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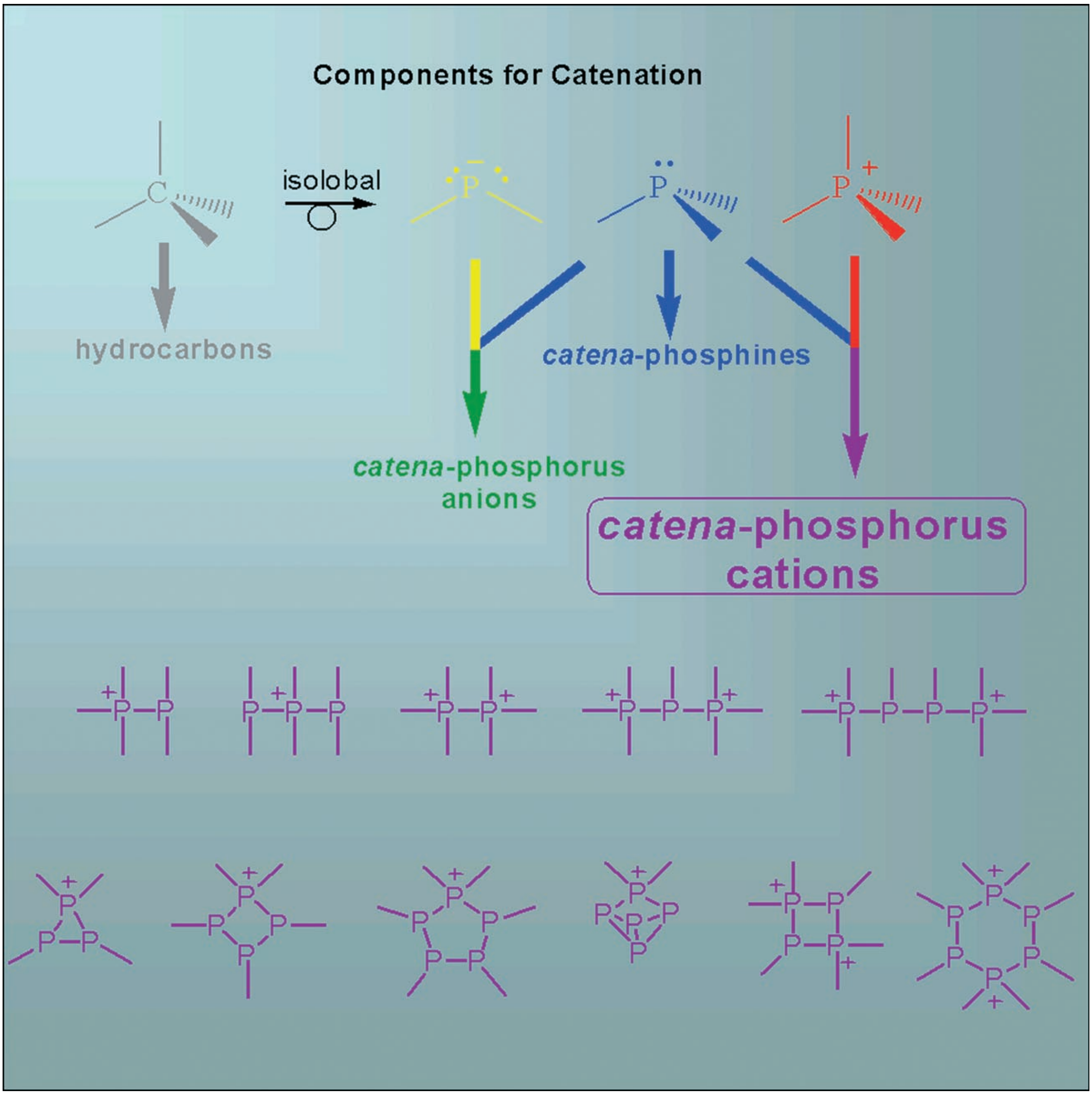
catena-Phosphorus Cations

C. Adam Dyker and Neil Burford*[a]



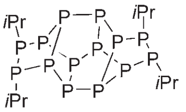
Abstract: Recent advances towards a systematic development of *catena*-phosphorus cations are reviewed. The cations represented in this new and developing chapter in fundamental phosphorus chemistry complement the series of neutral and anionic polyphosphorus compounds.

Keywords: catenation · cations · phosphines · phosphorus

1. Introduction

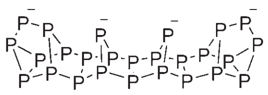
Catenation (homoatomic bonding) is a prominent feature of carbon chemistry that is also evident for phosphorus, consistent with the diagonal relationship (similar electronegativities) between carbon and phosphorus in the Periodic Table. Although the allotropic forms of phosphorus as well as the established series of *catena*-phosphines[1–4] and *catena*-phosphorus anions[1–3,5] represent an extensive *catena*-phosphorus chemistry, relatively few derivatives of *catena*-phosphorus cations have been reported.[6–28] Nevertheless, the isolobal nature of PH_4^+ and CH_4 highlights a potential for parallels to *catena*-carbon chemistry that are important in the context of fundamental understanding of catenation for phosphorus.

