Synthesis and Structural Characterization of the First Donor-stabilized Phosphanetriylphosphonium Cation: [Ar*PP(PPh3)]+ (Ar* = 2,4,6-But3C6H2)

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Reaction of Ar*P=PNR2 (Ar* = 2,4,6-But3C6H2) with CF3SO3H in the presence of triphenylphosphane in CH2Cl2 produces the isolable salt [Ar*PP(PPh3)]+ [CF3SO3]− which is characterized by X-ray crystallography; the triphenylphosphane ligand of [Ar*PP(PPh3)]+ readily participates in nucleophilic substitution reactions affording a novel entry to donor-stabilized phosphanetriylphosphonium cations and P-functionalized diphosphenes.

During the last few decades, compounds containing phosphorus engaged in (p–p)π triple bonds to main group elements have come under intensive investigation.[1] First synthesized in the early 1980s,[2] the stable phosphaalkynes A have been thoroughly investigated with regard to their chemical behaviour and spectroscopic properties.[3] Stable species with triply bonded σ3λ5-phosphorus atoms B have also been known for several years.[4] Many efforts have been directed towards the development of synthetic routes to phosphanitriles D.[5] Finally, the first representatives of a class of cationic compounds containing a P≡N triple bond, C, have recently been obtained.[6] In contrast, surprisingly little is known about phosphanetriylphosphonium cations E† in spite of the fact that the nitrogen analogues of (RPP)+ cations, diazonium ions, have been well known for many years and have occupied a central position in nitrogen cation chemistry. Here we report the first isolation of phosphanetriylphosphonium cations stabilized by donor–acceptor interactions, [Ar*PP←D]+, and their behaviour towards neutral and anionic nucleophiles.
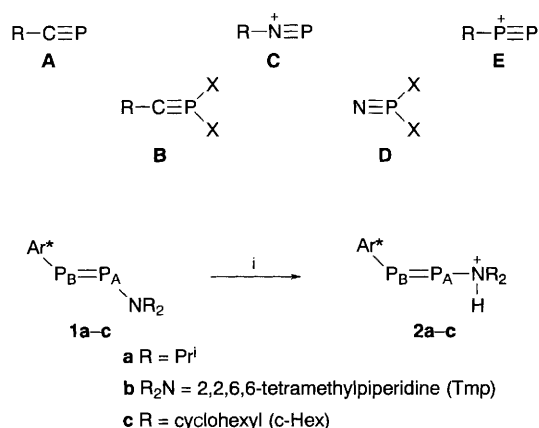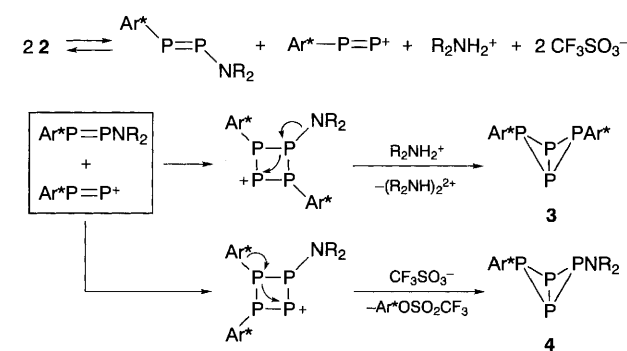
It is well known that diazonium salts can be generated by the reactions of diazoamino compounds, ArN=N–NR2, with strong acids,[7] and therefore it was reasonable to investigate the reactivity of P-aminodiphosphenes, Ar*P=P–NR2,[8] towards trifluoromethanesulfonic acid, which was selected as the proton source because of the low nucleophilicity of the triflate anion. We found that, in contrast with Ar*P=PAr*, which undergoes P–P bond cleavage upon the low temperature reaction with strong acids,[9] selective protonation of the nitrogen centre takes place when diphosphenes 1a–c are treated with 1 equiv. of CF3SO3H in dichloromethane at −50 °C (Scheme 1). The AX-type 31P NMR spectra of 2a–c and the large J(PAPB) coupling constants (Table 1) indicate the double linkage of two phosphorus atoms, while the sharp 19F NMR signal of the [CF3SO3]− anion at δ −79 (CCl3F, ext.) is in accord with the
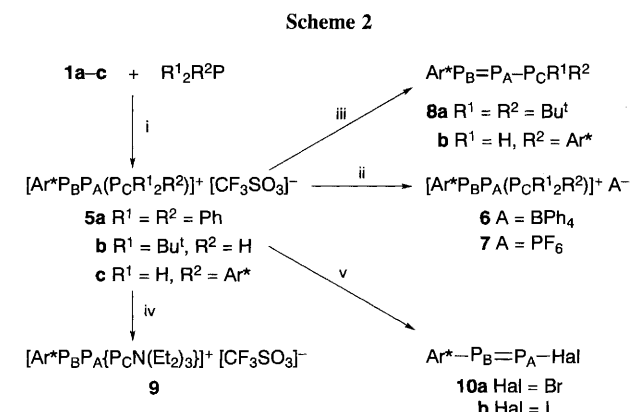
formation of the salt-like product. Unequivocal support for the structure of 2 comes from the routine 15N and 31P NMR spectral analyses of the 15N-labelled 2b [δ15N (MeNO2 ext.) −281, 1J(NPA) 69, 1J(NH) 71, 1J(PAPB) 606 Hz]. Theoretical calculations suggest that the N-protonated structure [HP=PNH3]+ is preferred over the P-protonated structure [H2P–P–NH2]+ by 34 kJ mol−1.

