Bifunctional diphosphorus Lewis acids from cyclodiphosphadiazanes†

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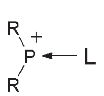
The quantitative displacement of triflate groups in 1,3-ditriflato-2,4-bis(2,6-dimethylphenyl)cyclodiphospha-2,4-diazane by DMAP (4-dimethylaminopyridine) or Me_3P gives dicationic complexes containing bifunctional diphosphorus Lewis acceptors.

Cationic phosphine centers are readily prepared from phosphines[1] bearing good anionic leaving groups that are displaced by neutral ligands. Chlorophosphines (in the presence of Me_3SiOTf) or Mes*NPOTf (Mes* = 2,4,6-tri-*tert*-butylphenyl; OTf = trifluoromethanesulfonate)[2] react with a wide variety of Lewis bases to give phosphenium cationic complexes of type **1**[3–8] and phosphadiazonium complexes of type **2**,[6,9–12] respectively.



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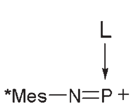

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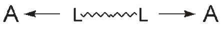

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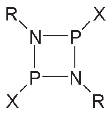

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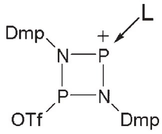
a: R = Mes*, X = OTf
b: R = Dmp, X = Cl
c: R = Dmp, X = OTf



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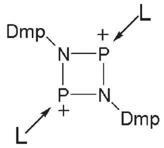

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a: L = DMAP
b: L = Me_3P

Analogous complexes with two charges have been realized using diphosphine and diamine ligands that tether two phosphorus cation acceptors, generically represented by **3**.[4,10] Moreover, reductive coupling of chloro- derivatives of **1** provide dications that behave as complexes involving a bifunctional P–P diphosphenium acceptor, generically represented by **4**,[3] demonstrating the ability of such compounds to accommodate more than one charge.

We have now exploited the well-established series of cyclodiphospha-2,4-diazanes **5** as synthetic origins for complexes of cyclophosphenium **6** and cyclodiphosphenium **7** frameworks that represent dimers of phosphadiazonium complexes of type **2**. Isolation of derivatives of **7** introduces the potential for development of oligomeric and polymeric polycationic systems.

Solution ^{31}P NMR spectra of reaction mixtures containing $DmpNH_2$ (Dmp = 2,6-dimethylphenyl) and PCl_3 in the presence of Et_3N[13] show two signals (intensity ratio ~95 : 5) assigned to 1,3-dichlorocyclodiphospha-2,4-diazane,[14–16] **5b**, with the chlorine substituents in a *cis* [$\delta(^{31}P)$ = 210.1 ppm] and *trans* [$\delta(^{31}P)$ = 295.4 ppm] configuration with respect to the approximate plane of the P_2N_2 ring. Reaction of **5b** with AgOTf in hexane gives an almost quantitative yield of 1,3-ditriflato-2,4-bis(2,6-dimethylphenyl)-cyclodiphospha-2,4-diazane **5c** as a *cis* (98%) [$\delta(^{31}P)$ = 182.8 ppm] and *trans* (2%) [$\delta(^{31}P)$ = 272.4 ppm] mixture. A crystalline sample of the *cis* isomer **5c** (Fig. 1a, Table 2) exhibits two ^{31}P CP/MAS NMR signals (Table 1), consistent with the observation of two crystallographically non-equivalent phosphorus centers.

Solution ^{31}P NMR spectra of a reaction mixture containing **5c** with one equivalent of DMAP show two doublets [$\delta(^{31}P)$ = 191.0 and 150.5 ppm, $^2J_{PP}$ = 48.7 Hz], consistent with a non-symmetric monocation in **6a**[OTf] (isolated 78%). Fig. 1b shows that cation **6a** contains a covalently bound OTf substituent at one phosphorus center that is *cis*-configured with a DMAP ligand at the other phosphorus center.

Solution ^{31}P NMR spectra of a mixture containing **5c** with two equivalents of DMAP show a single resonance [$\delta(^{31}P)$ = 149.1 ppm] assigned to **7a**$[OTf]_2$ (isolated 89%). The symmetric *cis*-configured dication **7a** (Fig. 1c) contains two crystallographically different phosphorus centers that are responsible for two resonances in the $^{31}P\{^1H\}$ CP/MAS NMR spectrum (Table 1).