As *catena*-phosphines and *catena*-phosphorus anions,[1–5,29,30] such as **1**[31] and **2**,[32,33] are formally derived by directly linking phosphine (**I**) and phosphide (**II**) units, *catena*-phosphorus cations (phosphinophosphonium ions) are envisaged as a combination of phosphine (**I**) and phosphonium (**III**) units. Herein we present the recent systematic development of *catena*-phosphorus cations, which represent a new direction in fundamental phosphorus chemistry.



$P_{14}iPr_4$

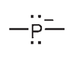
1



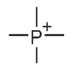
P_{26}^{4-}

2

I



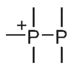
II



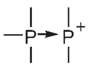
III

2. Phosphinophosphonium Ions

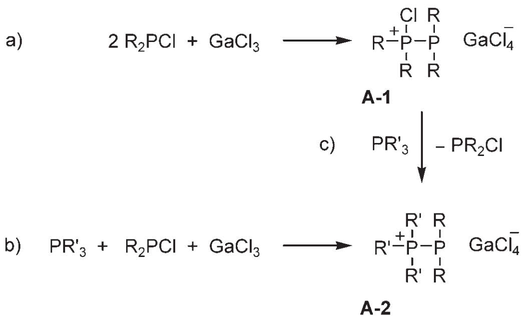
Phosphinophosphonium ions (**A**), which contain a single P−P bond between a phosphine and a phosphonium center, were first proposed as products of the reaction of a diphosphine with alkyl or aryl halides,[6] and in reactions of chlorophosphines with $AlCl_3$.[7–9,11–13,28] The solid-state structures of a number of derivatives recently confirmed the connectivity.[28] Chlorophosphonium derivatives (**A-1**) are prepared from a chlorophosphine and 0.5 equivalents of an appropriate halide-abstracting agent ($GaCl_3$ or TMSOTf (TMS = trimethylsilyl, OTf = trifluoromethanesulfonyl)) (Scheme 1a).



A



A'



Scheme 1. Synthetic approaches to phosphinophosphonium ions.

Phosphinophosphonium derivatives of type **A-2** can be prepared directly from combinations of a chlorophosphine, a phosphine, and a halide abstractor (Scheme 1b).[13,28] Derivatives of **A** exhibit two well-separated doublets in the ^{31}P NMR spectra with $\delta_{phosphine}$ in the range −23 to 3 ppm,

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$\delta_{phosphonium}$ in the range 15 to 80 ppm, and $^1J_{PP}$ in the range 320 to 360 Hz (see also Table 1).[13]

The solid-state structure of the phosphinophosphonium cation in [Me_3PPPh_2][OTf] is shown in Figure 1, illustrating the slightly distorted tetrahedral geometry of the tetracoordinate phosphorus center and the typical pyramidal geometry of the three-coordinate phosphorus center.[13] These geometrical parameters, coupled with the typical single P–P bond lengths in these species (Table 1), indicate the presence of a stereochemically active lone pair of electrons on the tricoordinate (phosphine) center and imply that no significant π-bonding is involved. In contrast to the typical covalent bonds in neutral and anionic polyphosphorus compounds, the P–P bond in phosphinophosphoniun ions is unusual in that it can be described as a homoatomic coordinate bond between a phosphine ligand and a phosphenium ion acceptor (**A′**). This model accounts for the extensive ligand-exchange chemistry that has been developed for derivatives of **A**.

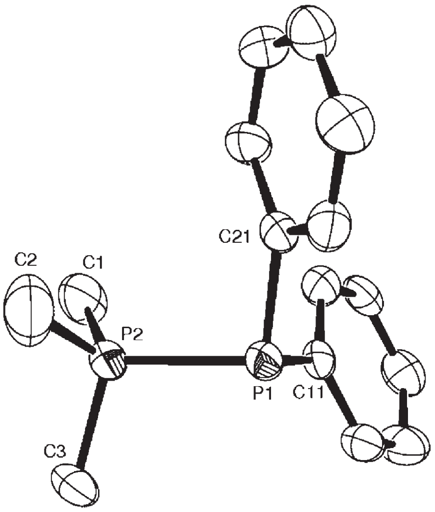
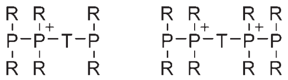


Figure 1. Solid-state structure of the cation in (Me_3PPPh_2)(OTf). Ellipsoids drawn at the 50 % probability level.

Ligand exchange at the phosphenium center can be effected by any neutral molecule that is a stronger donor than the stabilizing phosphine in the phosphinophosphonium cation (**A**),[13,28,34] as illustrated in Scheme 1 c by the replacement of R_2PCl in **A-1** for R'_3P. This is a versatile and convenient method for the formation of various element–phosphorus bonds.[34–36] Ligand exchange with diphosphines that bear a hydrocarbon tether (T) leads to polyphosphorus cations **3** and dications **4**.[37,38] The solid-state structure of the ethane-tethered octaphenylbis(phosphinophosphonium) dication (a derivative of **4**) of the bis(tetrachlorogallate) salt is shown in Figure 2.


