SHORT COMMUNICATION

Preparation and Characterization of a Ligand-Stabilized Trimethylphosphane Dication

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In memoriam of Prof. Dr. Nils Wiberg

The ditriflate salt of the DMAP-stabilized trimethylphosphane dication is formed from the reaction of chlorotrimethylphosphonium triflate with DMAP (4-dimethylaminopyridine) in the presence of trimethylsilyltriflate and also from the reaction of DMAP-dimethylphosphenium triflate with methyltriflate. The coordinative nature of the DMAP–phosphorus bond is demonstrated by a ligand exchange of DMAP for PMe$_3$ to give the hexamethyldiphosphonium dication. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Phosphorus exhibits a broad range of bonding environments and coordination numbers, and the chemistry of phosphorus is further diversified by the ability of compounds to accommodate negative or positive charges. Nevertheless, new electronic and structural arrangements for phosphorus are regularly reported. The Lewis acceptor properties of phosphorus have recently provided new synthetic approaches to new bonding environments.[1] Cations of phosphorus are the most versatile acceptors as classified in Figure 1 according to the coordination number and the charge.

Also summarized in Figure 1 are generic examples of donor–acceptor complexes that have been structurally characterized for monocations of type A,[2–8] B,[9–13] C,[1,14–18] D,[19–21] E[22,23] and F.[24] Complexes of a phosphorus dication of type G have been proposed on the basis of spectroscopic and chemical analysis data,[25–28] but solid-state structures have been confirmed for only two examples.[6,14,18] There are no structural reports of complexes involving cations of the type H, I, J, K, L or M.

We now report the preparation and isolation of complex 1 representing a 4-(dimethylamino)pyridine (DMAP) ligand

on the dication of trimethylphosphane, the first example of a ligand-stabilized bonding environment H. Two preparative reactions demonstrate synthetic versatility and the solid-state structure provides fundamental comparisons with the DMAP complex of the isoelectronic group 13 Lewis acid AlMe$_3$.

Reaction of [Me$_3$PCl][OTf] (OTf = trifluoromethanesulfonate; 2[OTf], δ^{31}P = 94.0 ppm, [D$_3$]MeCN, room temp.) with DMAP in the presence of Me$_3$SiOTf (Scheme 1, a) results in quantitative formation (isolated 93%) of the new salt 1[OTf]$_2$ (δ^{31}P = 89.0 ppm, [D$_3$]MeCN, room temp.). The reaction represents a chloride ion displacement or ligand (neutral DMAP for chloride ion) exchange from monocation 2 (OTf = trifluoromethanesulfonate). Compound 1[OTf]$_2$ is also formed quantitatively (isolated 95%) from the DMAP-phosphenium complex cation in 3[OTf] (δ^{31}P = 91.3 ppm, [D$_3$]MeCN, room temp.) by reaction with MeOTf in the absence of solvent (Scheme 1, b). As illustrated in part c of Scheme 1, DMAP·AlMe$_3$ (4) was prepared quantitatively by reaction of AlMe$_3$ with DMAP in hexane.

The solid-state structure of 2[OTf] (Figure 2) exhibits weak inter-ion contacts that give strands of alternating cations and anions along the *c* axis. The P–Cl distance [1.990(1) Å] is slightly shorter than that in [Ph$_3$P–Cl···Cl···Cl–PPh$_3$]Cl·2CH$_2$Cl$_2$ [2.015(9)].[29] The position of O1 [O1–P–Cl 178.33(5)°, P–O cation–anion contact 3.355(2) Å; cf. sum of the van der Waals radii r_w(P) + r_w(O) = 3.32 Å][30] is envisaged as the associative site for DMAP in an S$_N$2 displacement of chloride. The cation in the solid-state structure of 3(OTf) is shown in Figure 3, and is comparable to that of the previously reported (DMAP·PPh$_2$)(OTf).[15]

