Supplementary Information

"Phosphaalkene-substituted organo-group 15 compounds: Synthesis and characterisation of (NHC)P-E*t*Bu$_2$ (E = P, As, Sb, Bi)"

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Content

Experimental

All manipulations were performed under an inert argon atmosphere using standard *Schlenk* techniques. The solvents were dried by standard procedures and freshly destilled before used. The storage and use of moisture or air sensitive substances were carried out under an inert argon atmosphere in a glovebox. (SIMes)PK,[1] *t*Bu_2PCl,[2] *t*Bu_2AsCl,[3] *t*Bu_2SbCl,[4] *t*Bu_2BiBr[5] were prepared according to literature methods. NMR spectra were recorded on a Bruker AV II 300 or AV III HD 300. The coupling constants *J* were reported in Hertz (Hz) and the chemical shift (δ) is given in ppm relative to the standard (^{31}P: H_3PO_4; ^{1}H, ^{13}C: $SiMe_4$). IR-spectra were recorded on a Bruker ALPHA FT-IR with a diamond ATR (500-4000 cm^{-1}). Elemental analyses were performed on an ELEMENTAR Vario Microcube and the content is reported in %.

General procedure:

(SIMes)PK (50 mg, 0.133 mmol, 1 eq.) was added to *t*Bu_2EX (for E = P, As, Sb: X = Cl; for E = Bi: X = Br) (0.133 mmol, 1 eq.) in 8 mL toluene at –80 °C. The reaction mixture was slowly warmed to room temperature. The suspension was centrifuged and the obtained solution was concentrated *in vacuo*. Storage of the solution at –32 °C leads to crystals, which were separated and washed twice with pentane. The yields given billow are the yields of crystalline compounds. Higher yields (except compound **4**) are obtained from highly concentrated solutions as micro crystalline powders. However, in that case the samples always contain small amounts (up to 5%) of SIMesPH.

[(SIMes)PP*t*Bu_2] (1): Yield 17 mg, 0.035 mmol, 26%. Suitable crystals for X-ray measurements were obtained from toluene solution at –32 °C.
^{1}H NMR (300 MHz, C_6D_6): δ = 1.21 (d, $^{3}J_{P\text{-}H}$ = 10.7 Hz, 18 H, P(C(C*H*$_3$)$_3$)$_2$), 2.13 (s, 6H, mesityl-C*H*$_3$ para), 2.39 (s, 12 H, mesityl-C*H*$_3$ ortho), 3.19 (d, $^{4}J_{P\text{-}H}$ = 1.6 Hz, 4H, NC*H*$_2$C*H*$_2$N), 6.80 (s, 4H, mesityl-C*H* meta) ppm.
^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 18.9 (s, Mesityl-*C*H$_3$ ortho), 21.1 (s, Mesityl-*C*H$_3$ para), 31.7 (dd, $^{2}J_{C\text{-}P}$ = 5.9 Hz, $^{3}J_{C\text{-}P}$ = 15.2 Hz, P(C(*C*H$_3$)$_3$)$_2$), 32.5 (dd, $^{1}J_{C\text{-}P}$ = 28.4 Hz, 2JC-P = 8.8 Hz, P(*C*(CH$_3$)$_3$)$_2$), 49.8 (s, N*CC*N), 129.8 (s, mesityl-*C*H meta), 136.9 (s, mesityl C_{arom} para), 136.9 (s, mesityl C_{arom} ortho), 140.7 (s, mesityl C_{ipso}), 188.3 (dd, $^{1}J_{C\text{-}P}$ = 97.0 Hz, $^{2}J_{C\text{-}P}$ = 22.6 Hz, N*C*N) ppm.
^{31}P NMR (121 MHz, C_6D_6): δ = 18.5 (d-dec, $^{1}J_{P\text{-}P}$ = 252 Hz, $^{3}J_{P\text{-}H}$ = 10.7 Hz, *P*(C(CH$_3$)$_2$), –54.4 (d, $^{1}J_{P\text{-}P}$ = 252 Hz, SIMes-*P*) ppm.
IR: $\tilde{\nu}$ = 2961 (m), 2934 (m), 2885 (m), 2855 (m), 1607 (w), 1472 (m), 1397 (m), 1379 (m), 1358 (m), 1292 (m), 1258 (s), 1204 (m), 1173 (m), 1094 (m), 1071 (m), 1015 (s), 930 (m), 849 (m), 801 (s), 731 (w), 696 (w), 624 (w), 597 (w), 577 (m), 527 (m), 493 (m), 466 (m) cm^{-1}.
Elemental analysis calcd. (%) for $C_{29}H_{44}P_2N_2$ ([482.63 g/mol]): C 72.17, H 9.19, N 5.80; found: C 72.19, H 9.11, N 5.77.