Table 1 31P NMR spectral data for P-aminodiphosphenes Ar*PB=PANR2 1a–c and their N-protonated derivatives 2a–c (Gemini 200, 20% in CH2Cl2, −35 °C, H3PO4 ext.)

Compound	R2N	δ (PA)	δ (PB)	J(PAPB)/Hz
1a	Pri2N	442	276	537
1b	Tmp	455	332	574
1c	c-Hex2N	450	270	544
2a	Pri2N	433	544	596
2b	Tmp	435	550	604
2c	c-Hex2N	439	536	594

Scheme 2

Scheme 3 Reagents and conditions: i, CF3SO3H, R1 2R2P, CH2Cl2, −40 °C, 0.5 h; ii, NaBPh4 or NH4PF6 (2 equiv.), CH2Cl2, 20 °C, 24 h; iii, CH2Cl2, 20 °C, 0.5 h; iv, (Et2N)3P (1 equiv.), CH2Cl2, −78 °C, 2 h; v, Et3N·HHal, THF, −78 °C, 1 h

Scheme 1 Reagents and conditions: i, CF3SO3H (1 equiv.), CH2Cl2, −50 °C

Upon warming to 20 °C, the solutions of **2a–c** to 20 °C decompose to form *ca.* 50 : 50 mixtures of bicyclotetraphosphanes **3** and **4**. This mixture could be separated in the case of the products of decomposition of **2a** and the exact formulation of structures **3** and **4** (R = Pr^i) has been established by MS and ^{1}H, ^{13}C and ^{31}P NMR.‡ Although little is known about the mechanism of this process, we assume that the reaction proceeds through a cycloaddition of the generated [Ar*PP]$^+$ cation to the starting diphosphene to give a cationic cyclotetraphosphane intermediate, followed by PP coupling and reductive elimination of a bridgehead substituent (Scheme 2). It is noteworthy that reaction of the diphosphene [Ar*P=P–NHAr*] with CF$_3$SO$_3$H, even at −78 °C, leads immediately to the formation of **3** and unidentified products, thus indicating a high reactivity of the generated [Ar*PP]$^+$ cation.

The addition of CF$_3$SO$_3$H (2 equiv.) to a mixture of diphosphene **1a–c** and Ph$_3$P (1 equiv.) in dichloromethane at −78 °C, followed by warming to room temperature and standard workup, results in a near quantitative yield of the donor–acceptor adduct **5a** (Scheme 3). The ionic nature of **5a** was indicated by its low solubility in non-polar solvents and by anion exchange reactions with NaBPh$_4$ and NH$_4$PF$_6$ (isolated yields > 85%). In the ^{31}P NMR spectra of **5a**, **6** and **7** (30% in CDCl$_3$, H$_3$PO$_4$ ext.), an AMX pattern is observed [δ (P$_A$) 334 (dd), (P$_B$) 641 (dd), (P$_C$) 25 (dd), ^1J(P$_A$P$_B$) 580, ^2J(P$_A$P$_C$) 384, ^1J(P$_B$P$_C$) 71 Hz]. The X-ray structural analysis of **6** (Fig. 1)§ shows the absence of cation–anion contacts in the crystal. The central C(1)P(1)P(2)P(3) bond system is approximately planar [deviations from best least-squares plane do not exceed 0.039(3) Å],§ whereas the C(1)–C(6) benzene ring adopts an orientation almost orthogonal to this plane [corresponding dihedral angle 83.78(5)°]. Both the C(1)P(1)P(2) [98.8(2)°] and P(1)P(2)P(3) [96.78(5)°] bond angles, as well as the P(1)–P(2)