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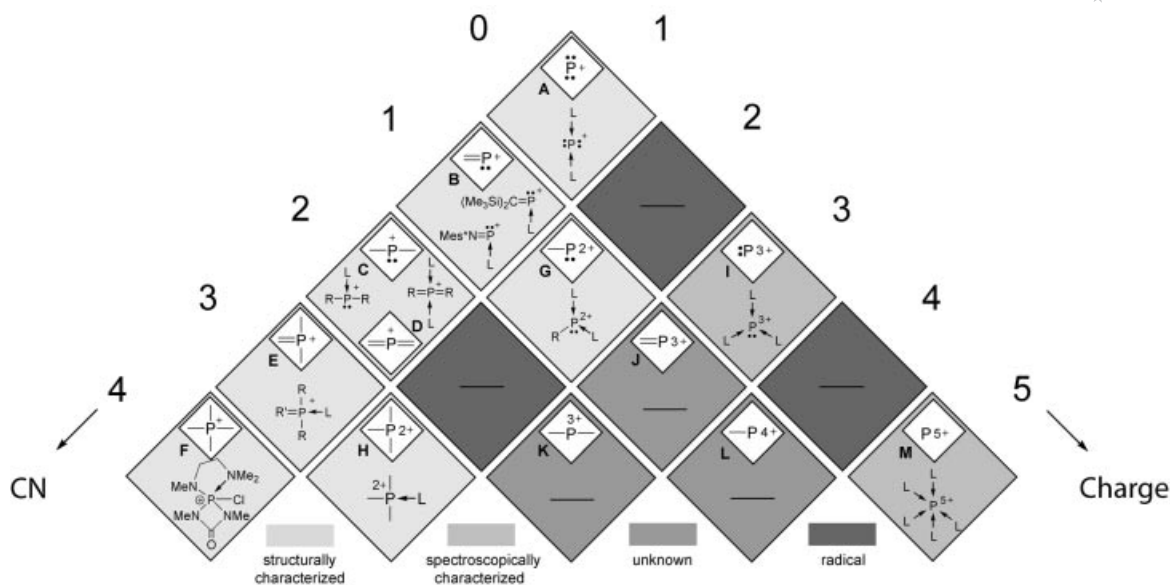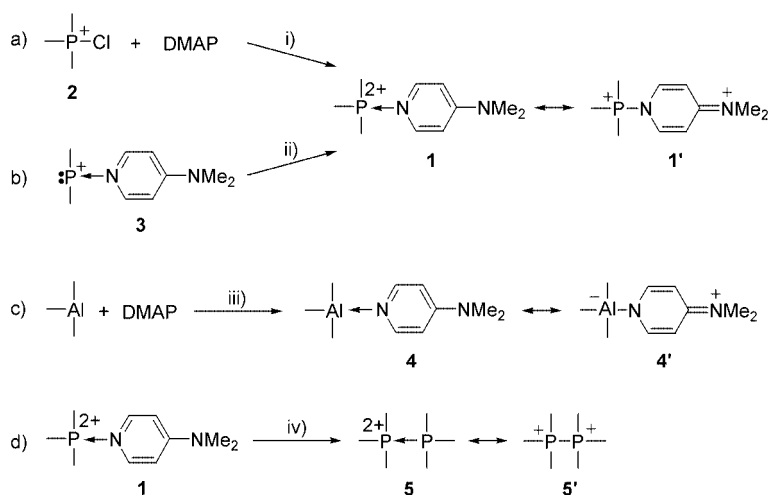
Figure 1. Bonding environments of cationic phosphorus centers and generic representations of isolated complexes.

Scheme 1. Preparative routes to **1**[OTf]₂, **4**, and **5**[OTf]₂ [i) Me₃SiOTf, MeCN, – Me₃SiCl; ii) MeOTf; iii) hexane; iv) excess. PMe₃, – DMAP, MeCN].

Figure 4 shows the ³¹P and ¹H NMR spectra for **1**[OTf]₂ as well as the bandshape analysis.[31] The phosphorus-coupled ¹H NMR spectrum exhibits a doublet centered at δ = 2.60 ppm assigned to the methyl groups attached to the phosphorus atom and the complex patterns at δ = 8.19 ppm and 7.13 ppm have been fitted as an AA′BB′M₉X spin system. The ¹H and ¹³C NMR signals for the *ortho* positions are upfield shifted, while those for the *meta* position are downfield shifted with respect to free DMAP (cf. δ¹H = 8.21 and 6.46 ppm, [D₃]MeCN, room temp.).[32]

