Synthesis and characterization of elusive cyclo-di- and -tri-phosphino-1,3-diphosphonium salts: fundamental frameworks in *catena*-organophosphorus chemistry†

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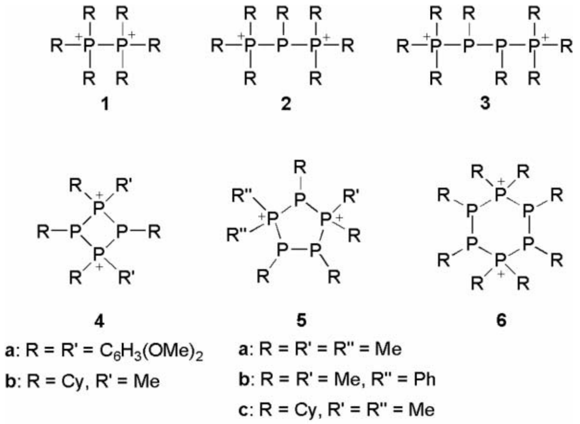
Reaction of a cyclophosphinophosphonium cation with neat MeOTf represents a general and high-yield synthetic approach to dications enabling the isolation of the first derivatives of 2,4,5-triphosphino-1,3-diphosphonium as bis-triflate salts.

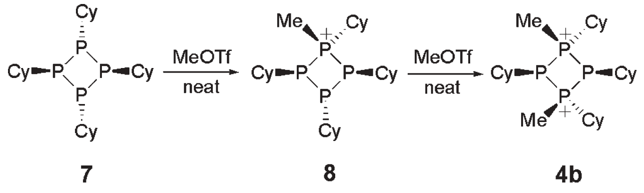


Despite the many parallels between the chemistry of carbon and phosphorus,[1] the established catenation chemistry of phosphorus is underdeveloped in comparison to hydrocarbon chemistry. We have recently exploited a variety of synthetic approaches to obtain series of phosphinophosphonium monocations that complement the previously known series of *catena*-phosphines[2] and *catena*-phosphinophosphide anions.[3] While phosphorus anions are commonly observed as multiply-charged species and many trianions are known (*e.g.* P_7^{3-}), polyphosphorus dications are represented by the few derivatives of frameworks **1**,[4] **2**,[5] **3**,[6] **4**[7] and **6**.[8] Preparative methods for these compounds are specific, few have been generally applied, and some provide low yields, as exemplified by the isolation of **4a**[Me_3SnF_2]$_2$ (1,1,2,3,3,4-hexakis(2,6-dimethoxyphenyl)-2,4-diphosphino-1,3-diphosphonium bis-difluorotrimethylstannate).[7]

Compounds based on framework **5** have not yet been reported despite the prevalence of cyclopentaphosphines and cyclotetraphosphinophosphonium species and the apparent thermodynamic preference for the P_5 framework.[3a,9] Additionally, recent isolation of [*cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$],[10] a neutral, isoelectronic analogue of a 3,4,5-triphosphino-1,2-diphosphonium framework, suggests that derivatives of **5** are viable synthetic targets. We have now used binary mixtures (in the absence of solvent) of cyclotetraphosphines, cyclopentaphosphines or cyclotetraphosphinophosphonium cations with MeOTf (OTf = trifluoromethanesulfonate or triflate) as high yield approaches to salts of cyclophosphinodiphosphonium dications.

$^{31}P\{^1H\}$ NMR spectra of a suspension composed of $(PCy)_4$ (**7**) in excess MeOTf initially (within 1 h) show only an A_2MX spin system that is characteristic of cyclotriphosphinophosphonium cation, **8** (Scheme 1).[11] After 17 h, two triplets characteristic of a higher symmetry A_2X_2 spin system are observed (Table S1, ESI†). The reaction mixture was recrystallized from acetonitrile (isolated yield 86%) as 1,2,3,4-tetracyclohexyl-1,3-dimethyl-2,4-diphosphino-1,3-diphosphonium (**4b**) bis-triflate. The symmetric (approximate C_{2v}) solid state structure‡ of the dication **4b**, shown in Fig. 3, is consistent with the A_2X_2 spin system observed in the solution $^{31}P\{^1H\}$ NMR spectrum. Table 1 compares selected structural parameters for **4b** with **4a**, as well as for precursors **7** and **8**.

