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Synthesis and Structural Characterization of the First Donor-stabilized Phosphanetriylphosphonium Cation: $[Ar^*PP(PPh_3)]^+$ (Ar^* = 2,4,6-$Bu^t_3C_6H_2$)

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Reaction of $Ar^*P{=}PNR_2$ (Ar^* = 2,4,6-$Bu^t_3C_6H_2$) with CF_3SO_3H in the presence of triphenylphosphane in CH_2Cl_2 produces the isolable salt $[Ar^*PP(PPh_3)]^+$ $[CF_3SO_3]^-$ which is characterized by X-ray crystallography; the triphenylphosphane ligand of $[Ar^*PP(PPh_3)]^+$ readily participates in nucleophilic substitution reactions affording a novel entry to donor-stabilized phosphanetriylphosphonium cations and P-functionalized diphosphenes.

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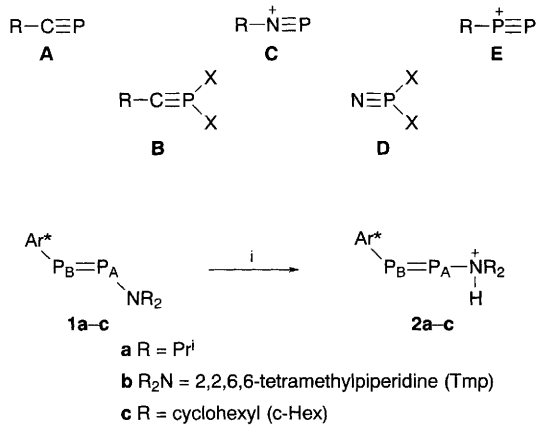
During the last few decades, compounds containing phosphorus engaged in $(p\text{–}p)_\pi$ triple bonds to main group elements have come under intensive investigation.[1] First synthesized in the early 1980s,[2] the stable phosphaalkynes **A** have been thoroughly investigated with regard to their chemical behaviour and spectroscopic properties.[3] Stable species with triply bonded $\sigma^3\lambda^5$-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, $[Ar^*PP{\leftarrow}D]^+$, and their behaviour towards neutral and anionic nucleophiles.

It is well known that diazonium salts can be generated by the reactions of diazoamino compounds, $ArN{=}N{-}NR_2$, with strong acids,[7] and therefore it was reasonable to investigate the reactivity of *P*-aminodiphosphenes, $Ar^*P{=}P{-}NR_2$,[8] towards trifluoromethanesulfonic acid, which was selected as the proton source because of the low nucleophilicity of the triflate anion.

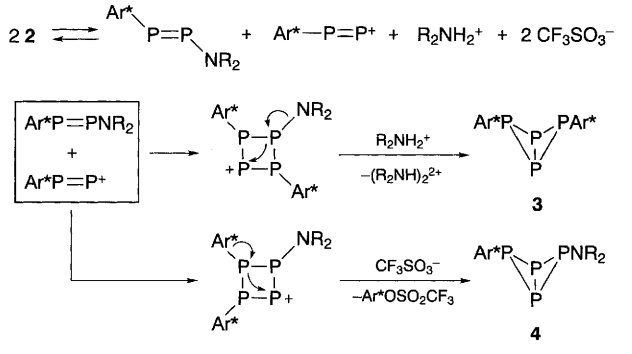
We found that, in contrast with $Ar^*P{=}PAr^*$, which undergoes P–P bond cleavage upon the low temperature reaction with strong acids,[9] selective protonation of the nitrogen centre takes place when diphosphenes **1a–c** are treated with 1 equiv. of CF_3SO_3H in dichloromethane at −50 °C (Scheme 1). The AX-type ^{31}P NMR spectra of **2a–c** and the large $J(P_AP_B)$ coupling constants (Table 1) indicate the double linkage of two phosphorus atoms, while the sharp ^{19}F NMR signal of the $[CF_3SO_3]^-$ anion at δ −79 (CCl_3F, ext.) is in accord with the formation of the salt-like product. Unequivocal support for the structure of **2** comes from the routine ^{15}N and ^{31}P NMR spectral analyses of the ^{15}N-labelled **2b** [δ_{15N} ($MeNO_2$ ext.) −281, $^1J(NP_A)$ 69, $^1J(NH)$ 71, $^1J(P_AP_B)$ 606 Hz]. Theoretical calculations suggest that the *N*-protonated structure $[HP{=}PNH_3]^+$ is preferred over the *P*-protonated structure $[H_2P{-}P{-}NH_2]^+$ by 34 kJ mol^{-1}.



