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A new family of silver(I) complexes stabilized by the phosphanylborane $(C_6H_5)_2PBH_2{\cdot}N(CH_3)_3$

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General

All manipulations were performed under an atmosphere of dry argon using standard glove-box and Schlenk techniques. All solvents were degassed and purified by standard procedures. The compounds $Ph_2PBH_2{\cdot}NMe_3$[1] and Ag[FAl{$OC_6F_{10}(C_6F_5)$}$_3$][2] were prepared according to literature procedures. $AgBF_4$ were obtained from Sigma was transferred to glove-box for storage and used as received. NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400.13 MHz, ^{31}P: 161.976 MHz, ^{11}B: 128.378 MHz, ^{13}C{^{1}H}: 100.623 MHz) with δ [ppm] referenced to external $SiMe_4$ (^{1}H, ^{13}C), H_3PO_4 (^{31}P), $BF_3{\cdot}Et_2O$ (^{11}B). IR spectra were recorded on a DIGILAB (FTS 800) FT-IR spectrometer. All mass spectra were recorded on a ThermoQuest Finnigan TSQ 7000 (ESI-MS). The C, H, N analyses were measured on an Elementar Vario EL III apparatus.

Synthesis of [Ag($Ph_2PBH_2{\cdot}NMe_3$)(MeCN)][FAl{$OC_6F_{10}(C_6F_5)$}$_3$] (1):

A solution of 12 mg (0.05 mmol) $Ph_2PBH_2{\cdot}NMe_3$ in 5 mL MeCN is added to a solution of 73 mg (0.05 mmol) Ag[FAl] in 5 ml MeCN and the solution is stirred for 1 day. After removal of all volatiles under reduced pressure the remaining solid is dissolved in 5 mL of CH_2Cl_2 and filtrated. The clear solution is over layered by a 6 fold amount of *n*-hexane. Compound **1** crystallises at r.t. as colourless needles. The crystals are separated, washed with *n*-hexane (3×5 mL) and dried under vacuum. Yield: 45 mg (52 %).

^{1}H NMR (CD_2Cl_2, 25 °C): δ = 2.36 (s, MeCN), 2.66 (m, 2H, BH_2), 2.69 (s, 9H, NMe_3), 7.35 – 7.46 (m, 6H, *m*- & *p*-Ph), 7.53 – 7.64 (m, 4H, *o*-Ph). ^{31}P NMR (CD_2Cl_2, 25 °C): δ = –25.8 (d, br, $^1J_{P,Ag}$ = 628 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): –25.8 (d, br, $^1J_{P,Ag}$ = 628 Hz). ^{11}B NMR (CD_2Cl_2, 25 °C): δ = –5.8 (m, br, BH_2). ^{11}B{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = –5.8 (m, br, BH_2). ^{19}F NMR (CD_2Cl_2, 25 °C): δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{F,F}$ = 18 Hz, 1F), –154.5 (t, $J_{F,F}$ = 22 Hz, 1F), –141.5 (d, $J_{F,F}$ = 277 Hz, 1F), –137.4 (d, $J_{F,F}$ = 277 Hz, 2F), –130.8 (d, $J_{F,F}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{F,F}$ = 277 Hz, 2F), –117.2 (d, $J_{F,F}$ = 277 Hz, 2F), –112.7 (d, $J_{F,F}$ = 283 Hz, 2F). ^{19}F{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{F,F}$ = 18 Hz, 1F), –154.5 (t, $J_{F,F}$ = 22 Hz, 1F), –141.5 (d, $J_{F,F}$ = 277 Hz, 1F), –137.4 (d, $J_{F,F}$ = 277 Hz, 2F), –130.8 (d, $J_{F,F}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{F,F}$ = 277 Hz, 2F), –117.2 (d, $J_{F,F}$ = 277 Hz, 2F), –112.7 (d, $J_{F,F}$ = 283 Hz, 2F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 2.7 (MeCN), 54.8 (d, $^3J_{C,P}$ = 7 Hz, NMe_3), 120.1 (s, MeCN), 129.5 (d, $^2J_{C,P}$ = 9 Hz, *p*-Ph), 130.4 (s, *m*-Ph), 132.4 (d, $^1J_{B,P}$ = 34 Hz, *i*-Ph), 134.5 (d, $^2J_{C,P}$ = 11 Hz, *o*-Ph). Several signals have been observed from 135-150 ppm for phenyl^F- and from 105 – 115 ppm for cyclohexyl^F-group of FAl-anion, cannot be exactly assigned. IR (KBr): $\tilde{\nu}$ = 3060 (vw, CH), 3019 (vw, CH), 2958 (vw, CH), 2850 (vw, CH), 2440 (w, br, BH), 2387 (w, br, BH), 2361 (w), 2321 (w), 2295 (w), 1653 (m), 1534 (m), 1486 (vs), 1324 (m), 1309 (m), 1268 (s), 1243 (s), 1205 (vs), 1186 (s), 1153 (s), 1104 (s), 1068 (w), 1020 (s), 955 (vs), 911 (m), 858 (w) , 811 (w), 770 (s), 751 (m), 741 (m), 730 (s), 696 (w), 667 (w), 647 (w), 635 (w), 625 (w), 600 (w), 535 (w), 527 (w), 519 (w), 500 (w), 490 (w), 468 (vw). ESI-MS (MeCN, pos): *m/z* = 405 (100%, $[\mathrm{Ag(Ph_2PBH_2{\cdot}NMe_3)(MeCN)}]^+$), 621 (88%, $[\mathrm{Ag(Ph_2PBH_2{\cdot}NMe_3)_2}]^+$). ESI-MS (MeCN, neg): *m/z* = 1381 (100%, $[\mathrm{FAl}]^-$). Elemental analysis (%) calculated for $\mathrm{C_{53}H_{24}AgAlBF_{46}N_2O_3P}$ (**1**): C: 35.76, H: 1.35, N: 1.56; found: C: 35.76, H: 1.60, N: 1.44.