The solid-state structure of the dication in **1**[OTf]₂ is compared in Figure 3 with the structures of the monocation in **3**[OTf] and the neutral compound **4**. Selected bond lengths for DMAP,[33] **1**[OTf]₂, **2**[OTf], **3**[OTf] and **4** are listed in Table 1. The distinctly pyramidal geometry at phosphorus in monocation **3** is comparable with that in the diphenyl deriva-

tive, as is the P–N distance [**3**(OTf), 1.801(2) Å; (Ph₂P·DMAP)⁺, 1.789(1) Å[15]]. The tetrahedral geometry of the phosphorus center in **1**[OTf]₂ is less distorted than that for the Al center in **4** (Figure 3). The DMAP ligand in all three complexes exhibits minimal structural adjustments with respect to free DMAP.[33] The Al–N distance [2.005(2) Å] in **4** is in the typical range for four-coordinate nitrogen-atoms involved in a donor–acceptor bond to an aluminium center (1.93–2.13 Å).[34] The P–N distance in **1**[OTf]₂ [1.720(3) Å] is significantly shorter than those in other DMAP complexes of phosphorus acceptors,[13,15,35] including **3**[OTf] [1.801(2) Å]. In addition, the P–C bonds in **1**[OTf]₂ [1.777(3), 1.772(3), 1.774(3) Å] are significantly shorter than those in **3**[OTf] [1.824(3), 1.826(3) Å] and in **4** [1.975(2), 1.971(2), 1.978(2) Å] (Table 1), all consistent with the greater positive molecular charge in **1**.
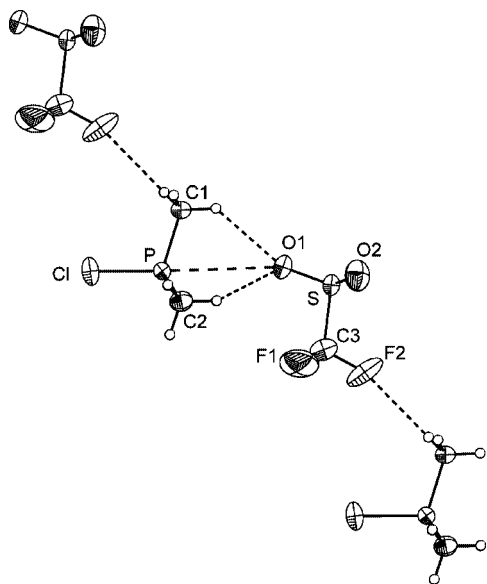
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Figure 2. ORTEP view of a portion of the solid-state structure for **2**[OTf] along the *c* axis. Atoms Cl, P, C1, C3, S and F2 lie on a mirror plane, and atoms C2′, F1′ and O2′ are not shown. Amplitude displacement ellipsoids are depicted at 50% probability and hydrogen atoms with arbitrary radii.

The quinoidal character of the pyridine framework (Scheme 1, **1′** and **4′**) is demonstrated in Table 1, by the C2–C3, C5–C6 and C4–N7 bonds being shorter in all complexes than in the free ligand. The trend in length for these bonds is **1** < **3** < **4** < DMAP, which we correlate with the relative strength of the N–E (E = P or Al) interaction in the complexes. Moreover, the N–E bond is shortest in the dicationic **1** and longest in **4**.

NBO analyses[36] and MO analyses of **4**, **3**, **1**, AlMe₃, PMe₂⁺ and PMe₃²⁺ at the B3LYP/6-31+G(d,p)[37] level provide charge-transfer and charge-distribution values that are summarized in Table 2. The donor–acceptor NP bond in **1** is purely σ in character and is strongly polarized (N: 75%,

P: 25%) with a partial charge of 1.806 *e* at phosphorus, representing a substantial increase with respect to neutral PMe₃ (0.734 *e*). The calculated charge at phosphorus in the free PMe₃²⁺ dication is 1.906 *e* (cf. 1.539 *e* at Al in AlMe₃) so that formation of **1** effects only a slight decrease in charge at phosphorus in the complex, although polarization of the P–C bonds in the PMe₃ fragment (P: 42%, C: 58%) contributes to the positive charge on phosphorus. The total charge transfer Q_{CT} (from DMAP to acceptor, Table 2) in dication **1** (0.540 *e*) is significantly greater than that in **4** (0.158 *e*) and only slightly greater than that in **3** (0.411 *e*) consistent with the relative positive charge in each acceptor.