$R_2P-\overset{+}{P}R_2-T-PR_2$ $\quad$ $R_2P-\overset{+}{P}R_2-T-\overset{+}{P}R_2-PR_2$

3 **4**

T = CH_2, C_2H_4, C_6H_{12}, p-C_6H_4

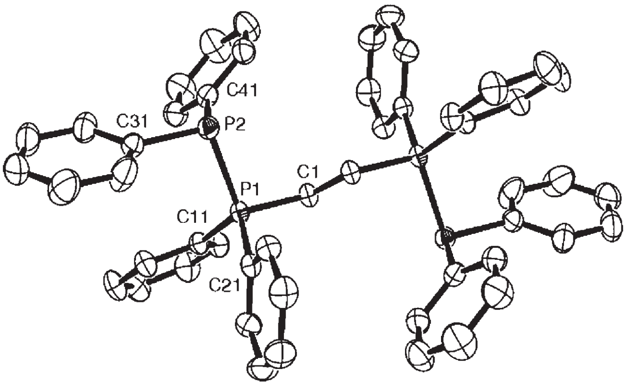
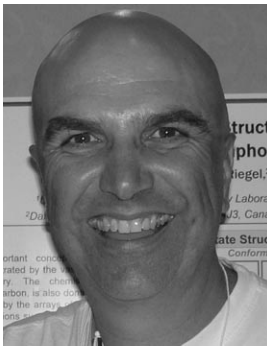


Figure 2. Solid-state structure of the dication in [$Ph_2PPh_2PCH_2CH_2PPh_2PPh_2$][$GaCl_4$]$_2$. Ellipsoids drawn at the 50 % probability level.

3. Diphosphinophosphonium Ions

Ligand-exchange reactions of phosphinophosphonium cations with P–P diphosphines give *catena*-diphosphinophosphonium ions (**B**), of which derivatives **B-1b** and **B-1c** can



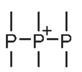
Neil Burford *is a native of Liverpool, U.K. He obtained a BSc(Hons) from Cardiff Univ. (1979) and a PhD at the Univ. of Calgary with Prof. Tristram Chivers. After postodoctoral studies with Prof. Ronald Cavell (Univ. of Alberta) and with Prof. Jack Passmore (Univ. of New Brunswick), he was appointed Assistant Prof. (1987) and later Prof. (1995) at Dalhousie Univ. He was an Alexander von Humboldt Fellow (1996), a Killam Professor (1998), Harry Shirreff Prof. of Chemical Research (2000), and a Canada Research Chair (Tier 1) (2001). His research is focused on the discovery of new structure and bonding through synthetic chemistry involving the heavy elements of group 15.*

Adam Dyker *obtained a BSc(Hons) degree from the Univ. of New Brunswick (2002) and a PhD at Dalhousie Univ. (2007) under the supervision of Prof. Neil Burford where his research focused on the development of catena-phosphorus cations. He is currently an NSERC Postdoctoral Fellow with Distinguished Prof. Guy Bertrand at the Univ. of California, Riverside.*

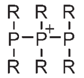
Table 1. Selected NMR parameters and structural data for one representative of each class of *catena*-phosphorus cation. Parameters in bold involve the phosphonium center(s).

