatives of $[\mathbf{10}\text{-R-R}'][\text{OTf}]_2$ have been isolated and comprehensively characterized.²⁰ The formation of both $[\mathbf{6}\text{-R-R}'][\text{OTf}]_2$ and $[\mathbf{10}\text{-R-R}'][\text{OTf}]_2$ has been previously noted by NMR spectroscopy of reactions involving P_2biphen (2,2'-bis(diphenylphosphino)-1,1'-biphenyl) or dppe with EtPCl_2 in the presence of SnCl_2 .³² This report now confirms that for some derivatives, formation of the triphosphorus dication $[\mathbf{6}\text{-R-R}']^{2+}$ and $[\mathbf{10}\text{-R-R}'][\text{OTf}]_2$ can be considered competitive processes. Depending on the reaction stoichiometry, derivatives of $[\mathbf{6}\text{-R-R}'][\text{OTf}]_2$ are formed quantitatively when $\text{R}' = \text{Me}$, as shown by ^{31}P NMR spectra of reaction mixtures. When $\text{R} = \text{Ph}$, mixtures of $[\mathbf{6}\text{-Ph-R}'][\text{OTf}]_2$ and $[\mathbf{10}\text{-Ph-R}'][\text{OTf}]_2$ are observed, and when $\text{R}' = \text{Et}$, analogous mixtures are formed, with a preference for $[\mathbf{10}\text{-R-Et}][\text{OTf}]_2$. Derivatives of $[\mathbf{1}][\text{OTf}]$ are formed immediately (< 5 min) upon combination of the reagents. Transformation to $[\mathbf{10}\text{-R-R}'][\text{OTf}]_2$ requires that $[\mathbf{1}][\text{OTf}]$ and $\text{R}'\text{PCl}_2$ are P-P coupled by a redox process effected by $\text{R}'_3\text{P}$ as the reducing agent and activated by TMSOTf as an abstracting agent. The resulting intermediate $[\mathbf{4}\text{-R-R}'][\text{OTf}]$ reacts further with TMSOTf to effect a second chloride abstraction and addition of a second phosphine to give $[\mathbf{10}\text{-R-R}'][\text{OTf}]_2$. In contrast, formation of $[\mathbf{6}\text{-R-R}'][\text{OTf}]_2$ precludes the redox process with abstraction of the chloride anion to facilitate interaction of a second phosphine ligand on the central phosphorus acceptor.

Scheme 2. Formation of phosphinodiphosphonium or diphosphinodiphosphonium salts from reaction of a dichlorophosphine with a trialkylphosphine and TMSOTf .



Summary

A series of 2-phosphino-1,3-diphosphonium bis-trifluoromethanesulfonate salts have been synthesized and comprehensively characterized, and ^{31}P NMR parameters have been obtained for a range of derivatives, examples of which were originally identified by Schmidpeter.¹² The compounds are formed in reactions of dichlorophosphines, tertiary phosphines and a halide abstracting agent. Depending on the substitution pattern and stoichiometry, formation of 2-phosphino-1,3-diphosphonium cations is competitive with formation of 2,3-diphosphino-1,4-

diphosphonium²⁰ cations, involving a redox process. This series of compounds augments the developing chemistry of *catena*-phosphorus cations.

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Supporting Information Available

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