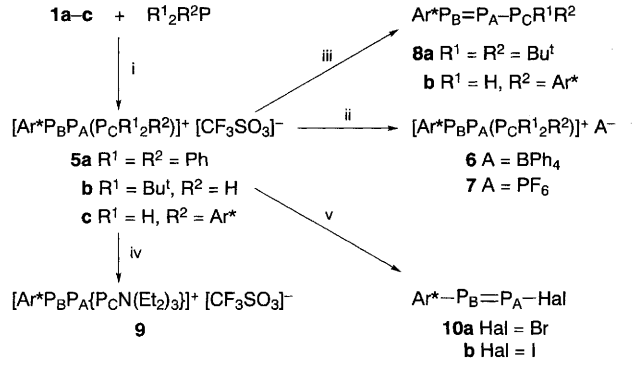
Scheme 1 *Reagents and conditions*: i, CF_3SO_3H (1 equiv.), CH_2Cl_2, −50 °C

Table 1 ^{31}P NMR spectral data for *P*-aminodiphosphenes $Ar^*P_B{=}P_ANR_2$ **1a–c** and their *N*-protonated derivatives **2a–c** (Gemini 200, 20% in CH_2Cl_2, −35 °C, H_3PO_4 ext.)

Compound	R_2N	δ (P_A)	δ (P_B)	$J(P_AP_B)$/Hz
1a	Pr^i_2N	442	276	537
1b	Tmp	455	332	574
1c	c-Hex_2N	450	270	544
2a	Pr^i_2N	433	544	596
2b	Tmp	435	550	604
2c	c-Hex_2N	439	536	594



Scheme 2



Scheme 3 *Reagents and conditions*: i, CF_3SO_3H, $R^1_2R^2P$, CH_2Cl_2, −40 °C, 0.5 h; ii, $NaBPh_4$ or NH_4PF_6 (2 equiv.), CH_2Cl_2, 20 °C, 24 h; iii, CH_2Cl_2, 20 °C, 0.5 h; iv, $(Et_2N)_3P$ (1 equiv.), CH_2Cl_2, −78 °C, 2 h; v, $Et_3N{\cdot}HHal$, THF, −78 °C, 1 h

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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 ^1H, ^{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_3SO_3H, 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_3SO_3H (2 equiv.) to a mixture of diphosphene **1a–c** and Ph_3P (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_4PF_6 (isolated yields > 85%). In the ^{31}P NMR spectra of **5a**, **6** and **7** (30% in $CDCl_3$, H_3PO_4 ext.), an AMX pattern is observed [δ (P_A) 334 (dd), (P_B) 641 (dd), (P_C) 25 (dd), $^1J(P_AP_B)$ 580, $^2J(P_AP_C)$ 384, $^1J(P_BP_C)$ 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 $Ph_3P{\rightarrow}ML_n$ [*e.g.* 1.820(2) Å in $Ph_3P{\rightarrow}AlMe_3$ and 1.821–1.834 (4) in $Ph_3P{\rightarrow}Cr(CO)_5$],[12] but are well within the range of 1.782–1.805(2) Å reported for triphenylphosphonium cations $[Ph_3P^+R]$.[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.

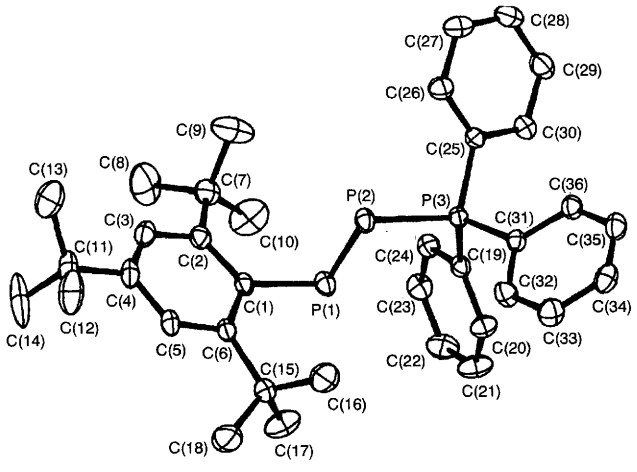

Fig. 1 Perspective view of cation **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.025(1), P(2)–P(3) 2.206(1), P(1)–C(1) 1.842(4), P(3)–C(19) 1.793(3), P(3)–C(25) 1.794(3), P(3)–C(31) 1.797(3), P(2)–P(1)–C(1) 98.8(2), P(1)–P(2)–P(3) 96.78(5), C(1)–P(1)–P(2)–P(3) −176.0(1).

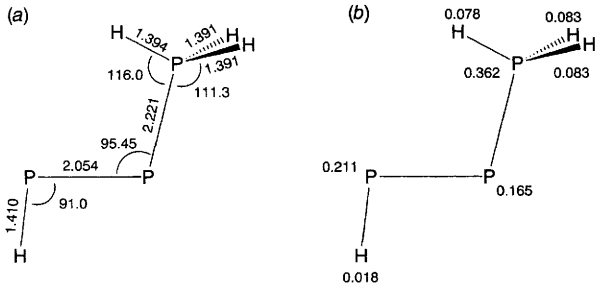

Fig. 2 (*a*) Calculated geometrical parameters (bond lengths in Å, bond angles in degrees) and (*b*) net atomic charges of the ion $[HPP(PH_3)]^+$

Reaction of **1a–c**/Bu^t_2PH (1 : 1 molar ratio) with CF_3SO_3H (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_3P ligand. Lastly, the high reactivity of **5a** towards nucleophiles is further demonstrated by the reaction with Et_3NHHal which afforded *P*-halodiphosphenes **10a,b** in almost quantitative yields.