Label	Formula	$^{31}P\{^1H\}$ Spin System	$^{31}P\{^1H\}$ δ [ppm]	$^1J_{PP}$ [Hz]	P–P [Å]	Ref.
A-2	$[Ph_3P\text{-}PPh_2][GaCl_4]$	AX	**13**	**−340**	**2.220(6)**	[13]
			−12			
B-1b	$[Me_2P\text{-}PMe_2\text{-}PMe_2][OTf]$	A_2B	**12**	**−298**	**2.2160(6)**	[39]
			−62		**2.1883(6)**	
C-1a	$[(tBuP)_2PtBuMe][OTf]$	AMX	**−20**	**−334**	**2.1465(6)**	[43,44]
			−51	**−317**	**2.1652(6)**	
			−110	−123	2.2306(6)	
D-1a	$[(tBuP)_3PtBuMe][OTf]$	AB_2X	**18**	**−275**	**2.204(2)**	[43,44]
			−29	−152	**2.203(2)**	
			−43		2.244(2)	
					2.246(2)	
E-1b	$[(MeP)_4PMe_2][OTf]$	AA′BB′X	**101**	**−346**	**2.206(1)**	[45]
			20	−277	**2.207(1)**	
			24	−263	2.185(1)	
					2.197(1)	
					2.189(1)	
F-1a	$[P_5Br_2][Al(OR)_4]$	A_2B_2X	**20**	**(−)320.9**	**2.156(7)**	[16,17]
	$R=C(CF_3)_3$		162	(−)148.7	2.239(8)	
			−237		2.211(8)	
G-1	$[Mes^*P=P(Mes^*)(Me)][OTf]$	AX	**237**	**(−)633**	**2.2024(2)**	[49]
			332			
H-1	$[Ph_3P\text{-}P=P\text{-}Mes^*][OTf]$	AMX	641	**(−)384**	**2.206(1)**	[50]
			334	(−)580	2.025(1)	
			25			
I-1	$[Ph_3P\text{-}P=PPh_3][AlCl_4]$	AX_2	**30**	**(−)502**	**2.137(6)**[b]	[52]
			−174		**2.2128(6)**[b]	
J-4b	$[Me_3P\text{-}PMe_3][OTf]_2$	A_2	**28.44**	**−19.9**	**2.198(2)**	[65]
K-1	$[Ph_3P\text{-}PH\text{-}PPh_3][AlCl_4]_2$	AB_2	**23**	**(−)286**	**2.205(1)**	[24]
			−120		**2.224(1)**	
L1a	$[Ph_3P\text{-}PPh\text{-}PPh\text{-}PPh_3][OTf]_2$[c]	AA′BB′	**24**	**−343**	**2.258(1)**	[69]
			−33	−124	2.221(1)	
M-1	$[\{2,6\text{-}(OMe)_2C_6H_4\}_6P_4][Me_3SnF_2]_2$	A_2B_2	**41.2**	**(−)287**	**2.231**	[27]
			2.2		**2.232**	
N-1b′	$[Me_2P(PPh)_4PMe_2][GaCl_4]_2$	AA′A″A‴BB′	**11.2**	**−295.2**	**2.2014(9)**	[71]
			−53.5	−4.0	**2.2081(9)**	
					2.2308(9)	

[a] Crystal data is of $(RO)_3Al\text{-}F\text{-}Al(OR)_3$ salt ($R=C(CF_3)_3$). [b] Values for one of two cations in the asymmetric unit. [c] NMR data presented for major diastereomer only

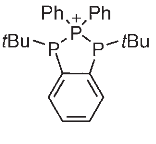


B

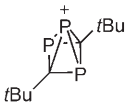


B-1

a: R = I
b: R = Me
c: R = Ph



B-2



B-3

also be prepared from the direct combination of diphosphine, chlorophosphine, and TMSOTf.[39] The solid-state structure of the prototypical cation in $[Me_6P_3][OTf]$ shown in Figure 3 reveals a crystallographic nonsymmetry (P1 ≠ P3) that is averaged by bond rotation in solution to give an AB_2 spin system in the ^{31}P NMR spectra. The $\delta_{phosphine}$, $\delta_{phosphonium}$, and $^1J_{PP}$ values are consistent with those observed for phosphinophosphonium cations (Table 1). Cation **B-1a** can be synthesized from an analogous direct reaction involving $I_2P\text{-}PI_2$, PI_3, and $AgAl[OC(CF_3)_3]_4$,[14] whereas the unique diphosphinophosphonium ions **B-2**[13] and **B-3**[15] can be prepared by alternative procedures. The triflate salt of **B-2** is formed in the complicated, but high-yielding reaction of 1,2-bis(di-*tert*-butylphosphino)benzene with the pentaphenyl

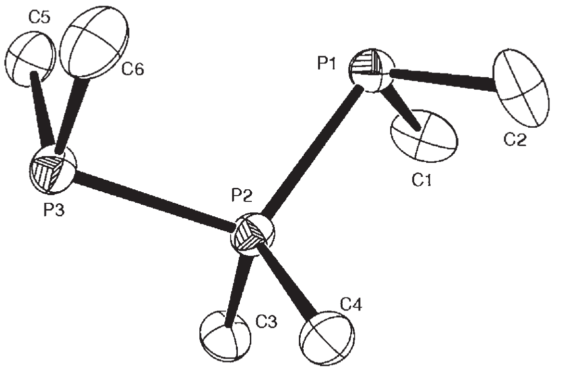
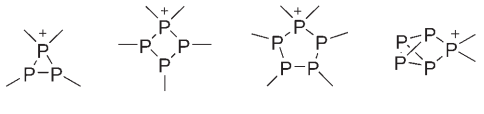


Figure 3. Solid-state structure of the cation in $[Me_6P_3][OTf]$. Ellipsoids drawn at the 50 % probability level.