[[SIMes)PA*st*Bu_2] (2): Yield 36 mg, 0.038 mmol, 29%. Suitable crystals for X-ray measurements were obtained from toluene solution at –32 °C.
^{1}H NMR (300 MHz, C_6D_6): δ = 1.25 (s, 18 H, As(C(C*H*$_3$)$_3$)$_2$), 2.12 (s, 6H, mesityl-*C*H$_3$ para), 2.39 (s, 12 H, mesityl-C*H*$_3$ ortho), 3.20 (d, $^{4}J_{P\text{-}H}$ = 1.6 Hz, 4H, NC*H*$_2$C*H*$_2$N), 6.80 (s, 4H, Mesityl-C*H* meta) ppm.
^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 18.8 (s, mesityl-*C*H$_3$ ortho), 21.1 (s, mesityl-*C*H$_3$ para), 31.5 (d, $^{3}J_{C\text{-}P}$ = 5.3 Hz, As(C(*C*H$_3$)$_3$)$_2$), 32.7 (d, $^{2}J_{C\text{-}P}$ = 7.3 Hz, As(*C*(CH$_3$)$_3$)$_2$), 49.9 (s, N*CC*N), 129.9 (s, mesityl-*C*H meta), 137.0 (s, mesityl C_{arom} para), 137.5 (s, mesityl C_{ipso}), 137.5 (s, Mesityl C_{arom} ortho), 187.9 (d, $^{1}J_{C\text{-}P}$ = 103.6 Hz, N*C*N) ppm.
^{31}P NMR (121 MHz, C_6D_6): δ = –46.6 (s, SIMes*P*) ppm.
IR: $\tilde{\nu}$ = 2915 (m), 2846 (m), 1607 (w), 1471 (m), 1381 (m), 1359 (m), 1259 (s), 1159 (m), 1096 (m), 1013 (m), 931 (w), 850 (m), 802 (m), 734 (w), 625 (w), 594 (w), 576 (m), 495 (w) cm^{-1}.
Elemental analysis calcd. (%) for $C_{29}H_{44}P_1N_2As_1$ ([526.58 g/mol]): C 66.15, H 8.42, N 5.32; found: C 66.03, H 8.26, N 5.39.

[[SIMes)PSb*t*Bu$_2$] (3): Yield 40 mg, 0.069 mmol, 52%. Suitable crystals for X-ray measurements were obtained from toluene solution at –32 °C.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.33 (s, 18H, Sb(C(C*H*$_3$)$_3$)$_2$), 2.12 (s, 6H, mesityl-*CH*$_3$ para), 2.36 (s, 12 H, mesityl-C*H*$_3$ ortho), 3.22 (d, $^4J_{P\text{-}H}$ = 1.4 Hz, 4H, NC*H*$_2$C*H*$_2$N), 6.80 (s, 4H, mesityl-C*H* meta) ppm.

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 18.6 (s, mesityl-*C*H$_3$ ortho), 21.1 (s, mesityl-*C*H$_3$ para), 26.2 (d, $^2J_{C\text{-}P}$ = 7.5 Hz, Sb(*C*(CH$_3$)$_3$)$_2$), 32.4 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, Sb(C(*C*H$_3$)$_3$)$_2$), 49.6 (d, $^3J_{C\text{-}P}$ = 2.6 Hz, N*CC*N), 130.2 (s, mesityl-*C*H meta), 137.2 (s, mesityl C$_{arom}$ ortho + s, mesityl C$_{arom}$ para), 137.9 (s, mesityl C$_{ipso}$), 188.1 (d, $^1J_{C\text{-}P}$ = 111.5 Hz, N*C*N) ppm.

^{31}P NMR (121 MHz, C_6D_6): δ = –72.6 (s, SIMes*P*) ppm.

IR: $\tilde{\nu}$ = 2913 (m), 2835 (s), 2698 (w), 1607 (w), 1463(m), 1402 (m), 1382 (m), 1358 (m), 1322 (w), 1292 (m), 1256 (s), 1149 (m), 1097 (s), 1031 (w), 1011 (w), 931 (m), 848 (s), 799 (s), 731 (w), 623 (w), 595 (m), 575 (s), 496 (m) cm^{-1}.

Elemental analysis calcd. (%) for $C_{29}H_{44}P_1N_2Sb_1$ ([573.42 g/mol]): C 60.74, H 7.73, N 4.89; found: C 60.54, H 7.71, N 4.91.

[[SIMes)PBi*t*Bu$_2$] (4): Yield 34 mg, 0.056 mmol, 38%. Suitable crystals for X-ray measurements were obtained from toluene solution at –32 °C. Due to instability of this compound towards light and temperature no satisfying elemental analysis could be obtained.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.87 (s, 18H, Bi(C(C*H*$_3$)$_3$)$_2$), 2.11 (s, 6H, mesityl-*CH*$_3$ para), 2.35 (s, 12 H, mesityl-C*H*$_3$ ortho), 3.24 (s, 4H, NC*H*$_2$C*H*$_2$N), 6.80 (s, 4H, mesityl-C*H* meta) ppm.

