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Interpnictogen Compounds with Polarised Phosphorus–Element Bonds

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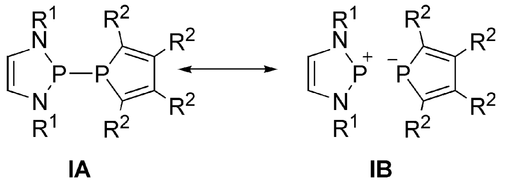
Dedicated to Professor Gerd Becker on the Occasion of His 70th Birthday

Keywords: N-heterocyclic compounds; Interpnictogen bonds; Donor-acceptor systems; Phosphorus; Pnictogens

Abstract. Metathesis of chloro-substituted N-heterocyclic phosphanes, arsanes, and stibanes with lithium tetraethylphospholide or -arsolide gave interpnictogen compounds **2**–**4** with As–P or Sb–P bonds, respectively. The products were characterised by analytical and spectroscopic data and single-crystal X-ray diffraction studies. All compounds feature central *E*–*E*' bonds that are notably longer (5–12 %) than standard bond lengths, and the As–P bond in the isomers **2** and **3** which are merely distinguished by formal exchange of the pnictogen atoms between both rings differ by some 4 pm. The observed structural features suggest that compounds **2**–**4** may, like the corresponding diphosphanes, be perceived as adducts of Lewis-pairs which are held together by a dative interpnictogen bond.

Introduction

Unsymmetrically substituted diphosphanes **I** (Scheme 1), which consist of an N-heterocyclic 1,3,2-diazaphospholene and a phosphole fragment are distinguished by unusually long P–P bonds whose distances (2.35–2.70 Å) exceed by far the standard single bond length of 2.21 Å [1], and a unique reactivity that enables these species to undergo insertion or addition reactions with concomitant cleavage of the P–P bond under extremely mild conditions [1, 2]. The structural and chemical properties have been attributed to a bonding situation which has been characterised in terms of bond/no bond resonance between covalent (**IA**) and ionic (**IB**) canonical structures, and led to describe diphosphanes **I** as Lewis-acid/base complexes with dative P–P interactions rather than molecules which are formally assembled by connecting two radical fragments with a covalent bond [1].



Scheme 1.

Regarding that bond energies decrease continually for covalent *E*–*E* bonds between the heavier pnictogen atoms [3], it is expected that the ionic character is further enhanced if one or both phosphorus atoms in **I** are formally replaced by an arsenic, antimony or bismuth atom. Unsymmetrical derivatives resulting from formal substitution of just one phosphorus atom in **I** are in this respect of particular interest as compounds with bonds between unlike pnictogen atoms are much less explored than derivatives with homonuclear bonds [4], and formal substitution of either of the two inequivalent phosphorus atoms of **I** may give rise to structural isomers where the bond polarisation implied by the bond/no bond resonance depicted in Scheme 1 is either enhanced or offset by the electronegativity difference between the bonding partners. As a consequence, the balance of both factors may affect the actually observable bond lengthening in the two isomeric molecules and thus constitute a special type of bond length isomerism. Following this outline, we report on the synthesis and structural characterisation of analogous compounds where both rings are linked by an $As^{(\delta+)}$–$P^{(\delta-)}$, $Sb^{(\delta+)}$–$P^{(\delta-)}$, or $P^{(\delta+)}$–$As^{(\delta-)}$ interpnictogen bond.

Results and Discussion

Diphosphane **1** is formed through metathesis between N-heterocyclic chlorophosphane **5a** and lithium phospholide **6a** [1]. By analogy, coupling of **6a** with chloroarsane **5b** [5] and chlorostibane **5c** [5] gave the expected products **2**, **3** with As–P and Sb–P bonds, and treatment of **5a** with lithium arsolide **6b** [6] produced **4** which is set apart from **2** by formal exchange of the two pnictogen atoms (Scheme 2). In contrast, reaction of chlorophosphane **5a** with the potassium stibolide [K(SbC_4Et_4)] (**6c**) [7] was found to be messy, and we were unable to obtain an isolable product. The interpnictogen compounds **2**–**4** were isolated in moderate to good yields of 50–72 % and characterised by analytical and spectroscopic data and single-crystal diffraction studies.