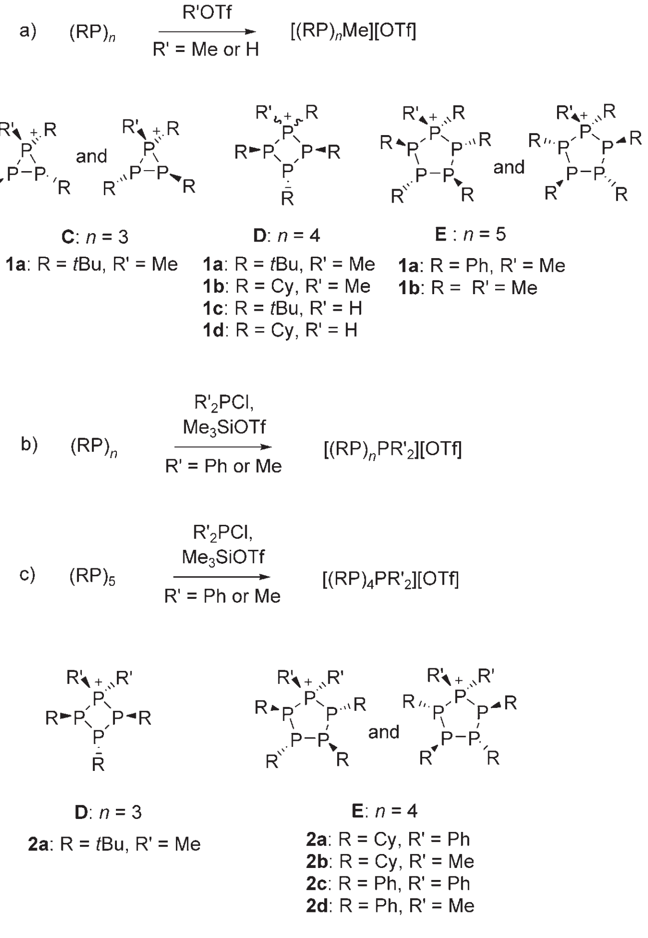
derivative of the phosphinophosphonium cation **A**. The tetrachloroaluminate salt of **B-3** is formed by the reaction of the unusual (tBuC)$_2$P$_3$Cl cage with AlCl$_3$.

4. Cyclopolyphosphinophosphonium Ions



C **D** **E** **F**

Triphosphinophosphonium (**D**) and tetraphosphinophosphonium (**E**) cations were first proposed on the basis of elemental analysis data for compounds isolated from the alkylation of cyclotetra- and cyclopentaphosphines with CCl$_4$ or MeI,[40–42] but examples have only recently been definitively characterized.[39,43–46] Triflate salts of cations with frameworks **C-1**,[44] **D-1**,[44] and **E-1**[45] can be prepared in high yields by methylation or protonation (**D-1** only) of cyclopolyphosphines (Scheme 2a). Frameworks **D-2** and **E-2** are also formed by insertion of a phosphenium ion into cyclotri- and tetraphosphines to give ring-expanded cations (Scheme 2b). In contrast, cyclopentaphosphines react with phosphenium cations with retention of the cyclopentaphosphorus ring (Scheme 2c), which indicates a redistribution process.[39,43] Solid-state structures of a number of derivatives (**C-1a, D-1a**, **D-1b**, **D-1c**, **D-2a E-1b**, **E-2b**, **E-2c**, **E-2d**) confirm the distinctly ionic formulations.[44,45]



Scheme 2. General synthetic methods for the preparation of *catena*-cyclopolyphosphinophosphonium ions. OTf = trifluoromethanesulfonate, Cy = cyclohexyl.

Whereas the ^{31}P{^{1}H} NMR spectra for derivatives of **C** and **D** are essentially first order, the five-membered frame of **E** necessarily imparts magnetic inequivalence and gives rise to complex second-order spectra. Interpretation of the experimental spectra for all derivatives of **E** has required iterative simulation as AA′BB′X (symmetrically substituted derivatives **E-1b** and **E-2a**, **E-2b**, **E-2c**, **E-2d**) or ABCDX (**E-1a**) spin systems. The averaged C_2 symmetry in solution, indicated by the AA′BB′X spin systems, contrasts the C_1 solid-state structures and imply a low-energy conformational pseudorotation process,[45] as understood for cyclopentane.[47] Unique conformations are observed in the solid state for each derivative, such as the envelope conformation (at P4) of **E-1b** shown in Figure 4.

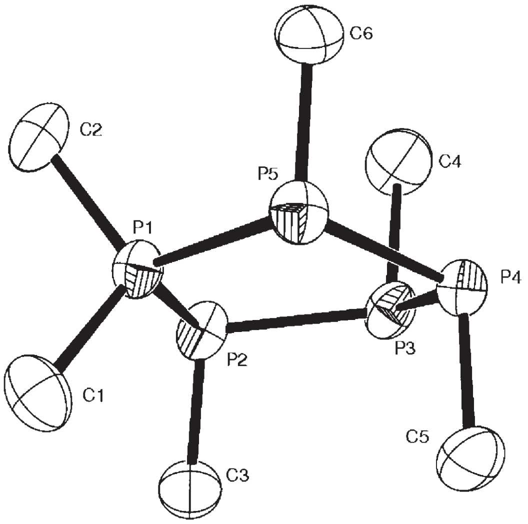
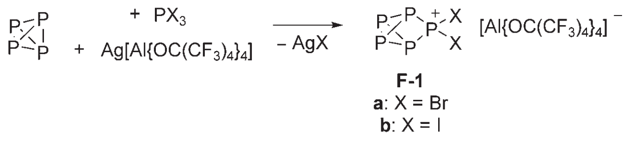


Figure 4. Solid-state structure of the cation in [cyclo-Me$_6$P$_5$][OTf]. Ellipsoids drawn at the 50 % probability level.