The presence of methyl groups at P1 and P3 in **4b** effects greater P–P–P angles at the phosphonium centers (bold values in Table 1) and a necessary contraction at the phosphine vertices relative to the neutral all-*trans* precursor, **7**.[12] The fold of the ring is essentially independent of the number of methylations [**4b**: P(4)–P(3)–P(2)–P(1) 23.11°, P(2)–P(3)–P(4)–P(1) 23.20°; *cf.* **8**: P–P–P–P 23.6–24.2°[11]] despite the sizeable compression observed on installation of the first methyl group (*cf.* **7**: P–P–P–P 31.4°).[12] In contrast, the sterically bulky substituents on the homoleptic derivative, **4a**, impose a planar P_4 conformation and an all-*trans* orientation of the substituents around the ring.[7] The P–P bond lengths in **4b** are typical for phosphinophosphonium cations (2.17–2.34 Å) and are generally shorter than those in the neutral **7**.[12] Similarly, the P–C bond lengths [1.793(2)–1.866(2) Å] in **4b**, are



Scheme 1

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† Electronic supplementary information (ESI) available: Synthetic procedures (**4b**, **5a–c** and **11**), $^{31}P\{^1H\}$ NMR data, and X-ray data for **4b**[OTf]$_2$·MeCN, **5b**[OTf]$_2$ and **5c**[OTf]$_2$. See DOI: 10.1039/b707741f

Table 1 Selected homoatomic distances (Å) and bond angles (°) for $\mathbf{4a}[SnMe_3F_2]_2$,[7] $\mathbf{4b}[OTf]_2$, **7**,[12] **8**[OTf],[11] $\mathbf{5b}[OTf]_2$, $\mathbf{5c}[OTf]_2$, **10**[OTf] and **12**[OTf][a]

	$\mathbf{4a}[Me_3SnF_2]_2$	$\mathbf{4b}[OTf]_2$	**7**	**8**[OTf]	$\mathbf{5b}[OTf]_2$	$\mathbf{5c}[OTf]_2$	**12**[OTf]
P–P Range	2.231–2.232	2.209–2.219	2.224(2)	2.1952(6)–2.2387(6)	2.199–2.238	2.193(2)–2.234(2)	2.183(1)–2.223(1)
P–P Avg	2.232	2.214	2.224(2)	2.215	2.228	2.213	2.204
P–P1–P	nr[b]	**92.76(3)**	85.47(6)	**91.05(2)**	**107.17(9)**	**109.58(8)**	**107.87(4)**
P–P2–P	nr	82.29(3)		84.92(2)	95.84(10)	95.05(8)	95.54(4)
P–P3–P	nr	**92.74(3)**		88.68(2)	**109.25(10)**	**106.26(8)**	104.56(4)
P–P4–P	nr	82.64(3)		85.07(2)	93.99(10)	105.23(7)	109.08(4)
P–P5–P					93.96(9)	101.79(7)	97.46(4)

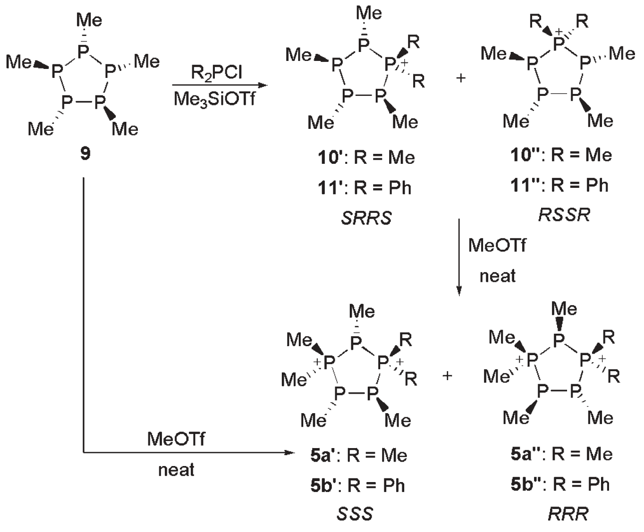
[a] Bold values correspond to the phosphonium centre. [b] nr = Not reported.

shorter than those in **7** [P–C 1.874(2) Å],[12] particularly in the case of the phosphonium P–C bonds.