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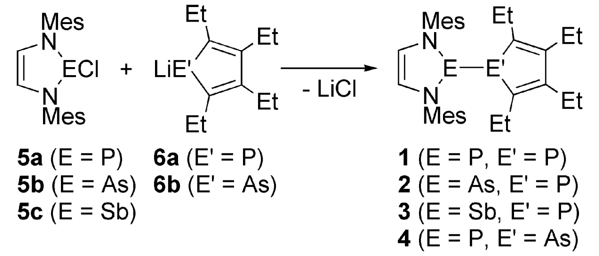

Scheme 2.

The spectroscopic data of **2**–**4** are unpeculiar. The ^{31}P NMR chemical shifts of **2** (δ^{31}P = 26.9) and **3** (δ^{31}P = 25.4) match closely the shift of the phosphorus atom in the phosphole ring of **1** (δ^{31}P = 23.1 [1]). The ^{31}P NMR signal of **4** (δ^{31}P = 160.1) is deshielded with respect to the corresponding resonance in **1** (δ^{31}P = 147.1) but lies still in the region between 135 and 170 ppm [1] covered by the chemical shifts of known diphosphanes (**I**). Mass spectra of **2**–**4** show molecular ion peaks of very low intensity (0.1–0.6 %) which indicate that the intact molecular species exist in the gas phase but have quite low stability, and the appearance of characteristic fragment ions attributable to N-heterocyclic cations $[(CH)_2(NMes)_2E]^+$ and ions $[C_{12}H_{19}E]^+$ (E = P, As) suggests cleavage of the central P–E bond as a prominent pathway for fragmentation.

Compounds **2** and **3** crystallise in the monoclinic space group $P2_1/n$ (**2**) or $P2_1/c$ (**3**), respectively, and show the same pattern for the packing of individual molecules in the crystal whereas crystals of **4** are triclinic and belong to the same space group $P\bar{1}$ as **1** [1]. Closer inspection reveals that single molecules of **1**, **2**–**4** are distinguished by subtle differences in the conformation of ethyl substituents at the phosphole ring (cf. Figure 1, Figure 2, and Figure 3) which alter the overall molecular shape and are presumably responsible for the observed differences in the crystal packing.

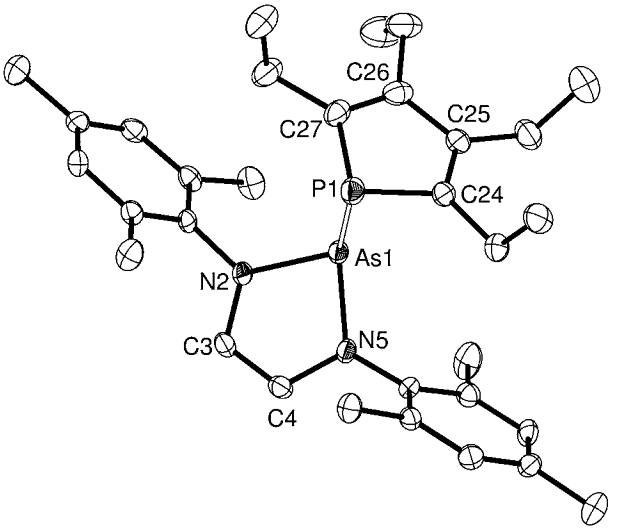

Figure 1. ORTEP-style representation of a molecule of **2** in the crystal (hydrogen atoms omitted for clarity; displacement parameters drawn at 50 % probability level). Selected bond lengths /Å and angles /° are listed in Table 1.

Comparison of significant bond lengths of **2**–**4** with each other and with the appropriate data for **1** (Table 1) reveals that the individual N–C, C–C and P–C bonds are essentially identical within experimental error and do not deviate significantly from the corresponding bond lengths in diphosphanes **I**. The As–N bonds in **2** and the Sb–N bonds in **3** are by some 5–6 pm longer than those in 2-halogeno-substituted N-heterocyclic arsanes (As–N 1.805–1.806 Å [5]) or stibanes (Sb–N 1.998–2.000 Å [5]), respectively. The same trend has also been noted for the P–N bond lengths in **I** [1] and was interpreted as indication of a more severe bond order alternation, and thus a lesser π-electron delocalisation, than in the 2-chloro derivatives. The As–C distances in the arsole ring of **4** (1.911–1.916 Å) are similar to those in known arsoles or η^1-arsole complexes (As–C 1.91–1.94 Å [8]), and the bond length distribution in this ring suggests that the π-electron structure is like in **1** closer to that of a conjugated diene rather than a delocalised aromatic heterocycle.