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 18.6 (d, $^5J_{C\text{-}P}$ = 2.3 Hz, mesityl-*C*H$_3$ ortho), 21.1 (s, mesityl-*C*H$_3$ para), 33.2 (d, $^3J_{C\text{-}P}$ = 3.7 Hz, Bi(C(*C*H$_3$)$_3$)$_2$), 37.5 (d, $^2J_{C\text{-}P}$ = 5.1 Hz, Bi(*C*(CH$_3$)$_3$)$_2$), 49.6 (d, $^3J_{C\text{-}P}$ = 2.0 Hz, N*CC*N), 130.2 (s, mesityl-*C*H meta), 137.2 (s, mesityl *C*$_{arom}$), 137.5 (s, mesityl *C*$_{arom}$), 137.9 (s, mesityl *C*$_{ipso}$), 186.4 (d, $^1J_{C\text{-}P}$ = 117.7 Hz, N*C*N) ppm.

^{31}P NMR (121 MHz, C_6D_6): δ = –50.7 (s, SIMes*P*) ppm.

IR: $\tilde{\nu}$ = 2908 (m), 2828 (s), 2754 (w), 2697 (w), 1726 (w), 1607 (w), 1482 (m), 1459 (m), 1400 (m), 1384 (m), 1358 (m), 1323 (m), 1307 (m), 1293 (m), 1254 (s), 1136 (s), 1097 (m), 1031 (m), 1011 (m), 966 (w), 931 (w), 849 (s), 795 (s), 732 (w), 695 (w), 622 (w), 596 (w), 575 (s), 498 (m), 414 (w) cm^{-1}.

NMR spectra

Compound 1

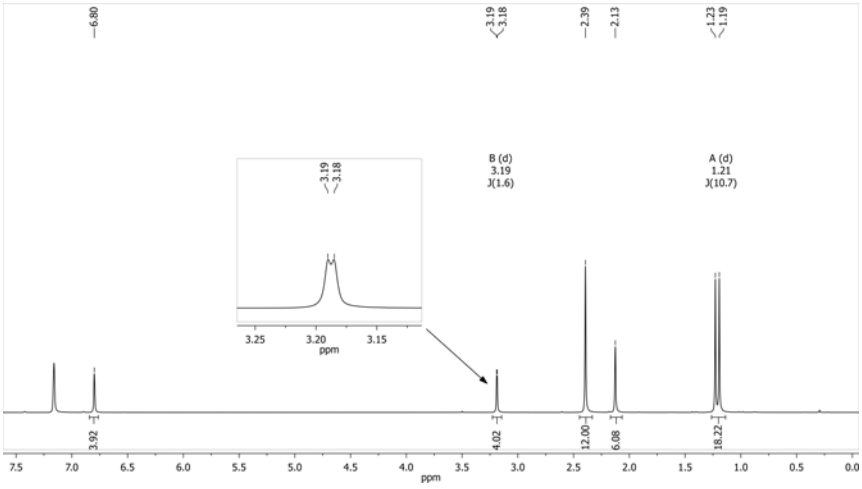

Figure S5: ^{1}H NMR spectrum of compound **1** in C_6D_6.

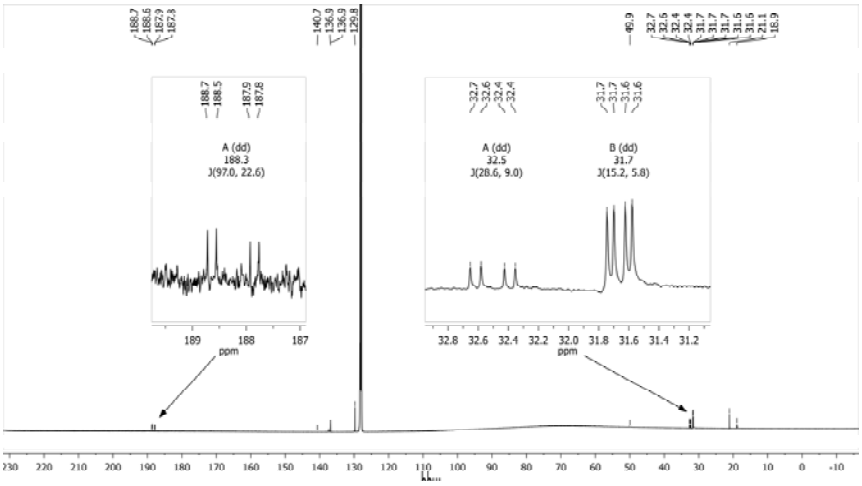

Figure S6: ^{13}C NMR spectrum of compound **1** in C_6D_6.