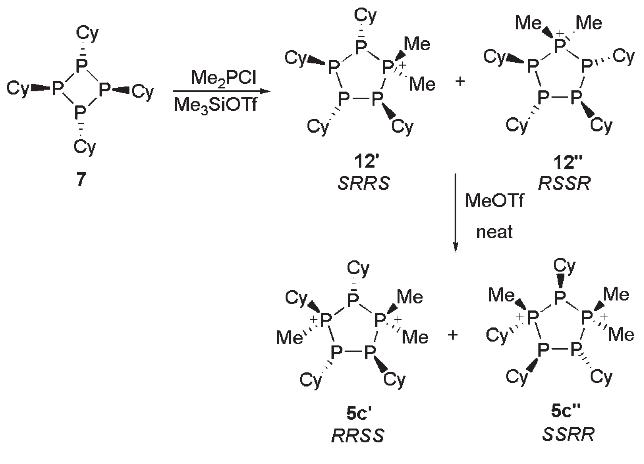
By analogy with the formation of **4b**, pentamethylcyclopentaphosphine (**9**) in neat MeOTf affords the first example of a cyclo-2,4,5-triphosphino-1,3-diphosphonium dication **5a** as a racemic mixture (Scheme 2). $\mathbf{5a}[OTf]_2$ was observed as the sole product in ^{31}P NMR spectra and was isolated in high yield (82%). Unlike the reaction of **7** to provide **4b**, a monocationic intermediate is not observed as **5a** is formed quantitatively in <1 min. However, the probable progression through **10** is evidenced by the formation of **5a** (*S,S,S* and *R,R,R*) in the reaction of **10**[OTf] (*S,R,R,S* and *R,S,S,R*)[13] with neat MeOTf.

As for **10**[OTf], a racemic mixture (*S,R,R,S* and *R,S,S,R*) of **11** is formed in the reaction of **9** with Ph_2PCl and Me_3SiOTf. Subsequent reaction of isolated **11**[OTf] with MeOTf, in the absence of solvent, results in a racemic mixture (*S,S,S* and *R,R,R*) of 2,4,5-trimethyl-1-diphenyl-3-dimethyl-2,4,5-triphosphino-1,3-diphosphonium (**5b**) bis-triflate (Scheme 2) with an isolated yield of 50%. Similarly, the analogous racemic mixture (*R,S,S,R* and *S,R,R,S*) of **12**, formed *via* the reaction of **7** with Me_2PCl and Me_3SiOTf,[13] reacts with neat MeOTf to give the *R,R,S,S* and *S,S,R,R* enantiomers of $\mathbf{5c}[OTf]_2$ in high yield (86%), as shown in Scheme 3.

Iterative simulations of $^{31}P\{^1H\}$ solution (d_3-MeCN) NMR spectra (Table S1, ESI†) of dications **5a** (Fig. 1) and **5c** (Fig. 2)



Scheme 2



Scheme 3

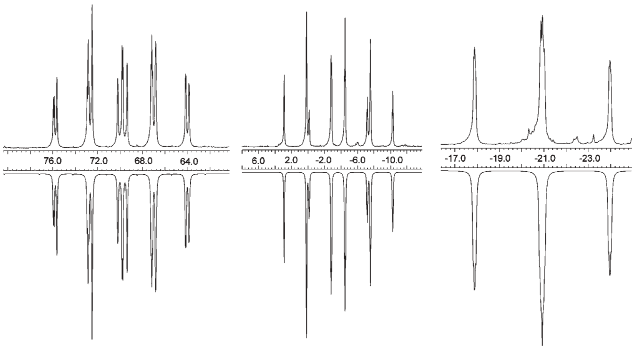


Fig. 1 Experimental (top) and simulated (inverted) expansions of $^{31}P\{^1H\}$ NMR spectrum at 101.3 MHz for $\mathbf{5a}[OTf]_2$. Appropriate parameters are given in ESI.†

