Unsymmetric dipnictenes—synthesis and characterization of MesP=EC$_6$H$_3$-2,6-Trip$_2$ (E = As or Sb; Mes = C$_6$H$_2$-2,4,6-Me$_3$, Trip = C$_6$H$_2$-2,4,6-Pr$^i_3$)

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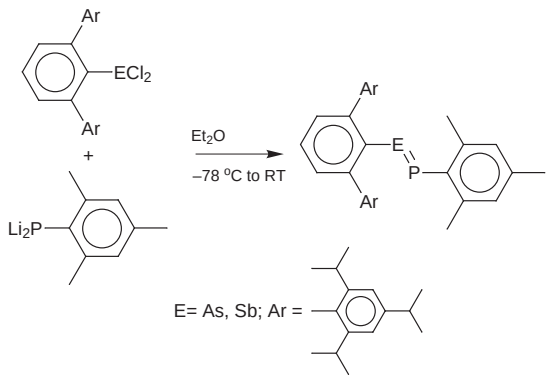
The use of terphenyl substituents enables the isolation of unsymmetrical dipnictenes with P=As or P=Sb double bonds by a new synthetic route.

The first stable diphosphene Mes*P=PMes* (Mes* = C$_6$H$_2$-2,4,6-Bu$^t_3$) was synthesized by Yoshifuji and coworkers in 1981, *via* the magnesium reduction of Mes*PCl$_2$ in THF.[1] Since that report many further examples of diphosphenes[2] have been synthesized. In contrast, the number of analogous compounds involving double bonds to the heavier pnictogens has remained quite small. For example, there are only two structurally characterized molecules with As–As double bonds,[3] and just one with a P–As double bond.[4] Stable compounds with Sb–Sb[5a] and Bi–Bi[5b] double bonds have only been reported recently. The latter were synthesized by a novel synthetic method involving the deselenation of 1,3,5,2,4,6-triselenatrispnictane (ArESe)$_3$ (Ar = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, E = Sb or Bi), whereas the related phosphorus or arsenic species, *i.e.* diphosphenes, diarsenes and phosphaarsenes, have usually been prepared *via* reduction with magnesium or sodium naphthalenide or in the case of the unsymmetrical compounds, by the coupling of ArECl$_2$ and Ar′E′H$_2$ in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).[4,6,7a] Other methods for synthesizing phosphaarsenes have used Me$_3$SiCl elimination[7b–d] or coupling of the RECl$_2$ (E = P, As) precursors in the presence of Bu^{t}Li.[7e] Currently, there is only one report of a phosphastibene, Mes*P=SbCH(SiMe$_3$)$_2$,[4,6] which was synthesized by the coupling of Mes*PH$_2$ with (Me$_3$Si)$_2$CHSbCl$_2$. However this compound is unstable under ambient conditions and it was characterized by high resolution mass spectrometry and ^{31}P NMR. Using a novel direct elimination method, we now report the isolation of the stable unsymmetric phosphastibene MesP=SbC$_6$H$_3$-2,6-Trip$_2$ (**1**) and phosphaarsene MesP=AsC$_6$H$_3$-2,6-Trip$_2$ (**2**) (Trip = 2,4,6-Pr$^i_3$).

Reaction of the dilithiophosphide Li$_2$PMes[8] in a 1:1 stoichiometry with 2,6-Trip$_2$H$_3$C$_6$ECl$_2$ (E = Sb, As) in Et$_2$O at −78 °C affords the corresponding phosphastibene MesP=SbC$_6$H$_3$-2,6-Trip$_2$ (**1**) and phosphaarsene MesP=AsC$_6$H$_3$-2,6-Trip$_2$ (**2**) (see Scheme 1). Both **1** and **2** were isolated† in low but reproducible yields of 1% and 7% respectively, and their structures were determined by X-ray crystallography (see Figs. 1 and 2).‡