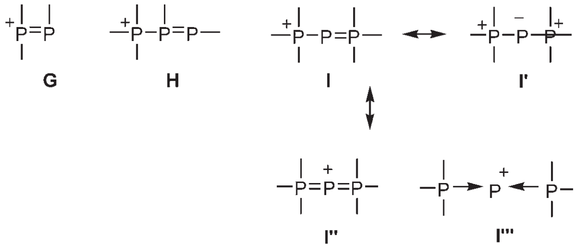
The cluster pentaphosphorus cations **F** have been prepared by the reaction of Ag[Al{OC(CF$_3$)$_4$}$_4$], PX$_3$ (X = Br, I), and white phosphorus, representing the insertion of the phosphenium ion PX$_2$$^+$ into a P–P bond of P$_4$ (Scheme 3).[17]



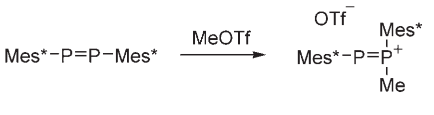
Scheme 3. Formation of cationic pentaphosporus clusters.

5. Unsaturated Phosphinophosphonium Ions

Diphosphenes with the generic formula RPPR contain a formal P=P double bond and represent catenated dicoordinate phosphorus frameworks that provide access to unsaturated phosphinophosphonium ions with topologies such as **G** and **H**. Methylation of the classical diphosphene[48]



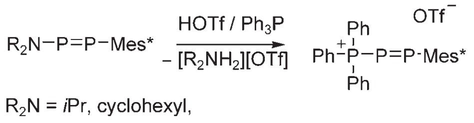
Mes*P=PMes* (Mes*=2,4,6-tri-*tert*-butylphenyl) (Scheme 4) gives **G-1**,[49] for which the coordination model implied for phosphinophosphonium cations **A′** does not apply. The cation features a planar C_3P_2 core and a characteristic P=P bond length of 2.024(2) Å.



G-1

Scheme 4. Methylation of a diphosphene. Mes=mesityl=2,4,6-trimethylphenyl.

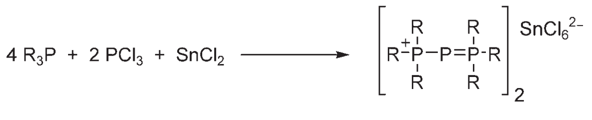
Cation **H-1**, composed of a phosphonium moiety and a diphosphene moiety, was prepared by the selective protonation at the nitrogen center of P-aminodiphosphenes in the presence of triphenylphosphine (Scheme 5).[50]



H-1

Scheme 5. Formation of the unsaturated monocation **H-1**.

As shown in Scheme 6, reduction of PCl_3 with $SnCl_2$ in the presence of a phosphine gives derivatives of framework **I**,[51–53] which can also be considered with bonding models **I′**, **I″**, or **I‴**. These frameworks have also been referred to as triphosphenium ions. Recent reports of cyclic derivatives represent chelate complexes of P^+, **I‴**,[26,51,53–60] and a synthetic source of P(I), as demonstrated by ligand-exchange reactions with stronger donors.[52,61] Cyclic derivatives of triphosphenium ions, with four- to seven-membered C_nP_3 rings ($n=1$–4) have also been prepared or observed in solution by means of ^{31}P NMR spectroscopy.[26,51,57–60]

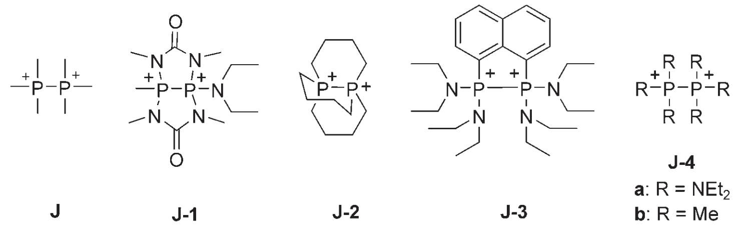


I-1

Scheme 6. Reduction of PCl_3 to give derivatives of **I**.

6. Diphosphonium Ions

The P–P-bonded diphosphonium unit **J** was first assigned on the basis of elemental analysis data and IR spectroscopy[62] for products isolated from reactions of red phosphorus with alkyl iodides.[63,64] Examples of the diphosphonium unit were definitively characterized in unique polycyclic frameworks (**J-1**,[18] **J-2**,[22] and **J-3**[26]) and in the presence of sterically bulky amine substituents (**J-4a**[19]). Alkylation reactions of diphosphines or phosphinophosphonium cations provide a general synthetic approach to hexaalkyl-1,2-diphosphonium dications such as the prototypical **J-4b**, a direct analogue of hexamethylethane, and a series of derivatives have been crystallographically characterized (Figure 5).[65] The ^{31}P NMR $\delta_{\text{phosphonium}}$ values for derivatives of **J** are consistent with those in phosphinophosphonium cations, but the $^1J_{PP}$ values (19–94 Hz) are smaller than for P–P bonds featuring at least one phosphine center.[65]