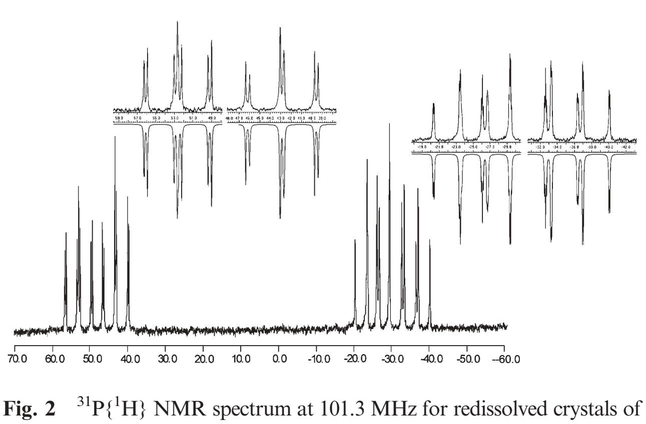


Fig. 2 $^{31}P\{^1H\}$ NMR spectrum at 101.3 MHz for redissolved crystals of $\mathbf{5c}[OTf]_2$ with expansions of the ABGMX spin system showing simulated data inverted. Parameters are given in ESI.†

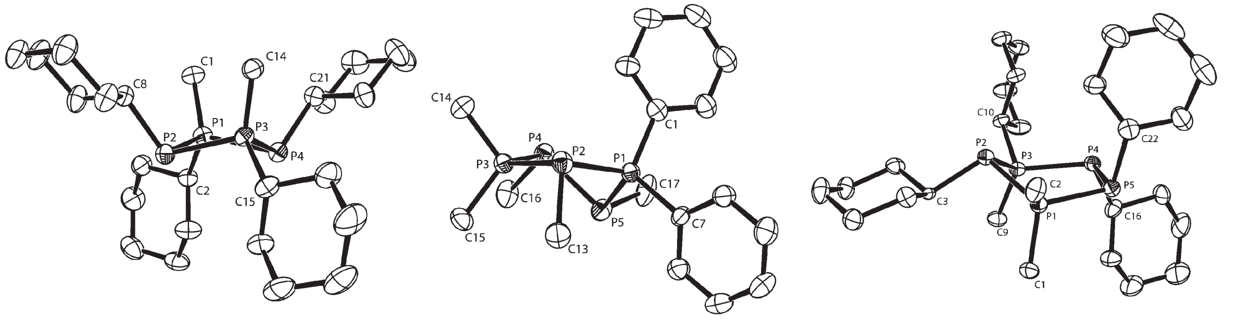


Fig. 3 ORTEP view of the dications in **4b**[OTf]$_2$·MeCN, (*R*,*R*,*R*)-**5b**[OTf]$_2$ and (*S*,*S*,*R*,*R*)-**5c**[OTf]$_2$ with hydrogen atoms omitted. Thermal ellipsoids are shown at 50% probability.

were successfully fit to ABGMX spin systems,[14] confirming the predicted C_1 symmetry. The values of both $^1J_{\mathrm{PP}}$ and $^2J_{\mathrm{PP}}$ are comparable with monocations **10**, **11** and **12**. $^1J_{\mathrm{PP}}$ and $^2J_{\mathrm{PP}}$ directly involving phosphonium centers are larger due to the increased presence of *cis* substituents, as has been previously described.[15] ^{31}P{^{1}H} NMR spectra for redissolved crystalline samples of **5b**[OTf]$_2$ show a complicated signal pattern that is essentially identical to that observed for reaction mixtures.

X-Ray crystallographic analysis‡ of **5b**[OTf]$_2$ (Fig. 3) confirms the presence of crystallographically equivalent enantiomers in the solid state. As determined by Cremer–Pople puckering analysis, **5b** adopts a twist conformation where the two adjacent phosphine centers (*i.e.* P4 and P5) are located out of the plane while **5c** assumes an envelope on P2.[16] Both conformations render the phosphonium centers in the same plane, minimizing steric repulsion between the *cis* substituents. Both the P–P and P–C bond lengths of **5b** and **5c** are similar to those in **4b**[OTf]$_2$ and the P–P–P angles for **5b** and **5c** are predictably wider than those in the more strained P_4 ring of **4b**[OTf]$_2$. As expected, P–P–P angles at phosphonium centers (bold values in Table 1) are significantly larger than those at phosphine centers (non-bold).