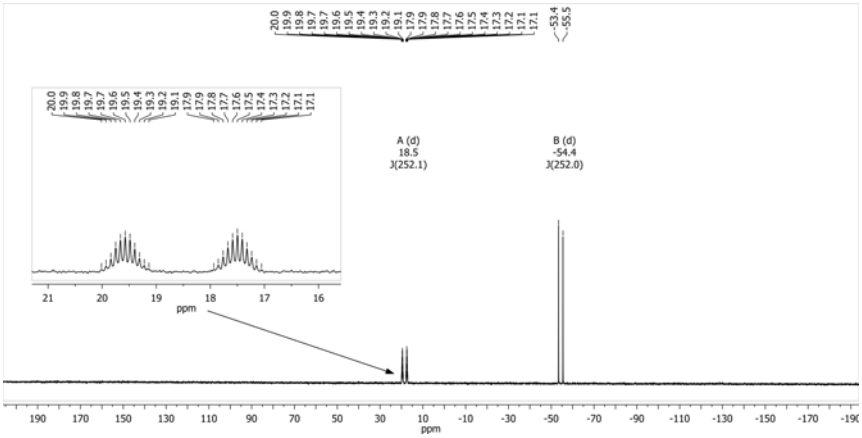

Figure S7: ^{31}P NMR spectrum of compound **1** in C_6D_6.

Compound 2

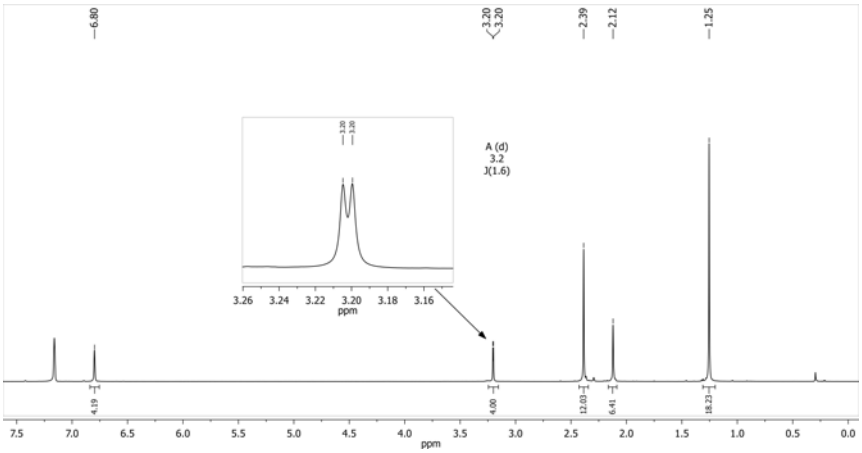

Figure S8: ^{1}H NMR spectrum of compound **2** in C_6D_6.

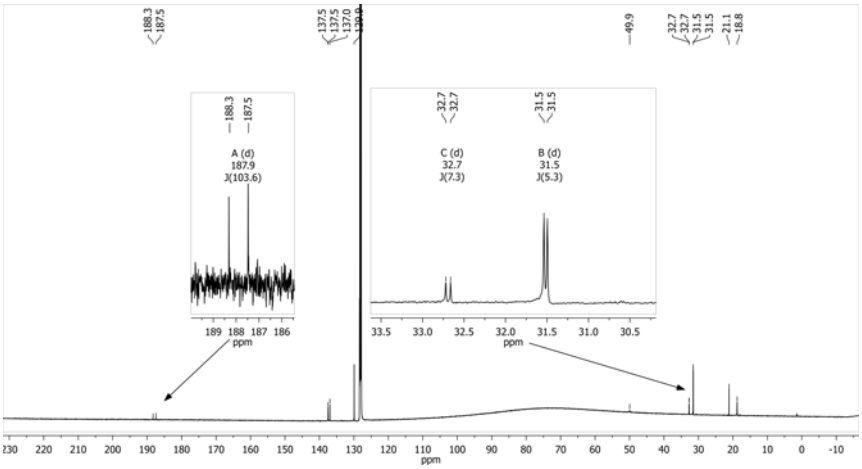

Figure S9: ^{13}C NMR spectrum of compound **2** in C_6D_6.