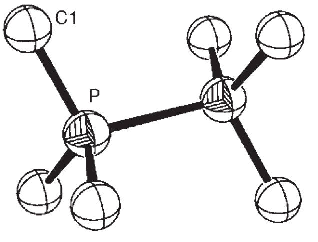
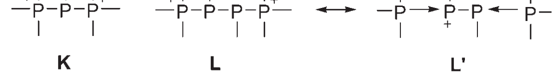
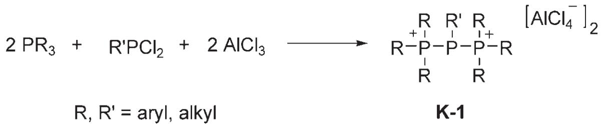


Figure 5. Solid-state structure of the diphosphonium dication in $[Me_6P_2]$-$[OTf]_2$. Ellipsoids drawn at the 50 % probability level.

7. Mono- and Diphosphinodiphosphonium Ions

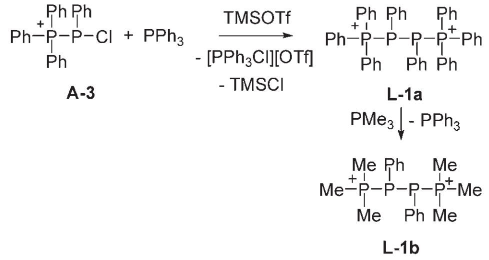
Dichlorophosphines react with 2 equivalents of a tertiary phosphine in the presence of $AlCl_3$ to give 2-phosphino-1,3-diphosphonium ions **K** (Scheme 7),[24] which can also be prepared by protonation or alkylation of derivatives of **I**.[24,66–68]





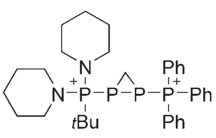
Scheme 7. Preparation of phosphinodiphosphonium ions K.

The analogous tetraphosphorus dicationic framework of type **L**, involving two phosphine centers between two terminal phosphonium centers, has been synthesized by reductive coupling of chlorophosphinophosphonium cations **A-3** (Scheme 8).[69] Unique derivatives of the tetraphosphorus

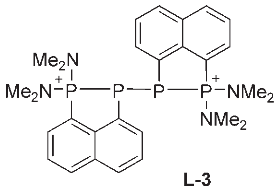


Scheme 8. Preparation of diphosphinodiphosphonium ions **L-1**. TMS = trimethylsilyl.

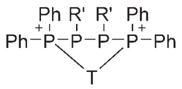
framework **L** have been reported, including **L-2**, which is prepared from a triphosphenium ion **I**,[25] and the bicyclic compound **L-3**.[26] Derivatives of **L-4** are prepared by a similar method to that for **L-1a** in that the reaction involves a reductive coupling between a chlorophophinophosphonium ion and dichlorophosphine before ring closure.[70]



L-2



L-3



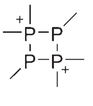
L-4

T = $(CH_2)_n$ (n = 1,2,4), etc
R' = Et, Ph

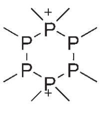
Importantly, derivative **L-1a** represents a bisphosphenium dication stabilized by two phosphine ligands (**L'**), and accordingly undergoes ligand exchange to provide **L-1b**, demonstrating a versatile approach to derivatization.[69] The solid-state structure of the dication **L-1b** is shown in Figure 6.

8. Cyclopolyphosphinodiphosphonium Ions

A cyclodiphosphinodiphosphonium ion **M**, the first cyclodiphosphonium cation, was isolated in low yield as the $[Me_3SnF_2]^-$ salt from the reaction of 2,6-dimethoxyphenyl(trimethyl)stannane with $PClF_2$.[27] However, high-yielding general synthetic routes to cyclotetraphosphinodiphosphonium ions **N** involve the stoichiometric combination of $(PhP)_5$, Ph_2PCl, and $GaCl_3$ in a melt mixture at 165 °C.[71] The previously mentioned hexaphenylpentaphosphorus monocation **E-2c** is observed by means of NMR spectroscopy as an intermediate at lower temperatures (Scheme 9). Whereas octaphenylcyclotetraphosphinodiphosphonium dication **N-1a** adopts a twist-boat conformation in the solid state, a conventional chair conformation is observed for the tetramethyl derivative **N-1b'**. Both configurational isomers **N-1b** and **N-1b'** are observed by using ^{31}P NMR spectroscopy upon dissolution of samples of crystalline **N-1b'**, and the spectra have been simulated as AA'A''A'''BB' spin systems.