In summary, methylation of cyclophosphines, or cyclophosphinophosphonium cations using MeOTf in the absence of solvent is a versatile high-yield approach to prepare cyclopolyphosphinodiphosphonium ions, including the first derivatives of 2,4,5-triphosphino-1,3-diphosphonium dications.

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Notes and references

‡ Crystallographic data for **4b**[OTf]$_2$·MeCN, **5b**[OTf]$_2$ and **5c**[OTf]$_2$ are provided in ESI.†

CCDC 640152–640154. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707741f

1 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley & Sons, Ltd, Chichester, 1998.
2 (*a*) M. Baudler and K. Glinka, *Chem. Rev.*, 1994, **94**, 1273; (*b*) M. Baulder and K. Glinka, *Chem. Rev.*, 1993, **93**, 1623.
3 (*a*) M. Baudler, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 419; (*b*) R. Wolf and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2006, **632**, 727.
4 (*a*) E. V. Nikitin, A. S. Romakhin, V. A. Zagumennov and Y. A. Babkin, *Electrochim. Acta*, 1997, **42**, 2217; (*b*) D. Schomburg, G. Bettermann, L. Ernst and R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 975; (*c*) R. W. Alder, C. Ganter, C. J. Harris and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 1172; (*d*) P. Kilian, A. M. Z. Slawin and J. D. Woollins, *Dalton Trans.*, 2006, 2175; (*e*) R. M. Siddique and J. M. Winfield, *Can. J. Chem.*, 1989, **67**, 1780; (*f*) J. J. Weigand, S. D. Riegel, N. Burford and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7969.
5 S. Lochschmidt, G. Muller, B. Huber and A. Schmidpeter, *Z. Naturforsch., Teil B*, 1986, **41**, 444.
6 C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2006, **128**, 9632.
7 L. Heuer, L. Ernst, R. Schmutzler and D. Schomburg, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1507.
8 J. J. Weigand, N. Burford, M. D. Lumsden and A. Decken, *Angew. Chem., Int. Ed.*, 2006, **45**, 6733.
9 (*a*) J. Hahn, M. Baudler, C. Kruger and Y.-H. Tsay, *Z. Naturforsch., Teil B*, 1982, **37**, 797; (*b*) N. Burford, C. A. Dyker and A. Decken, *Angew. Chem., Int. Ed.*, 2005, **44**, 2364; (*c*) J. Ma, A. Hozaki and S. Inagaki, *Inorg. Chem.*, 2002, **41**, 1876.
10 R. Wolf, M. Finger, C. Limburg, A. C. Willis, S. B. Wild and E. Hey-Hawkins, *Dalton Trans.*, 2006, 831.
11 N. Burford, C. A. Dyker, M. D. Lumsden and A. Decken, *Angew. Chem., Int. Ed.*, 2005, **44**, 6196.
12 J. C. J. Bart, *Acta Crystallogr., Sect B.*, 1969, **25**, 762.
13 C. A. Dyker, S. D. Riegel, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7464.
14 An appropriate designation of spin system is complicated for derivatives of **5**. Typically, the furthest downfield resonance is denoted by the latest letter in the alphabet, and the furthest upfield by the earliest letter. However, by convention the designation of the letter in the spin system is determined by calculating the ratio $\Delta\delta(\mathrm{P_iP_{ii}})/J_{\mathrm{P_iP_{ii}}}$. If the value exceeds 10, the resonances are considered to be pseudo-first order and the assigned letters are separated, however if the value is less than 10, consecutive letters are assigned. For **5**, it is not possible to comply with both of these conventions simultaneously and the spin systems have been assigned according to the latter convention.
15 (*a*) J. P. Albrand and D. Gagnaire, *Chem. Commun.*, 1970, 874; (*b*) J. P. Albrand and J. B. Robert, *J. Chem. Soc., Chem. Commun.*, 1974, 644.
16 (*a*) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (*b*) D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.