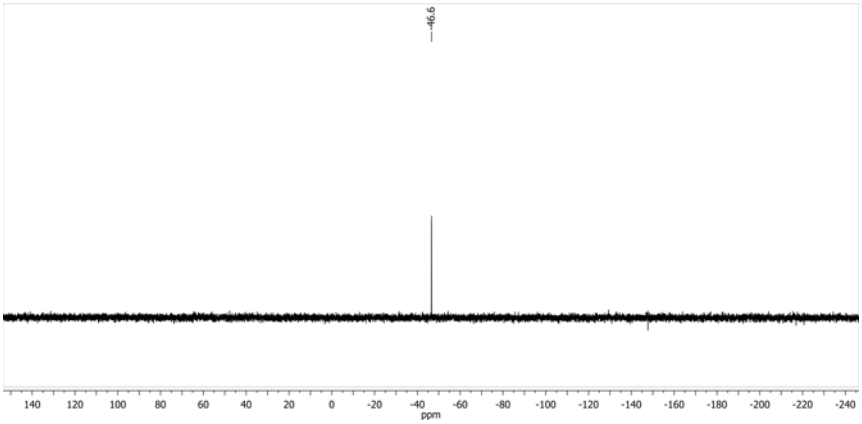

Figure S10: ^{31}P NMR spectrum of compound **2** in C_6D_6.

Compound 3

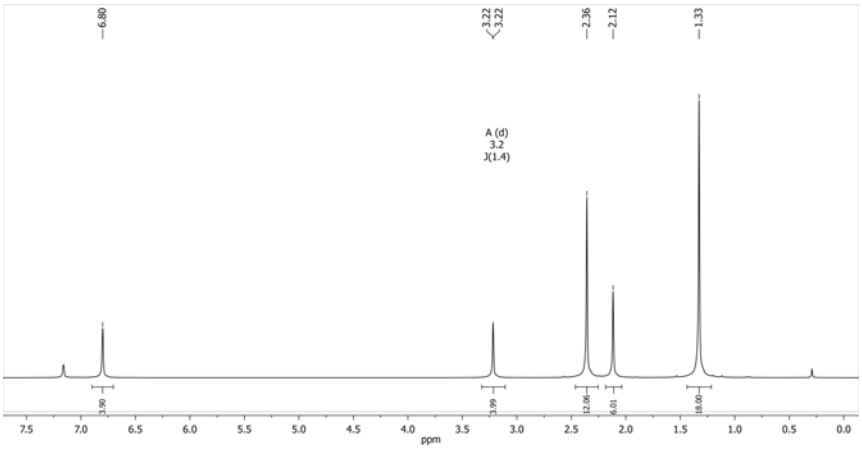

Figure S11: ^{1}H NMR spectrum of compound **3** in C_6D_6.

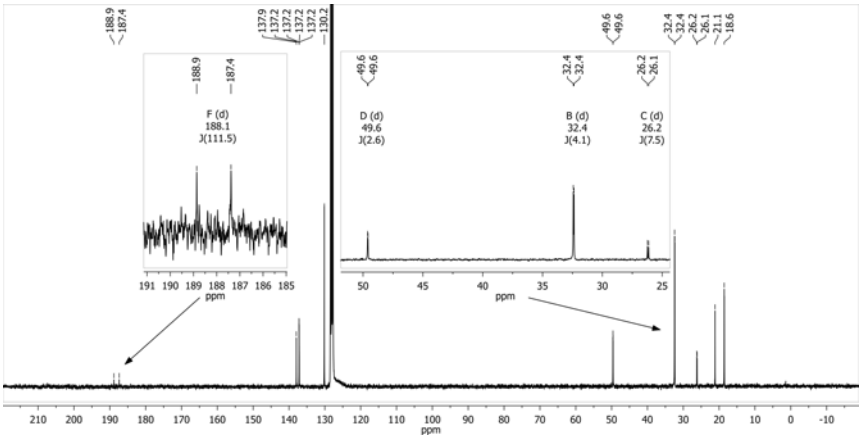

Figure S12: ^{13}C NMR spectrum of compound **3** in C_6D_6.

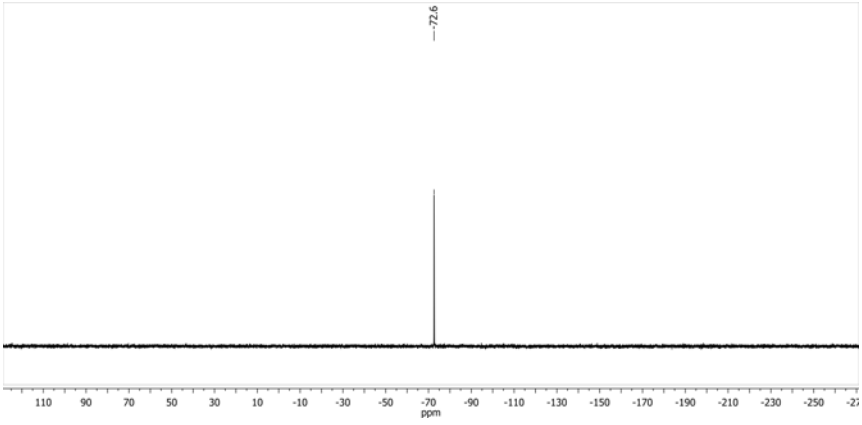

Figure S13: ^{31}P NMR spectrum of compound **3** in C_6D_6.