bond length of 2.025(1) Å, are unexceptional for diphosphenes,[10] whereas P(2)–P(3) [2.206(1) Å] corresponds to a single P–P bond.[11] The P(3)–C(Ph) bonds [1.793–1.793(3), av. 1.795 Å] are somewhat shorter than the respective distances in coordination compounds Ph$_3$P→ML$_n$ [*e.g.* 1.820(2) Å in Ph$_3$P→AlMe$_3$ and 1.821–1.834 (4) in Ph$_3$P→Cr(CO)$_5$],[12] but are well within the range of 1.782–1.805(2) Å reported for triphenylphosphonium cations [Ph$_3$P$^+$R].[13] These findings are in good agreement with the calculated charges and geometry of the parent molecule [HPPPH$_3$]$^+$ (Fig. 2) which clearly show that the phosphane–phosphanetriylphosphonium adduct has typical double and single P–P bonds.

Reaction of **1a–c**/Bu^t$_2$PH (1 : 1 molar ratio) with CF$_3$SO$_3$H (1 equiv.) leads to the immediate displacement of the amine and formation of **5b**, and the subsequent slow transformation to phosphanodiphosphene **8a** (yield > 95%). In a similar manner the diphosphene **8b** was a major product (yield > 80%) of the reaction of **5a** with Ar*PH$_2$ but we were not able to detect **5c** spectroscopically.

Treatment of **5a** with P(NEt$_2$)$_3$ in dichloromethane solution at −78 °C cleanly led to the formation of the adduct **9** (67% isolated yield) by elimination of the less nucleophilic Ph$_3$P ligand. Lastly, the high reactivity of **5a** towards nucleophiles is further demonstrated by the reaction with Et$_3$NHHal which afforded *P*-halodiphosphenes **10a,b** in almost quantitative yields.
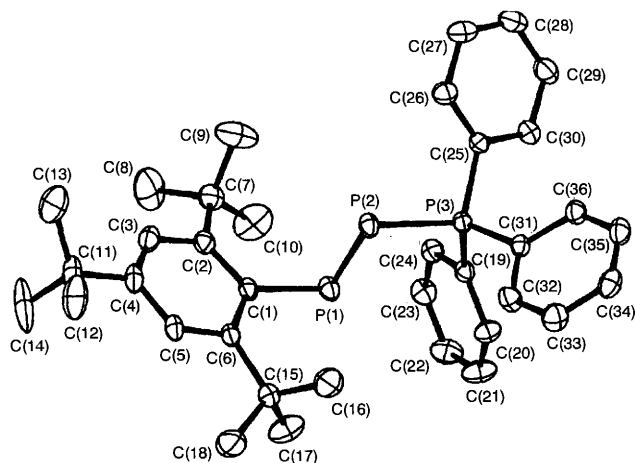
Fig. 1 Perspective view of cation **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.025(1), P(2)–P(3) 2.206(1), P(1)–C(1) 1.842(4), P(3)–C(19) 1.793(3), P(3)–C(25) 1.794(3), P(3)–C(31) 1.797(3), P(2)–P(1)–C(1) 98.8(2), P(1)–P(2)–P(3) 96.78(5), C(1)–P(1)–P(2)–P(3) −176.0(1).
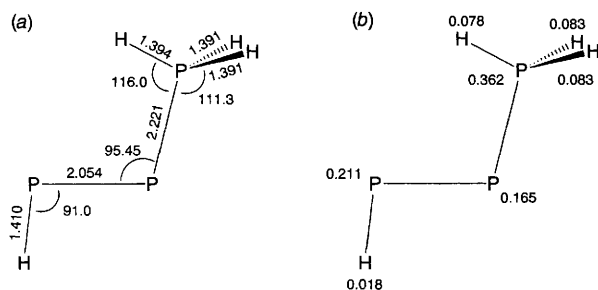

Fig. 2 (*a*) Calculated geometrical parameters (bond lengths in Å, bond angles in degrees) and (*b*) net atomic charges of the ion [HPP(PH$_3$)]$^+$

and thermal parameters. Corrections for Lorentz and polarisation effects and empirical absorption correction based on azimuthal scan data were applied. Crystallographic calculations were carried out using the SDP-PLUS program package[21] on a PDP-11/23 + computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 For a review, see *Muiltiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1990.