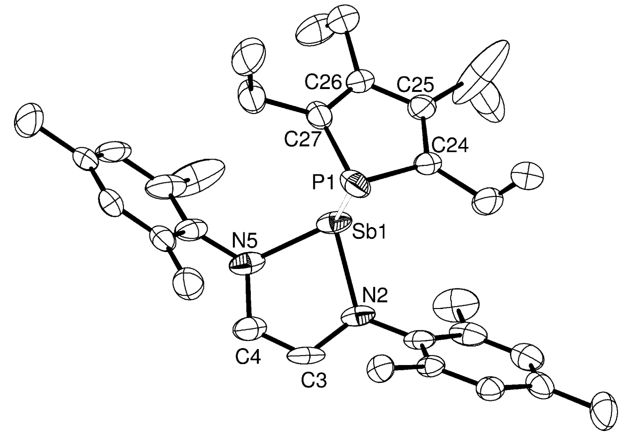

Figure 2. ORTEP-style representation of a molecule of **3** in the crystal (hydrogen atoms omitted for clarity; displacement parameters drawn at 50 % probability level). Selected bond lengths /Å and angles /° are listed in Table 1.

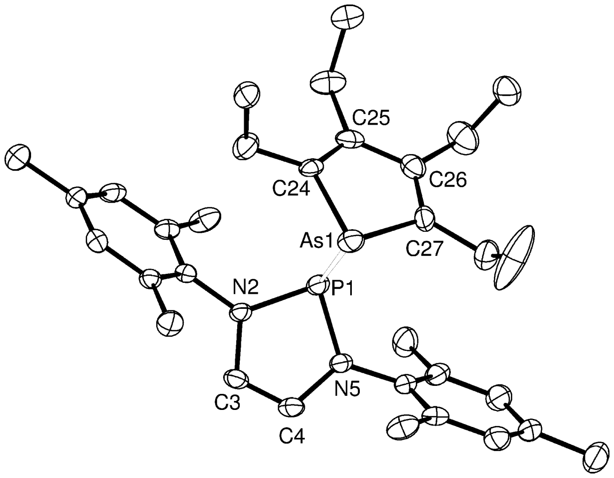

Figure 3. ORTEP-style representation of a molecule of **4** in the crystal (hydrogen atoms omitted for clarity; displacement parameters drawn at 50 % probability level). Selected bond lengths /Å and angles /° are listed in Table 1.

Table 1. Selected bond lengths /Å and angles /° for **2**–**4**. Data for **1** [1] are included for comparison.

	1 a)	**2**	**3**	**4**
E···*E*'	P1–P2	As1–P1	Sb1–P1	P1–As1
E–*E*'	2.484(1)	2.554(1)	2.667(2)	2.588(1)
E–N2	1.722(2)	1.867(2)	2.054(3)	1.725(3)
N2–C3	1.404(2)	1.385(3)	1.398(6)	1.399(3)
C3–C4	1.327(3)	1.334(3)	1.328(7)	1.309(4)
C4–N5	1.397(3)	1.403(3)	1.391(6)	1.411(4)
N5–*E*	1.716(2)	1.862(2)	2.053(4)	1.716(2)
E'–C24	1.789(2)	1.791(3)	1.782(5)	1.911(3)
C24–C25	1.371(3)	1.375(3)	1.369(7)	1.371(4)
C25–C26	1.446(3)	1.455(3)	1.428(7)	1.454(5)
C26–C27	1.371(3)	1.376(3)	1.369(7)	1.364(5)
C27–*E*'	1.788(2)	1.791(3)	1.785(6)	1.916(3)
C24–*E*'–*E*	81.1(1)	79.0(1)	79.3(2)	79.1(1)
C27–*E*'–*E*	81.9(1)	81.2(1)	79.8(2)	80.0(1)
N2–*E*–*E*'	109.7(1)	110.8(1)	105.9(1)	108.6(1)
N5–*E*–*E*'	110.9(1)	109.2(1)	108.6(1)	110.4(1)

a) Data from ref. [1]