Scheme 1 Synthesis route to unsymmetric dipnictenes

Compound **1** is the first example of a stable species with a P–Sb double bond [P–Sb = 2.335(2) Å]. The molecule has a *trans* configuration with a Sb–C bond distance of 2.174(7) Å and C–Sb–P and C–P–Sb angles of 100.9(2) and 95.7(3)°. There is a torsion angle of 4.2° in the C(37)–P(1)–Sb(1)–C(1) array. The ^{31}P NMR spectrum displays a singlet at 543 ppm which is 77 ppm upfield from Mes*P=SbCH(SiMe$_3$)$_2$ (620 ppm),[4,6] which demonstrates the shielding effect of the bulky terphenyl substituent. In the solid state **2**, which also has a *trans* conformation, has an As–P bond distance of 2.134(2) Å. The As–C bond distance is 1.975(6) and C–As–P and C–P–As angles are 101.4(2)° and 96.7(2)° respectively. These parameters are in reasonable agreement with the only other structurally characterized analogue Mes*P=AsCH(SiMe$_3$)$_2$[4,6] which has an

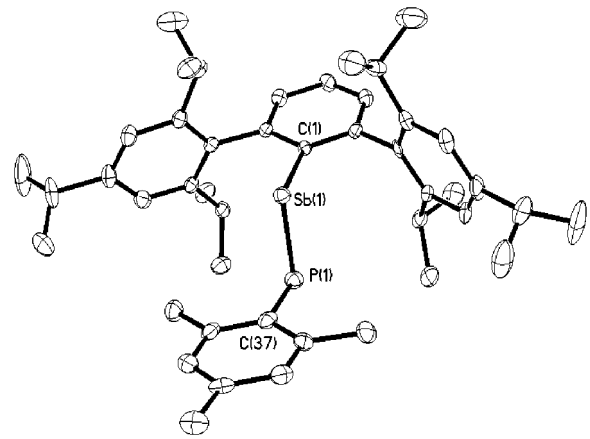


Fig. 1 ORTEP diagram of the structure of **1** (30% probability). H atoms omitted for clarity.

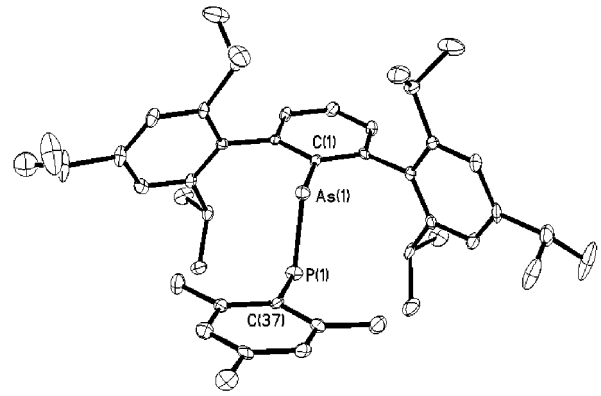


Fig. 2 ORTEP diagram of the structure of **2** (30% probability). H atoms omitted for clarity.

As–P distance of 2.125(1) Å, and C–As–P, C–P–As angles of 101.35(9)°, 96.37(9)°. **2** has a torsion angle of 3.2° for the array C(37)–P(1)–As(1)–C(1). The ^{31}P NMR spectrum of **2** shows a sharp singlet at 534 ppm which is 41 ppm upfield from that of Mes*P=AsCH(SiMe$_3$)$_2$ (575 ppm) and is almost identical to those of (Me$_3$Si)$_2$CHP=AsMes* (533 ppm),[6] and ArP=AsAr (537 ppm) Ar = 2,6-dimesityl-4-methylphenyl.[7a]

The As–P and Sb–P bonds are *ca.* 8% shorter than the calculated covalent single bond distances (2.33 and 2.54 Å)[9] which indicates considerable double bond character. The percentage shortening is comparable to that seen in symmetrical double bonded compounds.[2] In addition **1** and **2** display bond angles of 100.9(2) and 101.35(9)° at antimony and arsenic and narrow angles of 95.7(3) and 96.7(2)° at the phosphorus atoms. The wider angles at arsenic and antimony are somewhat surprising but are probably due to the larger size of the aryl substituents at these atoms. It may be noted that the angles at all the pnictogens are considerably smaller than would be expected for approximately sp^2 hybridization, indicating a concentration of s-character in the lone pair orbitals.