The reaction of **5c** with two equivalents of PMe_3 in benzene at RT gives **7b**$[OTf]_2$ (isolated 91%) containing a dication with *trans*-configuration of two PMe_3 ligands at the two acceptor phosphorus centers (Fig. 1d). Reaction mixtures containing equimolar amounts of **5c** and PMe_3 give solution ^{31}P NMR spectra showing a mixture of **7b**$[OTf]_2$ and **5c**.

Consistent with a C_i symmetric framework of **7b** observed in the solid state (Fig. 1d), the $^{31}P\{^1H\}$ NMR spectrum has been fitted as an AA′XX′ spin system (Table 1, Fig. 2). The relatively large $^4J_{XX'}$ and the high field resonance of P_A is in agreement with a transoid arrangement of the phosphorus lone pairs in the P_2N_2 ring. The solid state CP/MAS ^{31}P NMR spectrum of **7b**$[OTf]_2$ shows two signal groups for the AA′XX′ pattern as poorly resolved doublets (Fig. 2) that have been simulated using the *J* values obtained from the liquid state NMR spectrum with adjustment of shift offset and line width.

Selected structural parameters for **5c**, **6a**[OTf], **7a**$[OTf]_2$ and **7b**$[OTf]_2$ are presented in Table 2. The endocyclic interatomic

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† Electronic supplementary information (ESI) available: Experimental details and crystallographic data in CIF format for **5c**, **6a**[OTf], **7a**$[OTf]_2$ and **7b**$[OTf]_2$ (CCDC 650721, 650722, 650720 and 650811, respectively). See DOI: 10.1039/b710853b

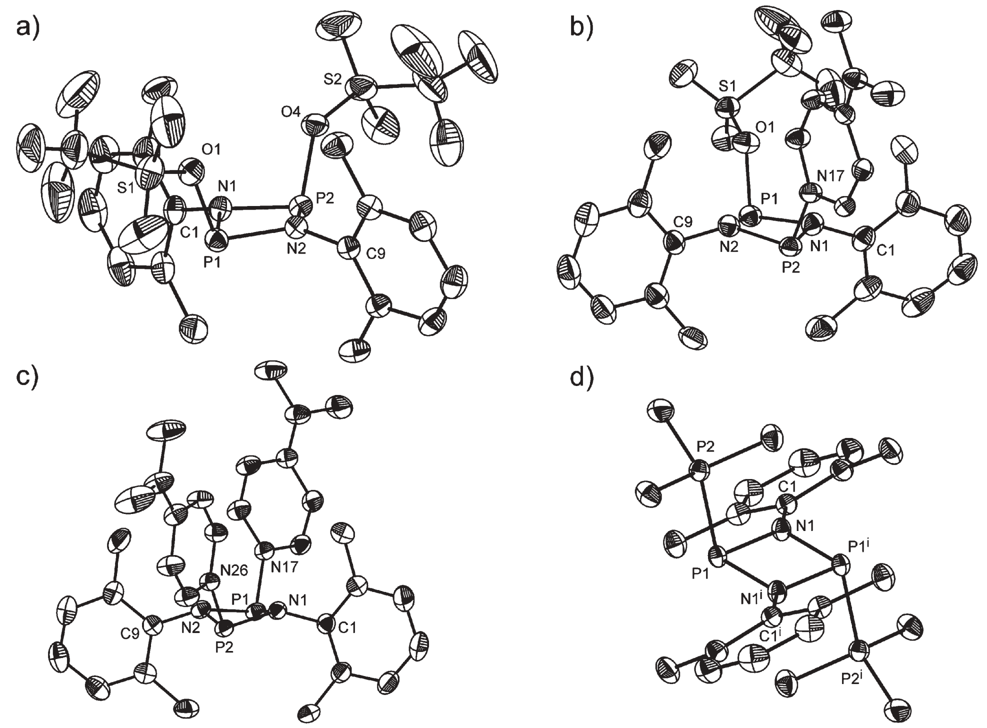

Fig. 1 ORTEP plots of the solid state structures for (a) **5c**, (b) the cation in **6a**[OTf], (c) the dication in **7a**[OTf]$_2$ and (d) the dication in **7b**[OTf]$_2$. Thermal ellipsoids with 50% probability at 173(2) K (hydrogen atoms are omitted) [symmetry code: (i) $-x + 1$, $-y$, $-z + 1$].