The most interesting structural parameters are beyond doubt the *E*–*E*' distances of the bonds connecting the two pnictogen atoms. Like in the diphosphanes **I**, the As–P and Sb–P bonds in **2**–**4** are generally longer than standard bond lengths (As–P 2.338 ± 0.023 Å, Sb–P 2.541 ± 0.026 Å [9]) but the relative lengthening decreases continually from **1**, where the distance of 2.484 Å exceeds a standard bond length by 12 %, to 9 % for the As–P bonds in **2** and **4** and 6 % for the Sb–P bond in **3**. The same trend had previously been observed in a series of 2-chloro-substituted N-heterocyclic phosphanes and their heavier congeners [5] and owes presumably to the fact that the standard values reflect with growing electronegativity difference of *E* and *E*' likewise an increasing ionicity so that these systems are therefore getting more similar (ionic) to the reported molecules and, as a consequence, the deviations become smaller. The P–As bonds in the isomers **2** and **4** differ by a margin of 3.5 pm which exceeds appreciably the sum of estimated errors. It is further an interesting aspect to note that the C–*E*2–*E*1 bond angles in **2**–**4** (79–82°) lie right through at the lower end of the range found for diphosphanes **I** (79–89°) [1] and impose therefore a molecular conformation in which the pnictogen atom in the EN_2C_2-ring resides above the EC_4-ring and is close to its centroid. The EC_4-rings deviate not significantly from planarity and the EN_2C_2-rings display very flat envelope conformations (fold angles between C_2N_2 and N_2E-units 5.5–7.5°). The five-membered rings in **2**–**4** exhibit angles of 34–40° between least-squares planes drawn through the atoms in each ring.

The presence of lengthened and highly flexible P–P bonds in combination with acute phosphorus bond angles was identified as characteristic structural signature of the special bonding situation in diphosphanes **I** that led to perceive these compounds as phosphenium–phospholide contact ion pairs [1]. As compounds **2**–**4** display essentially the same features, we consider them likewise as adducts of Lewis pairs that are held together by a dative donor-acceptor interaction rather than a genuine covalent bond. The notable deviation in the P–As distances in the isomers **2** and **4** may then be traced to the higher Lewis-acidity of the *N*-heterocyclic arsenium as compared to the corresponding phosphenium cation [5], however, regarding that very minute energetic forces suffice to induce far larger variations of P–P distances in **I** [1], the difference must be regarded as chemically insignificant. The trend in Lewis-acidities of the cation fragments can likewise serve to explain the effect that the relative bond lengthening (i.e. the difference between actually observed *E*–*E*' distances in **1**, **2** and **3** and the appropriate standard bond lengths) shrinks with increasing atomic number of the pnictogen atom in the cation fragment although, in view of the importance of steric effects for the molecular structures of **I** [1], it must be conceded that part of this effect is also attributable to a decrease of repulsive interactions between substituents with increasing atomic radius of the central pnictogen atoms.

Conclusions

Higher congeners of diphosphanes with interpnictogen *E*–*E*' bonds were prepared in a controlled way by metathesis reactions. The results of single-crystal X-ray diffraction studies reveal that the *E*–*E*' bonds are longer than standard distances and show a certain elasticity which is highlighted by the observed deviation of As–P distances in the isomers **2**, **4**. The structural features suggest to perceive the molecules, like the analogous diphosphanes, as donor-acceptor adducts of Lewis-pairs that are held together by dative *E*–*E*' bonds.

Experimental Section

General remarks: All manipulations were carried out under argon using Schlenk techniques. Solvents were dried prior to use by common procedures. NMR spectra were recorded with Bruker Avance 250 (^{1}H: 250.1 MHz, ^{13}C: 62.8 MHz, ^{31}P: 101.2 MHz) or Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{31}P: 161.9 MHz) spectrometers at 303 K. Chemical shifts were referenced to ext. TMS (^{1}H, ^{13}C) or 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P). EI-MS: Varian MAT 711, 70eV. Elemental analysis: Perkin–Elmer 24000 CHN/O Analyser. Melting points were determined in sealed capillaries.