M



N

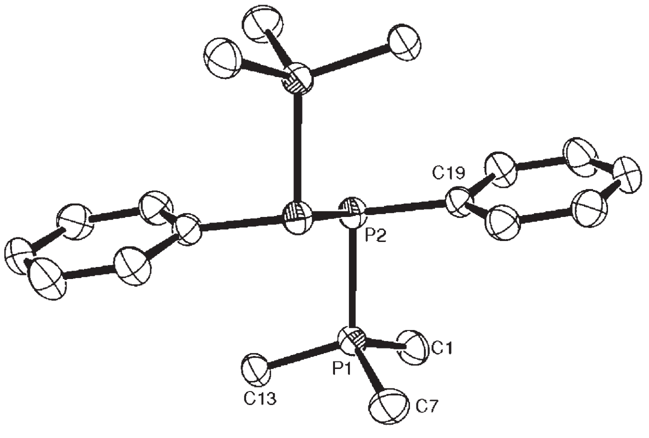
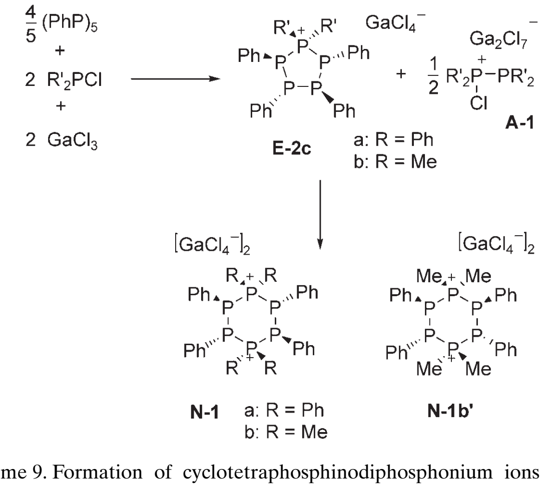


Figure 6. Solid-state structure of the dication in $[Me_3PPPhPPhPMe_3][OTf]_2$. Ellipsoids drawn at the 50 % probability level.



Scheme 9. Formation of cyclotetraphosphinodiphosphonium ions **N** via cyclotetraphosphinophosphonium ions in a molten mixture.

Conclusions

The diagonal relationship between carbon and phosphorus, and the isolobal relationship between methane and phosphine and/or phosphide has often been invoked in drawing comparisons between the chemistry of carbon and phosphorus.[1–4,72–74] In this context, the development of *catena*-phosphorus cations represents a new direction in fundamental phosphorus chemistry that complements the established series of neutral and anionic *catena*-phosphorus compounds. Figure 7 catalogues the potential topologies for acyclic phosphinophosphonium monocations and dications (up to four phosphorus atoms) and cyclic phosphinophosphonium monocations and dications (up to six phosphorus atoms). Less than half of the potential topologies have been reported, defining a number of synthetic objectives and promising a diverse array of structural arrangements and reactivity. Currently, the degree of charge and catenation for *catena*-phosphorus cations are much lower than for the corresponding neutral and anionic species, and cations that contain more than three positive charges and/or six phosphorus atoms represent important targets in this new field. The first cyclotriphosphinodiphosphonium cations have been reported.[75]

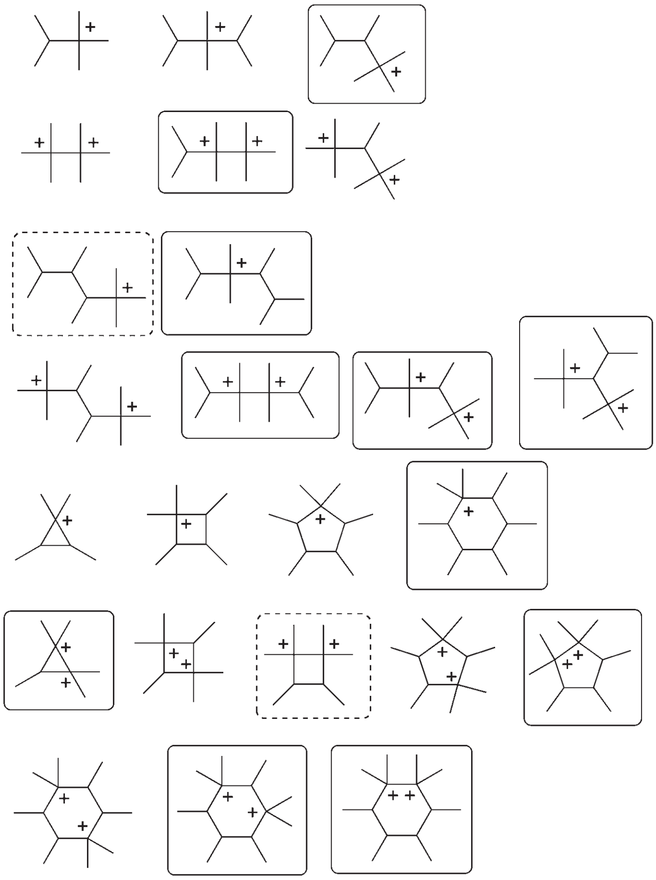


Figure 7. Phosphinophosphonium frameworks (each vertex represents a phosphorus center). Frameworks in solid boxes have not been reported; frameworks in dotted boxes have been observed and will be reported in due course.

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