2 G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., B. Chem. Sci.*, 1981, **36**, 16.

3 M. Regitz, *Chem. Rev.*, 1990, **90**, 191.

4 A. Baceiredo, G. Bertrand and G. Sicard, *J. Am. Chem. Soc.*, 1985, **107**, 4781; H. Keller, G. Maas and M. Regitz, *Tetrahedron Lett.*, 1986, **27**, 1903.

5 G. Sicard, A. Baceiredo, G. Bertrand and J.-P. Majoral, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 459; J. Böske, E. Niecke, M. Nieger, E. Ocando, J.-P. Majoral and G. Bertrand, *Inorg. Chem.*, 1989, **28**, 499.

6 E. Niecke, M. Nieger and F. Reichert, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1715; R. Detsch, E. Niecke, M. Nieger, F. Reichert and W. W. Schoeller, *Bull. Soc. Chim. Fr.*, 1993, **130**, 25; N. Burford, J. A. C. Clyburne, P. K. Bakshi and T. S. Cameron, *J. Am. Chem. Soc.*, 1993, **115**, 8829; A. B. Drapailo, A. N. Chernega, V. D. Romanenko, R. Madhouni, J.-M. Sotiropoulos, L. Lamandé and M. Sanchez, *J. Chem. Soc., Dalton Trans.*, 1994, 2925.

7 P. Gries, *Liebigs Ann. Chem.*, 1862, **121**, 257; Th. L. Gilchrist, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, London, 1991, vol. 7, pp. 735–736.

8 A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov and V. D. Romanenko, *Zh. Struct. Khim.*, 1990, **31**, 108; E. O. Klebanskii, PhD. Thesis, Institute of Organic Chemistry, Kiev, 1989.

9 A. H. Cowley, J. F. Kilduff, N. C. Norman, M. Pakulski, J. L. Atwood and W. E. Hunter, *J. Am. Chem. Soc.*, 1983, **105**, 4845.

10 M. Yoshifuji, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Stuttgart, 1990, p. 321; A. N. Chernega, M. Yu. Antipin and Yu. T. Struchkov, *Zh. Struct. Khim.*, 1989, **29**, 122.

11 V. A. Naumov and L. V. Vilkov, *Molecular Structure of Organophosphorus Compounds*, Nauka, Moscow, 1986, p. 320.

12 G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton. Trans.*, 1989, 1; D. A. Wierda and A. R. Barron, *Polyhedron*, 1989, **8**, 831; H. J. Plastas, J. M. Stewart and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.

13 H. Banbery and T. A. Hamor, *Acta Crystallogr., Sect. C*, 1988, **44**, 1683; S. Belanger and A. L. Beauchamp, *Acta Crystallogr., Sect. C*, 1993, **49**, 388; N. Brinckebank, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard, *Acta Crystallogr., Sect. C*, 1993, **49**, 1017; H. J. Haupt, F. Huber, C. Kruger, H. Preut and D. Thiebach, *Z. Anorg. Allg. Chem.*, 1977, **436**, 229.

14 T. Busch, W. W. Schoeller, E. Niecke, M. Nieger and H. Westermann, *Inorg. Chem.*, 1989, **28**, 4334; T. Busch and W. W. Schoeller, *Chem. Phys. Lett.*, 1992, **200**, 26.

15 M. T. Nguyen and N. J. Fitzpatrick, *Chem. Phys. Lett.*, 1988, **146**, 524.

16 R. Glaser, *J. Phys. Chem.*, 1989, **93**, 7993; R. Glaser, C. J. Horan, G. S.-C. Choy and B. L. Harris, *J. Phys. Chem.*, 1992, **96**, 3689.

17 E. Niecke, R. Streubel, M. Nieger and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1673.

18 E. Fluck, R. Riedel, H.-D. Hausen and G. Heckmann, *Z. Anorg. Allg. Chem.*, 1987, **551**, 85.

19 L. N. Markovskii, V. D. Romanenko, M. I. Povolotskii, A. V. Ruban and E. O. Klebanskii, *Zh. Obshch. Khim.*, 1986, **56**, 2157.

20 P. Jutzi and U. Meyer, *Phosphorus Sulfur*, 1988, **40**, 275.

21 B. A. Frenz, in *Computing in Crystallography*, ed. H. Schenk, R. Olthof-Hazekamp, H. van Konigsveld and G. C. Bassi, Delft University Press, Delft, 1976, pp. 64–71.