Compound 4

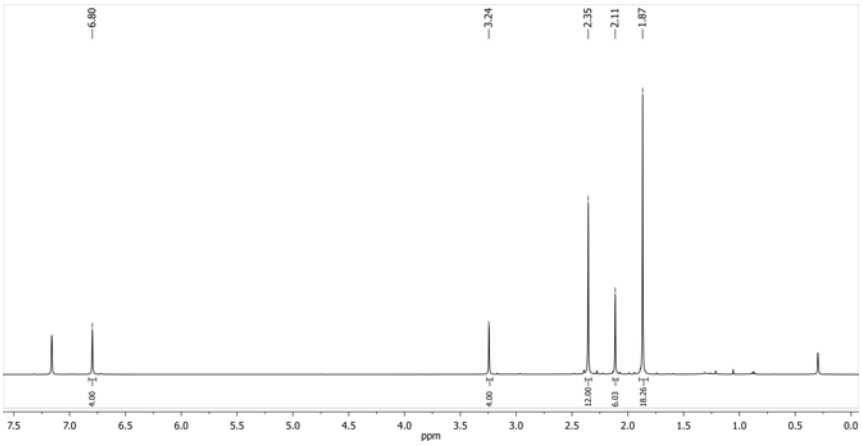

Figure S14: ^{1}H NMR spectrum of compound **4** in C_6D_6.

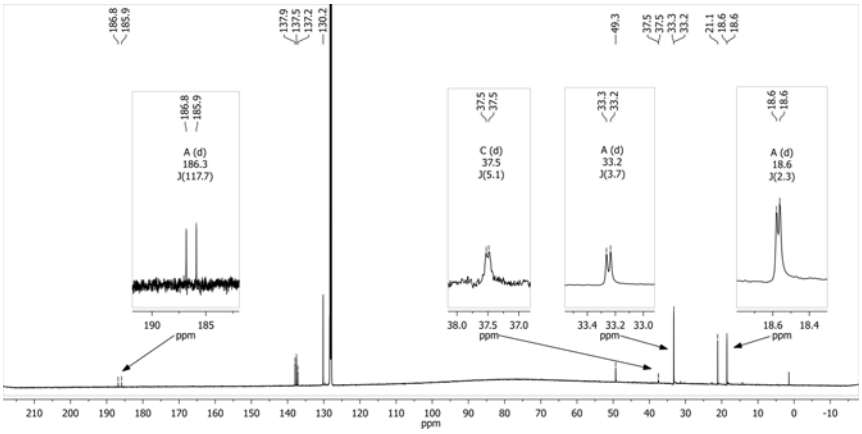

Figure S15: ^{13}C NMR spectrum of compound **4** in C_6D_6.

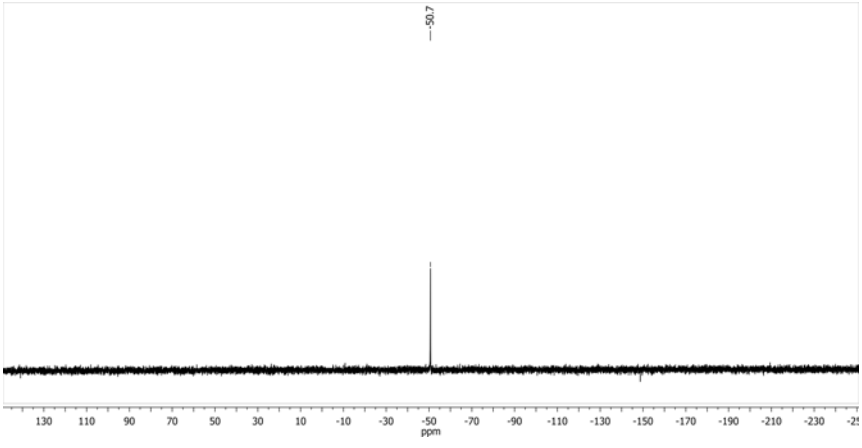

Figure S16: ^{31}P NMR spectrum of compound **4** in C_6D_6.

X-ray structure analysis

Data were collected on a Bruker D8 Quest diffractometer using monochromatic Mo-Kα radiation. The solution of the structure was performed with direct methods with the SHELXT-2015 solution programme, while for the structure refinement with full-matrix least-squares against F^2 the SHELXL-2015 package was used, both within the OLEX^2 environment.[6–8]

Crystal data of 1: $C_{29}H_{44}N_2P_2$, 482.60 g·mol^{-1}, 100 K, monoclinic, $P2_1/n$, a = 976.12(4) pm, b = 2445.04(10) pm, c = 1435.95(6) pm, α = 90°, β = 94.6105(15)°, γ = 90°, V = 3416.0(2) Å^3, Z = 4, ρ = 0.938 g·cm^{-3}, μ = 0.143, *F(000)* = 1048.0, *GooF* = 1.056. A total of 122745 reflections was collected of which 6214 were unique (R(int) = 0.0419). R_1 (wR_2 all data) = 0.0381 (0.1069) for 320 parameters and 5639 reflections ($I > 2\sigma(I)$). CCDC 1584231.