General Procedure for the Reaction of 5b,c with Lithium-tetraethylphospholide

Lithium shavings (14 mg, 2.0 mmol) were added to a solution of 1-chloro-2,3,4,5-tetraethylphosphole [10] (230 mg, 1.0 mmol) in THF (20 mL) and the mixture was allowed to stir for 3 h at ambient temperature. Unreacted lithium was removed by filtration and the solution added dropwise to a cooled (–78 °C) solution of **5b** [5] (403 mg, 1.0 mmol) or **5c** [5] (450 mg, 1.0 mmol) in THF (50 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. Solvent was removed under reduced pressure and the residue dispersed in hexane (100 mL). Precipitated salts were removed by filtration through Celite. The volume of the filtrate was reduced to 20 mL under reduced pressure and the remaining solution stored at –20 °C for crystallisation. The yellow crystalline precipitate was collected by filtration and dried in vacuo.

1,3-Di-mesityl-2-(2',3',4',5'-tetraethylphospholyl)-1,3,2-diazaarsolene (2): Yield 347 mg (0.62 mmol, 62 % yield); m.p. 162 °C. $C_{32}H_{44}AsN_2P$ (562.61): calcd. C 68.32 H 7.88 N 4.98; found C 68.03 H 7.96 N 4.69 %. **^{1}H NMR** (C_6D_6): $\delta = 6.80$ (s, 4 H, *m*-CH), 6.06 (s, 2 H, N–CH), 2.41 (s, 12 H, *o*-CH_3), 2.35 (q, 4 H, $^3J_{HH}$ = 7,6 Hz, CH_2), 2.14 (s, 6 H, *p*-CH_3), 1.98 (qd, 2 H, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 7.6 Hz, CH_2); 1.40 (qd, 2 H, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 7.6 Hz, CH_2), 1.05 (t, 6 H, $^3J_{HH}$ = 7.6 Hz, CH_3), 1,04 (t, 6 H, $^3J_{HH}$ = 7.6 Hz, CH_3). **^{13}C{^{1}H} NMR** (C_6D_6): $\delta = 151.9$ (d, $^2J_{PC}$ = 3.4 Hz, $C_{Phosphole}$), 144.9 (d, $^1J_{PC}$ = 27.6 Hz, $C_{Phosphole}$), 139.7 (d, $^3J_{PC}$ = 1.5 Hz, *i*-C), 136.4 (s, *p*-C), 135.8 (d, $^4J_{PC}$ = 1.5 Hz, *o*-C), 129.8 (s, *m*-CH), 122.4 (d, $^3J_{PC}$ = 1.4 Hz, N–CH), 21.4 (d, $^3J_{PC}$ = 1.0 Hz, CH_3), 21.3 (d, $^3J_{PC}$ = 22.4 Hz, CH_2), 21.0 (s, CH_3), 19.9 (s, *o*-CH_3), 19.8 (s, *o*-CH_3), 18.6 (d, $^2J_{PC}$ = 6.8 Hz, CH_2), 17.8 (s, CH_3). **^{31}P{^{1}H} NMR** (C_6D_6): $\delta = 26.9$ (s). **MS:** (EI, 70 eV, 420K): m/e (%) = 562.1 ([M]$^+$, 0.5), 488.2 ([M–C_5H_{14}]$^+$, 0.6); 367.0 ([M–$C_{12}H_{20}P$]$^+$, 24), 277.1 ([M–$C_{13}H_{23}PAs$]$^+$, 100), 194.0 ([M–$C_{20}H_{25}N_2As$]$^+$, 54).