Reaction of **1** in MeCN with an excess of PMe₃ results in the displacement of DMAP and formation of **5**[OTf]₂ ($\delta^{31}P$ = 28.4 ppm, [D₃]MeCN, room temp.; isolated by Et₂O diffusion into the reaction mixture)[38] (Scheme 1, d), which is understood in terms of a ligand exchange of DMAP in **1** by Me₃P.

Summary

Compound **1**[OTf]₂ has been prepared by two methods and represents a ligand-stabilized PMe₃²⁺, which is compared with the isoelectronic group 13 analog AlMe₃. The synthetic versatility of the first phosphane dication bodes well for the discovery and development of a series of ligand-stabilized multiply-charge phosphorus cations.
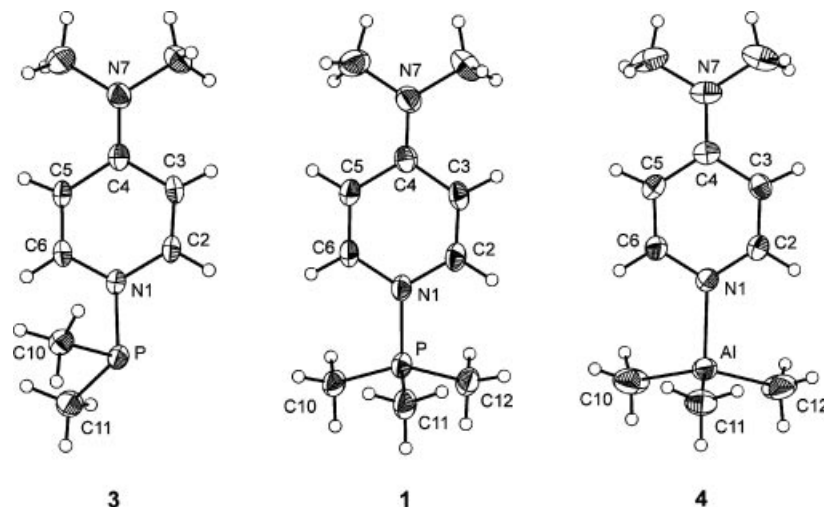
Figure 3. ORTEP views of the cations in **3**[OTf] and **1**[OTf]₂, and the neutral **4**. Amplitude displacement ellipsoids are depicted at 50% probability and hydrogen atoms with arbitrary radii.
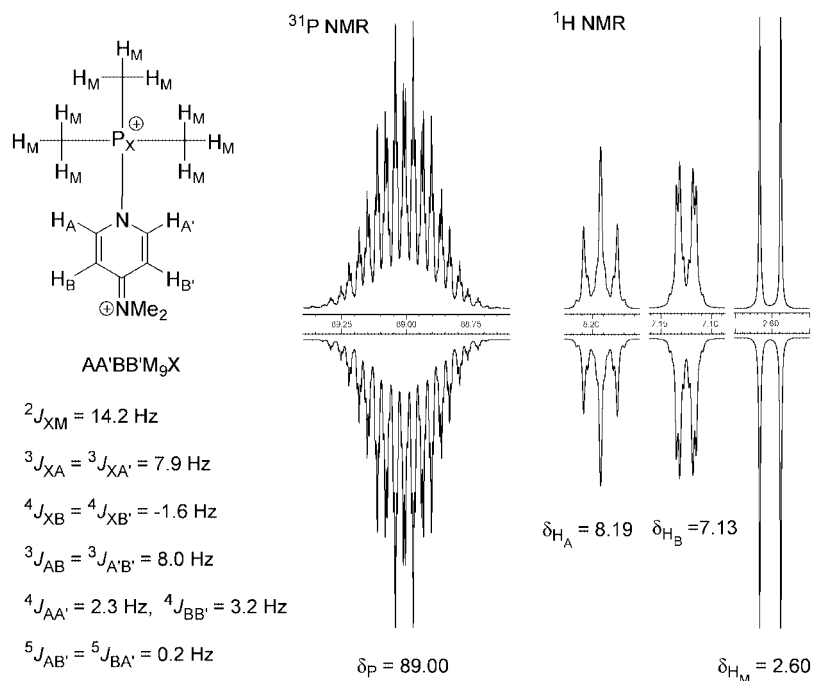
Figure 4. Experimental (upper) and simulated (lower) ^{31}P and ^1H NMR spectra of **1**[OTf]$_2$ (in [D$_3$]MeCN, room temp. [ppm]), cf. free DMAP, 8.21, 6.46 (in [D$_3$]MeCN).