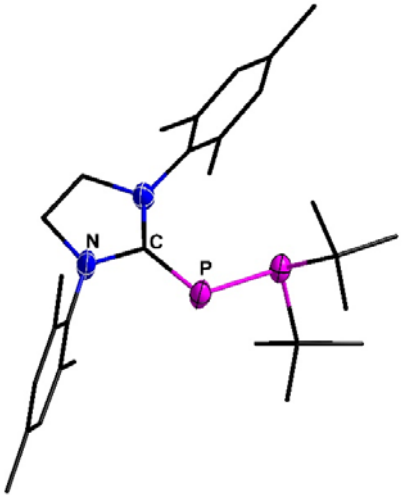

Figure S1. Molecular structure of **1**. Carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids for **1** represent a 90% probability level, carbon atoms are shown as balls and sticks for better visibility. Selected bond lengths /pm and angles /°: P-P 219.38(6); P-C_{NHC} 175.96(17); C_{NHC}-P-P 104.11(6).

Crystal data of 2: $C_{29}H_{44}AsN_2P{\cdot}C_7H_8$, 618.69 g·mol^{-1}, 100K, triclinic, *P-1*, a = 943.13(5) pm, b = 1176.13(7) pm, c = 1651.08(9) pm, α = 88.700(2)°, β = 82.678(3)°, γ = 71.476(2)°, V = 1722.09(17) Å^3, Z = 2, ρ = 1.193 g·cm^{-3}, μ = 1.059, *F(000)* = 660.0, *GooF* = 1.045. A total of 38793 reflections was collected of which 7311 were unique (R(int) = 0.0267). R_1 (wR_2 all data) = 0.0273 (0.0688) for 439 parameters and 6681 reflections ($I > 2\sigma(I)$). CCDC 1584230.

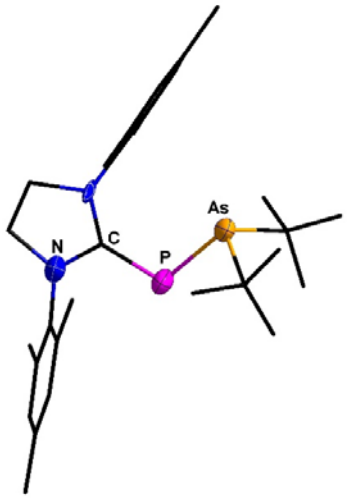

Figure S2. Molecular structure of **2**. Carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids for **2** represent a 90% probability level, carbon atoms are shown as balls and sticks for better visibility. Selected bond lengths /pm and angles /°: P-As 231.33(4); P-C_{NHC} 175.93(16); C_{NHC}-P-As 105.21(6).

Crystal data of 3: $C_{29}H_{44}N_2PSb \cdot C_7H_8$, 665.53 g·mol^{-1}, 100K, triclinic, *P-1*, *a* = 958.16(5) pm, *b* = 1177.84(7) pm, *c* = 1674.85(9) pm, *α* = 88.332(2)°, *β* = 80.966(3)°, *γ* = 70.456(2)°, *V* = 1758.61(17) Å^3, *Z* = 2, *ρ* = 1.257 g·cm^{-3}, *μ* = 0.855, *F(000)* = 696.0, *GooF* = 1.058. A total of 42678 reflections was collected of which 8956 were unique (*R*(int) = 0.0344). R_1 (wR_2 all data) = 0.0262 (0.0544) for 416 parameters and 7836 reflections ($I > 2\sigma(I)$). CCDC 1584228.

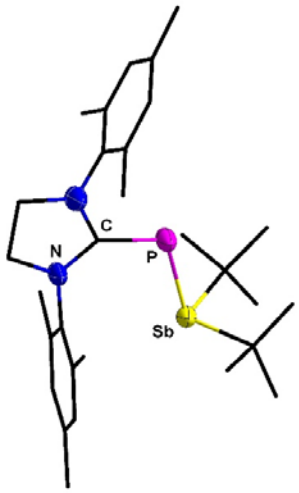

Figure S3. Molecular structure of **3**. Carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids for **3** represent a 90% probability level, carbon atoms are shown as balls and sticks for better visibility. Selected bond lengths /pm and angles /°: P-Sb 250.31(5); P-C_{NHC} 176.35(18); C_{NHC}-P-Sb 106.90(6).