distances and bond angles in the P_2N_2 ring are essentially independent of the substituents or ligands attached to phosphorus, and the distances are typical of those observed for neutral diphosphadiazanes.[19–22] For example, all of the P–N distances within the P_2N_2 ring are within normal ranges (1.68–1.74 Å). The P–N_{DMAP} bonds in the ligand-stabilized monocation **6a**[OTf] (1.774(2) Å) and dication **7a**[OTf]$_2$ (1.790(3) and 1.775(3) Å) are consistent with that in [DMAP·PPh_2][OTf][6] (1.789(1) Å) and are significantly shorter than the two P–N_{DMAP} distances (1.873(2) and 1.879(2) Å) in [Mes*N=P(DMAP)$_2$][OTf].[10] The dication in **7a**[OTf]$_2$ lies on a center of inversion (crystallographically imposed), resulting in a planar P_2N_2 diphosphadiazanium framework, while the *cis*-configurations of **5c**, **6a**[OTf] and **7a**[OTf]$_2$ impose puckering.

The dimeric N_2P_2 structures of the bis-donor–bis-phosphenium dications in **7a**[OTf]$_2$ and **7b**[OTf]$_2$ contrast the monomeric phosphadiazonium complex cations of type **2**. While the formula Mes*NPOTf is observed as both a monomer and a dimer (**5a**) in the solid state, only structural type **2** is observed in the presence of Lewis bases (ligands). Retention of the P_2N_2 framework in the ionic complexes **6** and **7** illustrates the significance of the sterically bulky substituents (Mes*) in restricting dimerization of derivatives of **2**. The sterically mild Dmp substituent is insufficient to effect dissociation of the dimeric N_2P_2-ring arrangement in solution and in the solid state. Consequently, the accommodation of a

Table 1 ^{31}P NMR data (202.46 MHz, 300 K) for **5b**, **5c**, **6a**[OTf], **7a**[OTf]$_2$ and **7b**[OTf]$_2$

	Ligand	^{31}P NMR (solution)^c	^{31}P NMR (solid state)
trans-**5b**^{a}	—	295.4 (A_2)	—^{d}
cis-**5b**^{a}	—	210.1 (A_2)	212.8, 207.8
trans-**5c**^{a}	—	276.9 (A_2)	—^{d}
cis-**5c**^{a}	—	182.8 (A_2)	180.3, 178.3
6a[OTf]^a	DMAP	191.0, 150.5 (AX)^f	193.6, 147.4
7a[OTf]$_2^a$	DMAP	149.1 (A_2)	136.9, 132.5
7b[OTf]$_2^b$	Me_3P	279.5, 17.5 (AA′XX′)^e	280.5, 19.5 (AA′XX′)

[a] In $CDCl_3$. [b] In d_3-MeCN. [c] An $\Delta\nu/J \geqslant 10$ (AX); $0 < \Delta\nu/J < 10$ (AB); $\Delta\nu/J \rightarrow 0$ (A_2). [d] Not observed in the solid state NMR experiment. [e] $^1J_{AX} = {}^1J_{A'X'} = -474.2$, $^2J_{AA'} = 21.4$, $^3J_{AX'} = {}^3J_{XA'} = 41.2$, $^4J_{XX'} = 107.0$ Hz (a negative value for $^1J_{PP}$ in agreement with other observations[17,18]). [f] $^1J_{PP} = 48.7$ Hz.

Table 2 Selected interatomic distances and bond angles for **5c**, **6a**[OTf] and **7a**[OTf]$_2$, and **7b**[OTf]$_2$