1,3-Di-mesityl-2-(2',3',4',5'-tetraethylphospholyl)-1,3,2-diazastibolene (3): Yield 303 mg (0.50 mmol, 50 % yield); m.p. 159 °C. $C_{32}H_{44}N_2PSb$ (609.44): calcd. C 63.07 H 7.28 N 4.60, found C 62.94 H 7.28 N 4.59 %. **^{1}H NMR** (C_6D_6): $\delta = 6.84$ (s, 4 H, *m*-CH), 6.37 (s, 2 H, N–CH), 2.46 (s, 12 H, *o*-CH_3), 2.28 (q, 4 H, $^3J_{HH}$ = 7.5 Hz, CH_2), 2.18 (s, 6 H, *p*-CH_3), 1.58 (qd, 4 H, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 4.7 Hz, CH_2), 1.00 (t, $^3J_{HH}$ = 7.5 Hz, CH_3), 0.97 (t, $^3J_{HH}$ = 7.5 Hz, CH_3). **^{13}C{^{1}H} NMR** (C_6D_6): $\delta = 146.8$ (d, $^2J_{PC}$ = 3.7 Hz, $C_{Phosphole}$), 139.2 (d, $^1J_{PC}$ = 29.5 Hz, $C_{Phosphole}$), 137.2 (d, $^3J_{PC}$ = 1.3 Hz, *i*-C), 129.7 (s, *o*-C), 124.4 (s, *m*-CH), 124.4 (s, *p*-C), 119.3 (d, $^3J_{PC}$ = 1.3 Hz, N–CH), 16.8 (s, CH_3), 16.1 (d, $^2J_{PC}$ = 12.9 Hz, CH_2), 15.5 (s, *o*-CH_3), 14.6 (d, $^3J_{PC}$ = 2.9 Hz, CH_2), 12.9 (s, CH_3), 12.8 (d, $^3J_{PC}$ = 1.0 Hz, CH_3). **^{31}P{^{1}H} NMR** (C_6D_6): $\delta = 25.4$ (s). **MS:** (EI, 70 eV, 420K): m/e (%) = 608.2 ([M]$^+$, 0.6), 413.0 ([M–$C_{12}H_{20}P$]$^+$, 16), 277.0 ([M–$C_{21}H_{23}PSb$]$^+$, 100), 194.0 ([M–$C_{20}H_{25}N_2Sb$]$^+$, 74).

1,3-Di-mesityl-2-(2',3',4',5'-tetraethylarsolyl)-1,3,2-diazaphospholene (4): Potassium shavings (390 mg, 10 mmol) were added to a solution of 1-chloro-2,3,4,5-tetraethylarsole [10] (1.37 g, 5.0 mmol) in THF (20 mL) and the mixture was allowed to stir for 5 d at ambient temperature. Unreacted metal was removed by filtration and the solution added dropwise to a cooled (–78 °C) solution of **5a** [11] (1.80 g, 5.0 mmol) in THF (50 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. Solvent was removed under reduced pressure and the residue dispersed in hexane (100 mL). Precipitated salts were removed by filtration through Celite. The volume of the filtrate was reduced to 20 mL under reduced pressure and the remaining solution stored at –20 °C for crystallisation. The orange crystalline precipitate was collected by filtration and dried in vacuo to give 1.97 g (3.5 mmol, 70 % yield) of **4** of m.p. 178 °C. $C_{32}H_{44}AsN_2P$ (562.61): calcd. C 68.32 H 7.88 N 4.98; found C 67.99 H 7.91 N 4.60 %. **^{1}H NMR** (C_6D_6): $\delta = 6.77$ (s, 4 H, *m*-CH), 5.84 (s, 2 H, N–CH), 2.43 (s, 6 H, *p*-CH_3), 2.33 (q, 4 H, $^3J_{HH}$ = 7.3 Hz, CH_2), 2.01 (q, 4 H, $^3J_{HH}$ = 7.3 Hz, CH_2), 1.23 (s, 12 H, *o*-CH_3), 1.06 (t, 6 H, $^3J_{HH}$ = 7.3 Hz, CH_3), 0.88 (t, 6 H, $^3J_{HH}$ = 7.3 Hz, CH_3). **^{13}C{^{1}H} NMR** (C_6D_6): $\delta = 152.0$ (d, $^2J_{PC}$ = 14.7 Hz, C_{Arsole}), 143.4 (d, $^3J_{PC}$ = 8.2 Hz, C_{Arsole}), 136.6 (d, $^2J_{PC}$ = 6.8 Hz, *i*-C), 136.4 (d, $^5J_{PC}$ = 2.0 Hz, *p*-C), 135.8 (d, $^3J_{PC}$ = 3.4 Hz, *o*-C), 129.7 (d, $^4J_{PC}$ = 1.1 Hz, *m*-C), 121.4 (d, $^2J_{PC}$ = 8.9 Hz, N–CH), 22.7 (s, *p*-CH_3), 20.7 (d, $^5J_{PC}$ = 0.8 Hz, CH_3), 19.7 (d, $^3J_{PC}$ = 5.5 Hz, CH_2), 18.8 (d, $^4J_{PC}$ = 2.2 Hz, CH_2), 16.6 (d, $^4J_{PC}$ = 1.4 Hz, CH_3), 14.0 (s, *o*-CH_3). **^{31}P{^{1}H} NMR** (C_6D_6): $\delta = 160.6$ (s). **MS:** (EI, 70 eV, 430K): m/e (%) = 562.0 ([M]$^+$, 0.1), 478.0 ([M–C_6H_{12}]$^+$, 31), 323.1 ([M–$C_{12}H_{20}As$]$^+$, 27), 238.0 ([M–$C_{20}H_{42}N_2P$]$^+$, 100).