Crystal data of 4: $C_{29}H_{44}BiN_2P$, 660.69 g·mol^{-1}, 100K, triclinic, *P-1*, *a* = 852.19(7) pm, *b* = 1007.62(8) pm, *c* = 3731.9(3) pm, *α* = 85.580(2)°, *β* = 87.360(3)°, *γ* = 68.332(2)°, *V* = 2968.7(4) Å^3, *Z* = 4, *ρ* = 1.478 g·cm^{-3}, *μ* = 6.011, *F(000)* = 1320.0, *GooF* = 1.142. A total of 80403 reflections was collected of which 13143 were unique (*R*(int) = 0.0517). R_1 (wR_2 all data) = 0.0497 (0.1046) for 588 parameters and 13143 reflections ($I > 2\sigma(I)$). CCDC 1584229.

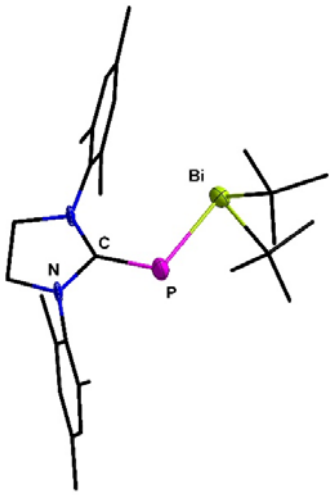

Figure S4. Molecular structure of **4**. Carbon-bound hydrogen atoms are omitted for clarity. Thermal ellipsoids for **4** represent a 90% probability level, carbon atoms are shown as balls and sticks for better visibility. Selected bond lengths /pm and angles /°: P-Sb 260.32(16); P-C_{NHC} 174.73(69); C_{NHC}-P-Bi 109.1(2).

Computational Details

DFT calculations were performed at the BP86/def2-TZVP level of theory with the TURBOMOLE software suite.[9–14]

Table 1. Computational data on compounds 1-4.

	(SIMes)PH	1	2	3	4
WBI (C-P)	1.6411	1.5063	1.5157	1.5040	1.5190
WBI (P-E)	-	1.0763	1.0612	1.0363	0.9922
HOMO-LUMO gap /eV	2.716	2.769	2.759	2.732	2.66

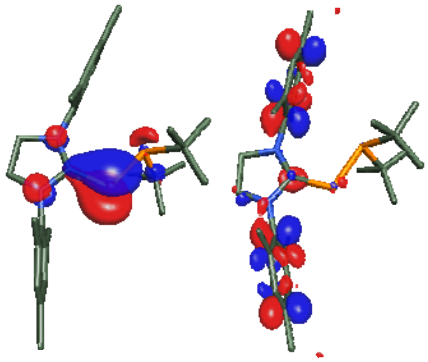

Figure S17: HOMO (left) and LUMO (right) of compound **1** with orbital threshold of 0.055 a.u.

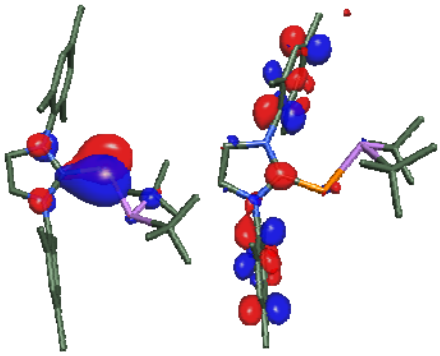

Figure S18: HOMO (left) and LUMO (right) of compound **2** with orbital threshold of 0.055 a.u.

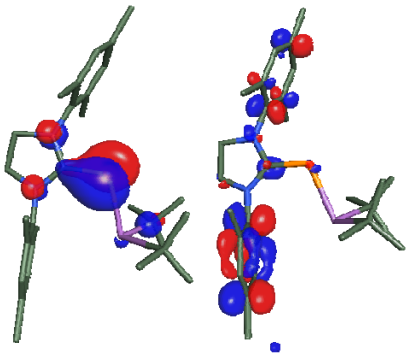

Figure S19: HOMO (left) and LUMO (right) of compound **3** with orbital threshold of 0.055 a.u.

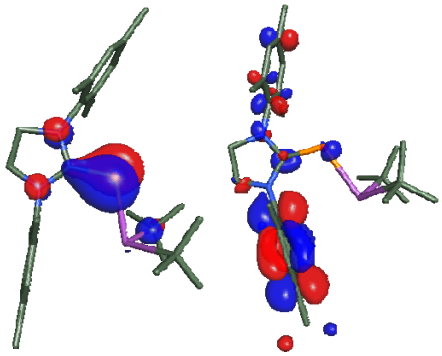

Figure S20: HOMO (left) and LUMO (right) of compound **4** with orbital threshold of 0.055 a.u.

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