	5c X1 = O1 X2 = O4	**6a**[OTf] X1 = O1 X2 = N17	**7a**[OTf]$_2$ X1 = N17 X2 = N26	**7b**[OTf]$_2$ X1 = P2
[Å]				
P1–N1	1.704(2)	1.696(2)	1.735(3)	1.741(1)
P1–N2(1^i)	1.701(2)	1.702(2)	1.730(3)	1.726(1)
P2–N1	1.697(2)	1.717(2)	1.717(3)	
P2–N2	1.698(2)	1.724(2)	1.740(3)	
P1–P2(1^i)	2.556(1)	2.568(1)	2.559(2)	2.6101(4)
P1–X1	1.750(2)	1.799(2)	1.790(3)	2.2832(5)
P2–X2	1.749(2)	1.774(2)	1.775(3)	
[°]				
P1–N1–P2(1^i)	97.4(1)	97.6(1)	95.7(2)	97.67(5)
P1–N2–P2	97.53(9)	97.1(1)	95.0(2)	
N1–P1–N2(1^i)	81.82(9)	82.3(1)	81.5(2)	82.33(5)
N1–P2–N2	82.11(9)	81.1(1)	81.7(2)	
P1–N1–P2(1^i)–N2(1^i)	−8.07(9)	−10.6(1)	−18.5(2)	0.0
Puckering angle in [°]^a	10.6(1)	14.02(9)	24.7(1)	0.0

[a] Puckering angle between the N1–N2(1^i)–P1 and N1–N2(1^i)–P2(1^i) planes; [symmetry code: (i) $-x + 1$, $-y$, $-z + 1$].

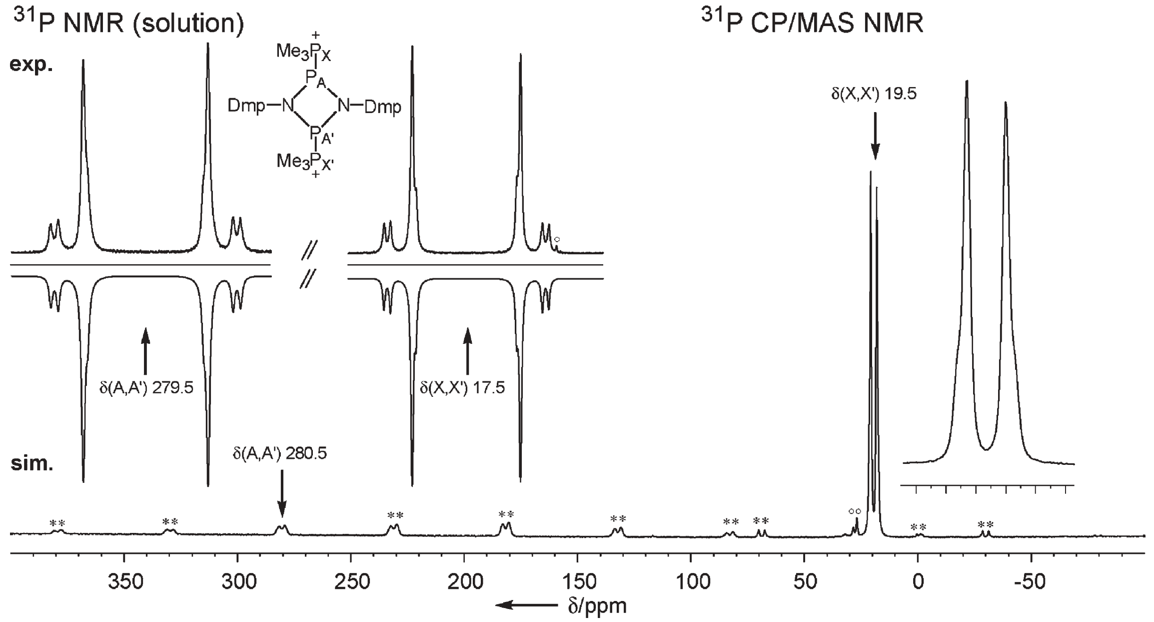

Fig. 2 ^{31}P NMR spectra for **7b**[OTf]$_2$: experimental solution spectrum (exp.) in d_3-MeCN at 202.46 MHz (25 °C, external H_3PO_4) and simulated solution spectrum (sim.). ^{31}P CP/MAS NMR spectrum, broad resonances indicated by ↓ are modeled as an AA′XX′ spin system (* spinning side bands, ° impurity).

dicationic charge in derivatives of **7** provides examples of bifunctional phosphorus Lewis acceptors of type **4** and complements the previously reported dicationic complexes of a bifunctional donor on two phosphorus acceptors, of type **3**.[4,10] In this context, the new dications provide insight for the development of extended systems towards cationic polymers.

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