Table 1. Selected interatomic distances [Å] for DMAP, **4**, **3**[OTf], **1**[OTf]$_2$, and **2**[OTf].

	DMAP	**4** (E = Al, X = N1)	**3**[OTf] (E = P, X = N1)	**1**[OTf]$_2$ (E = P, X = N1)	**2**[OTf] (E = P, X = Cl)
E–C10(C1)[a]	–	1.975(2)	1.824(3)	1.777(3)	1.772(2)
E–C11(C2)[a]	–	1.971(2)	1.826(3)	1.772(3)	1.773(3)
E–C12(C2^i)[a]	–	1.978(2)	–	1.774(3)	1.773(3)
E–X	–	2.005(2)	1.801(2)	1.720(3)	1.990(1)
C2–C3	1.381(3)	1.369(2)	1.354(3)	1.340(4)	–
C3–C4	1.403(2)	1.418(2)	1.437(3)	1.431(4)	–
C4–C5	1.404(3)	1.409(2)	1.416(3)	1.432(4)	–
C5–C6	1.375(3)	1.368(2)	1.349(3)	1.342(4)	–
C2–N1	1.337(3)	1.348(2)	1.367(3)	1.380(3)	–
C6–N1	1.335(3)	1.350(2)	1.374(3)	1.386(4)	–
C4–N7	1.367(2)	1.350(2)	1.339(3)	1.319(4)	–

[a] Atom labeling for **2**[OTf] in brackets [symmetry code: i) x, $0.5 - y$, z].

Table 2. Charge-transfer (Q_{CT}) values and selected NPA charges in the DMAP complexes **4**, **3**, and **1** in e.

	4	**3**	**1**	PMe$_3$
Q_{CT}[a,b]	–0.158	–0.411	–0.540	1.387
Q_{CT}(E)[c,d]	–0.056	–0.316	–0.100	1.073
Q_{CT}(N1$_{ring}$)[e]	–0.094	–0.098	–0.178	–
Q_{CT}(N7$_{amino}$)[e]	0.019	0.064	0.125	–
E[f]	1.538[g]	1.003[h]	1.806[i]	0.734
N1[j]	–0.599	–0.617	–0.697	–
N7[j]	–0.431	–0.382	–0.321	–

[a] For **1** and **4**: Q_{CT} = –Σ q(E, DMAP, adduct), (i) = Σ q(E, AlMe$_3$, adduct), (ii) = [Σ q(E, PMe$_3$, adduct)] – 2 = Σ [q(E, PMe$_3$$^{2+}$)] (charge transfer based on PMe$_3$$^{2+}$) and for **3**: Q_{CT} = –Σ q(E, DMAP, adduct). [b] In **1**: Q_{CT} = Σ [q(E, PMe$_3$, adduct) – q(E, PMe$_3$)] charge transfer based on neutral PMe$_3$. [c] In **1**: Q_{CT}(P) = q(P, adduct) – q(P, PMe$_3$$^{2+}$), in **3**: Q_{CT}(P) = q(P, adduct) – q(P, PMe$_2$$^+$) and in **4**: Q_{CT}(Al) = q(Al, adduct) – q(Al, AlMe$_3$). [d] Q_{CT}(P) = q(P, adduct) – q(P, PMe$_3$), q(P, PMe$_3$) – q(P, PMe$_3$$^{2+}$) = 1.173 e. [e] Q_{CT}(N) = q(N, adduct) – q(N, DMAP). [f] E = P in **3** and **1**, Al in **4**. [g] 1.593 e In AlMe$_3$. [h] 1.319 e In PMe$_2$$^+$. [i] 1.906 e In PMe$_3$$^{2+}$. [j] –0.520 (N1) and –0.441 (N7) e in neutral DMAP.

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[37] Single point calculations were computed with a tight conversion criterion using the program package Gaussian 98. For computational details see Supporting Information; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, Mennucci, B. C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, Morokuma, K. D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revision A7 and A11, Gaussian Inc., Pittsburgh PA, **1998**.

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