The electronic spectra for **1** and **2** each exhibit two absorption maxima, 512 nm (ε 373), 397 nm (ε 3417) and 467 nm (ε 216), 356 nm (ε 2477) respectively. The spectrum of **2** closely matches those of Mes*P=AsCH(SiMe$_3$)$_2$ [454 nm (ε 280), 353 nm (ε 7500],[4] and ArP=AsAr [463 nm (ε 870), 385 nm (ε 9549) (Ar = 2,6-dimesityl-4-methylphenyl)], [7a] whereas the spectrum of **1** shows a characteristic red-shift for double-bond systems of heavier group 15 elements as seen in *e.g.* ArSb=SbAr,[5a] 599 nm (ε 170), 466 nm (ε 5200) and ArBi=BiAr,[5b] 660 nm (ε 100), 525 nm (ε 4000), where Ar = C$_6$H$_2$-2,4,6-{CH(SiMe$_3$)$_2$}$_3$.

The reaction of 2,6-Trip$_2$H$_3$C$_6$BiCl$_2$ with either Li$_2$PMes or H$_2$PMes with DBU does not lead to the formation of the bismuth analogue MesP=BiC$_6$H$_3$-2,6-Trip$_2$. Instead, the purple symmetrical dibismuthene 2,6-Trip$_2$H$_3$C$_6$Bi=BiC$_6$H$_3$-2,6-Trip$_2$ is formed. The details of this structure as well as those of the corresponding distibenes, diarsenes, and diphosphenes will be reported in the near future.