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Footnotes

† These species can also be formulated as phosphinidenediylphosphenium cations [R–P=P+]. *Ab initio* calculations of the model molecules $[RPP]^+$, performed using the GAUSSIAN 92 program at the MP2/6-31G** level, have emphasised that the importance of the mesomeric form $[RP^+{\equiv}P]$ decreases in the sequence (R): F > OH > NH_2 > Me > H > PH_2 (to be submitted for publication). See also refs. [14,15] The ion $[H_3CPP]^+$ is predicted to be a stable molecule that should be detectable in the gas phase.[16] The free $[Pr^i_2NPP]^+$ cation has been observed by MS.[17]

‡ *Selected ^{31}P NMR data*: For **3**, ^{31}P (C_6D_6) δ −272 (t, $^1J_{PP}$ 176 Hz), −127 (t, $^1J_{PP}$ 176 Hz).[18] For **4b**, ^{31}P (CD_2Cl_2), δ −219 (dd, $^1J_{PP}$ 232, $^2J_{PP}$ 211 Hz), −93 (td, $^1J_{PP}$ 211, $^2J_{PP}$ 30 Hz), −54 (td, $^1J_{PP}$ 232, $^2J_{PP}$ 30 Hz). For **5b**, ^{31}P (CH_2Cl_2), δ 63 (dm, $^1J_{PP}$ 384 Hz, P_C), 310 (dd, $^1J_{PP}$ 574, 384 Hz, P_A), 647 (dd, $^1J_{PP}$ 574, $^2J_{PP}$ 85 Hz, P_B). For **8a**, ^{31}P (CH_2Cl_2), δ 53 (dd, $^1J_{PP}$ 209, $^2J_{PP}$ 288 Hz, P_C), 485 (dd, $^1J_{PP}$ 575, 209 Hz, P_A), 599 (dd, $^1J_{PP}$ 575, $^2J_{PP}$ 288 Hz, P_B).[19] For **8b**, ^{31}P (CH_2Cl_2), −60 (ddd, $^1J_{PP}$ 218, $^2J_{PP}$ 203, $^1J_{PH}$ 199 Hz, P_C), 495 (dd, $^1J_{PP}$ 567, 218 Hz, P_A), 553 (ddd, $^1J_{PP}$ 567, $^2J_{PP}$ 203, $^3J_{HP}$ 16 Hz, P_B).[20] For **9**, ^{31}P (CH_2Cl_2), δ 71 (dd, $^1J_{PP}$ 383, $^2J_{PP}$ 81 Hz, P_C), 382 (dd, $^1J_{PP}$ 588, $^2J_{PP}$ 81 Hz, P_A), 621 (dd, $^1J_{PP}$ 588, $^2J_{PP}$ 81 Hz, P_B); ^{19}F (CH_2Cl_2, CCl_3F ext.) δ −79. For **10a**, ^{31}P (CH_2Cl_2), δ 458 (d, $^1J_{PP}$ 586 Hz, P_B), 532 (d, $^1J_{PP}$ 586 Hz, P_A). For **10b**, ^{31}P (CH_2Cl_2), δ 431 (d, $^1J_{PP}$ 574 Hz, P_B), 560 (d, $^1J_{PP}$ 574 Hz, P_A).

§ *Crystal data* for **6**: $C_{60}H_{64}BP_3$, M = 888.91, triclinic, space group $P\bar{1}$, a = 11.228(8), b = 12.028(4), c = 19.615(5) Å, α = 91.27(3), β = 93.36(5), γ = 100.93(5)°, V = 2595(4) Å^3, $F(000)$ = 948, Z = 2, D_c = 1.14 g cm^{-3}, μ = 13.1 cm^{-1}, crystal size *ca.* 0.66 × 0.38 × 0.16 mm, 8167 total (7710 independent) reflections, R = 0.042 and R_w = 0.041 from 5118 reflections with $I > 3\sigma(I)$ (577 variables, observations/variables 8.87), maximum and minimum peaks in final Fourier difference synthesis 0.22(3) and −0.23(3) e Å^3. A crystal of **6** was sealed under nitrogen in a Lindemann capillary and this was transferred to the goniometer head. Data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite monochromated Cu-Kα radiation (ω/2θ scan mode, ratio of scan rates ω/θ = 1.2, θ_{max} = 60°). The structure was solved by direct methods and refined by full-matrix least-squares techniques in the anisotropic approximation (unit weighting scheme). All hydrogen atoms were located in the difference Fourier maps and included in the final refinement with the fixed positional

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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.

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