X-ray Crystallography

The crystals were investigated with a Nonius Kappa-CCD diffractometer at 123(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97 [12]) were used for structure solution and full-matrix least-squares refinement on F^2 (SHELXL-97 [12]). Hydrogen atoms were localised by difference Fourier synthesis and refined using a riding model.

2: orange crystals, $C_{32}H_{44}AsN_2P$, M = 562.58, crystal size 0.30 × 0.20 × 0.10 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 8.1286(2) Å, b = 20.5683(5) Å, c = 18.1360(4) Å, β = 100.036(1)°, V = 2985.79(12) Å^3, Z = 4, ρ(calcd) = 1.252 Mg·m^{-3}, F(000) = 1192, μ = 1.21 mm^{-1}, 14695 reflexes ($2\theta_{max}$ = 50°), 5258 unique [R_{int} = 0.050], semi-empirical absorption correction from multiple reflections, max. and min. transmission 0.7959 and 0.7220, 331 parameters, $R1$ [$I > 2\sigma(I)$) = 0.033, $wR2$ (*all data*) = 0.070, GooF = 0.93, largest diff. peak and hole 0.403 and –0.354 e·Å^{-3}.

3: red crystals, $C_{32}H_{44}N_2PSb$, M = 609.41, crystal size 0.20 × 0.10 × 0.05 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 8.5475(3) Å, b = 20.7642(7) Å, c = 17.6826(7) Å, β = 103.865(1)°, V = 3046.90(19) Å^3, Z = 4, ρ(calcd) = 1.329 Mg·m^{-3}, F(000) = 1264, μ = 0.98 mm^{-1}, 13737 reflexes ($2\theta_{max}$ = 50°), 5369 unique [R_{int} = 0.055], semi-empirical absorption correction from equivalents, max. and min. transmission 0.9498 and 0.7952, 331 parameters, 18 restraints, $R1$ [$I > 2\sigma(I)$) = 0.045, $wR2$ (*all data*) = 0.119, GooF = 0.97, largest diff. peak and hole 1.261 and –1.290 e·Å^{-3}.

4: yellow crystals, $C_{32}H_{44}AsN_2P$, M = 562.58, crystal size 0.15 × 0.10 × 0.03 mm, triclinic, space group $P\bar{1}$(No. 2): a = 8.1693(3) Å, b = 8.9044(3) Å, c = 20.4802(8) Å, α = 96.304(2)°, β = 90.302(2)°, γ = 94.501(2)°, V = 1476.07(9) Å^3, Z = 2, ρ(calcd) = 1.266 Mg·m^{-3}, F(000) = 596, μ = 1.23 mm^{-1}, 12039 reflexes ($2\theta_{max}$ = 50°), 5354 unique [R_{int} = 0.081], semi-empirical absorption correction from equivalents, max. and min. transmission 0.9619 and 0.8005, 331 parameters, $R1$ [$I > 2\sigma(I)$) = 0.048, $wR2$ (*all data*) = 0.078, GooF = 0.86, largest diff. peak and hole 0.530 and –0.405 e·Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-757208 (**2**), -757209 (**3**), 757210 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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[9] Result of a query in the CSD database (version 5.31 of Nov. 2009) for compounds featuring the generic fragment X_2P–EX_2 (E = As, Sb; X = any non-metal) with three-coordinate P and E atoms. The given values are the mean value and standard deviation of a sample of 8 (for E = As) or 9 compounds (for E = Sb), respectively.

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