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Notes and References

† *Experimental:* **1**: under anaerobic and anhydrous conditions, a solution of 2,6-Trip$_2$H$_3$C$_6$SbCl$_2$ (0.5 g, 0.74 mmol), in Et$_2$O (40 mL) was added to a suspension of MesPLi$_2$ (0.122 g, 0.74 mmol) in Et$_2$O (20 mL) at −78 °C, dropwise (10 min). The mixture was stirred at −78 °C (1 h) before warming to room temperature and stirred overnight. The solvent was removed *in vacuo* and the orange residue was extracted with hexane (40 mL) and filtered through Celite to give a deep orange solution. Concentration of the solution and prolonged cooling at −25 °C for 15 days yielded orange crystalline **1**, 62 mg, 1%. Mp 184–188 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.15 [d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.23 [d, 12H, *p*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.36 [d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.97 (s, 6H *o*-Me), 2.18 (s, 3H, *p*-Me), 2.798 [sept., 2H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 3.20 [sept., 4H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 6.73 (s, 2H, *m*-Mes), 7.13 (s, 4H, *m*-Trip), 7.32 [t, 1H, *p*-C$_6$H$_3$, $^3J_{HH}$ = 7.4 Hz], 7.46 (d, 2H, *m*-C$_6$H$_3$, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$) δ 20.66 (Mes-*C*H$_3$), 22.3 [*o*-CH(*C*H$_3$)$_2$], 24.29 [*p*-CH(*C*H$_3$)$_2$], 26.53 [*o*-CH(*C*H$_3$)$_2$], 31.33 [*o*-*C*H(CH$_3$)$_2$], 34.78 [*p*-*C*H(CH$_3$)$_2$], 121.14 (*m*-Trip), 128.28 (*p*-C$_6$H$_3$), 129.27 (*m*-C$_6$H$_3$), 130.02 (*m*-Mes), 137.43 (*i*-Trip), 137.73 (*o*-C$_6$H$_3$), 138.69 (*o*-Mes), 146.78 (*p*-Trip, *p*-Mes), 147.19 (*o*-Trip), 149.32 (d, *i*-Mes-P, J_{CP} = 5.7 Hz), 201.56 (*i*-C$_6$H$_3$). ^{31}P{^{1}H} NMR (121.7 MHz C$_6$D$_6$) δ 543. UV–VIS. (λ_{max}, ε) 512 nm, 373; 398 nm, 3417. **2**: this compound was prepared in a similar manner to that described for **1**; 2,6-Trip$_2$H$_3$C$_6$AsCl$_2$ (0.5 g. 0.79 mmol) and MesPLi$_2$ (0.131 g. 0.79 mmol) were reacted in Et$_2$O and **2** was isolated as pale orange crystals 40 mg, 7%. Mp 239–241 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.16 [d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz], 1.25 [d, 12H, *p*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.32 [d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.82 (s, 6H, *o*-Me), 2.04 (s, 3H, *p*-Me), 2.82 [sept., 2H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 3.16 [sept., 4H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 6.62 (s, 2H, *m*-Mes), 7.13 (s, 4H, *m*-Trip), 7.28 (t, 1H, *p*-C$_6$H$_3$, $^3J_{HH}$ = 7.35 Hz), 7.38 (d, 2H, *m*-C$_6$H$_3$, $^3J_{HH}$ = 7.35 Hz). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$) δ 20.86 (Mes-CH$_3$), 22.6 [*o*-CH(*C*H$_3$)$_2$], 24.37 [*p*-CH(*C*H$_3$)$_2$], 26.4 [*o*-CH(*C*H$_3$)$_2$], 31.43 [*o*-*C*H(CH$_3$)$_2$], 34.783 [*p*-*C*H(CH$_3$)$_2$], 121.06 (*m*-Trip), 128.15 (*p*-C$_6$H$_3$), 128.85 (*m*-C$_6$H$_3$), 130.03 (*m*-Mes), 137.63 (*i*-Trip), 137.99 (*o*-C$_6$H$_3$), 138.4 (*o*-Mes), 146.68 (*p*-Trip, *p*-Mes), 147.07 (*o*-Trip), 144.59 (d, *i*-Mes-P, J_{CP} = 4.3 Hz). ^{31}P{^{1}H} NMR (121.7 MHz C$_6$D$_6$) δ 534. UV–VIS. (λ_{max}, ε) 467 nm, 216; 356 nm, 2477.

‡ *Crystal data* at 130 K with Cu-Kα (λ = 1.54170 Å) radiation: **1** C$_{45}$H$_{60}$PSb, M = 753.65, triclinic, space group $P\bar{1}$, a = 12.848(3), b = 13.095(3), c = 13.642(3) Å, α = 102.97(3), β = 112.31(3), γ = 96.31(3)°, V = 2020.2(7) Å^3, Z = 2, D_c = 1.239 Mg m^{-3}, μ = 5.986 mm^{-1}, scan type 2θ, θ range 3.55 to 56.25°. GoF on F^2 1.027 for 5307 unique observed data and 434 parameters, R_1 6.04%, wR_2 13.46%; **2** C$_{45}$H$_{60}$PAs, M = 706.82, triclinic, space group $P\bar{1}$, a = 12.846(2), b = 12.918(3), c = 13.806(4) Å, α = 114.606(16), β = 102.508(17), γ = 93.932(16)°, V = 2000.7(8) Å^3, Z = 2, D_c = 1.173 Mg m^{-3}, μ = 1.725 mm^{-1}, scan type 2θ, θ range 3.58 to 56.45°. GoF on F^2 1.017 for 5272 unique observed data and 439 parameters, R_1 6.96%, wR_2 13.31%. Solution and refinement (full matrix least-squares on F^2) were performed using SHELXTL Plus 1994. CCDC 182/967.

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