Synthesis of $[\mathrm{Ag(Ph_2PBH_2{\cdot}NMe_3)_2}][\mathrm{FAl\{OC_6F_{10}(C_6F_5)\}_3}]$ (2):

A solution of 24 mg (0.1 mmol) $\mathrm{Ph_2PBH_2{\cdot}NMe_3}$ in 5 mL MeCN is added to a solution of 73 mg (0.05 mmol) Ag[FAl] in 5 ml MeCN. Upon addition the solution turns slightly red, the solution is stirred for 1 day. After removal of all volatiles under reduced pressure the remaining solid is dissolved in 5 mL of $\mathrm{CH_2Cl_2}$ and filtrated. The clear solution is over layered by a 6 fold amount of *n*-hexane. Compound **2** crystallises at r.t. as colourless needles. The crystals are separated, washed with *n*-hexane (3×5 mL) and dried under vacuum. Yield: 66 mg (33 %).
^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = 2.66 (s, 9H, $\mathrm{NMe_3}$), 2.67 (m, 2H, $\mathrm{BH_2}$), 7.36 – 7.46 (m, 6H, *m*- & *p*-Ph), 7.61 (s, br, 4H, *o*-Ph). ^{31}P NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –25.6 (d, br, $^1J_{\mathrm{P,Ag}}$ = 415 Hz). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): –25.6 (d, br, $^1J_{\mathrm{P,Ag}}$ = 415 Hz). ^{11}B NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –5.6 (m, br, $\mathrm{BH_2}$). ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –5.6 (m, br, $\mathrm{BH_2}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{\mathrm{F,F}}$ = 18 Hz, 1F), –154.5 (t, $J_{\mathrm{F,F}}$ = 22 Hz, 1F), –141.5 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 1F), –137.4 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –130.8 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –117.2 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –112.7 (d, $J_{\mathrm{F,F}}$ = 283 Hz, 2F). ^{19}F{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{\mathrm{F,F}}$ = 18 Hz, 1F), –154.5 (t, $J_{\mathrm{F,F}}$ = 22 Hz, 1F), –141.5 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 1F), –137.4 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –130.8 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –117.2 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –112.7 (d, $J_{\mathrm{F,F}}$ = 283 Hz, 2F). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = 54.7 (s, $\mathrm{NMe_3}$), 129.5 (s, *p*-Ph), 130.3 (s, *m*-Ph), 133.1 (m, *i*-Ph), 134.5 (s, *o*-Ph). Several signals have been observed from 135-150 ppm for phenyl$^{\mathrm{F}}$- and from 105 – 115 ppm for cyclohexyl$^{\mathrm{F}}$-group of FAl-anion, cannot be exactly assigned. IR (KBr): $\tilde{\nu}$ = 3080 (w, CH), 3059 (w, CH), 3012 (w, CH), 2955 (w, CH), 2920 (w, CH), 2845 (vw, CH), 2435 (m, br, BH), 2410 (m, br, BH), 1653 (s), 1534 (s), 1484 (vs), 1436 (s), 1407 (w), 1325 (s), 1309 (s), 1268 (s), 1243 (s), 1204 (vs), 1185 (s), 1154 (s), 1134 (s), 1105 (s), 1068 (s), 1030 (s), 1018 (s), 1005 (s), 956 (vs), 910 (s), 857 (s) , 810 (m), 768 (s), 749 (s), 729 (s), 695 (s), 666 (w), 646 (m), 635 (m), 624 (m), 599 (m), 535 (m), 527 (m), 519 (m), 495 (w), 468 (m). ESI-MS (MeCN, pos): *m/z* = 621 (100%, $[\mathrm{Ag(Ph_2PBH_2{\cdot}NMe_3)_2}]^+$). ESI-MS (MeCN, neg): *m/z* = 1381 (100%, $[\mathrm{FAl}]^-$). Elemental analysis (%) calculated for $\mathrm{C_{66}H_{42}AgAlB_2F_{46}N_2O_3P}$ (**2**): C: 39.56, H: 2.11, N: 1.40; found: C: 39.58, H: 2.31, N: 1.35.

Synthesis of $[\mathrm{Ag(Ph_2PBH_2{\cdot}NMe_3)_3}][\mathrm{FAl\{OC_6F_{10}(C_6F_5)\}_3}]$ (3):

A solution of 78 mg (0.3 mmol) $\mathrm{Ph_2PBH_2{\cdot}NMe_3}$ in 5 mL MeCN is added to a solution of 150 mg (0.1 mmol) Ag[FAl] in 5 ml MeCN. Upon addition the solution turns slightly red, the solution is stirred for 1 day. After removal of all volatiles under reduced pressure the remaining solid is dissolved in 5 mL of $\mathrm{CH_2Cl_2}$ and filtrated. The clear solution is over layered by a 6 fold amount of *n*-hexane. Compound **3** crystallises at r.t. as colourless needles. The crystals are separated, washed with *n*-hexane (3×5 mL) and dried under vacuum. Yield: 116 mg (53 %).
^{1}H NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = 2.52 (s, 9H, $\mathrm{NMe_3}$), 2.12 – 2.32 (m, 2H, $\mathrm{BH_2}$), 7.27 – 7.36 (m, 6H, *m*- & *p*-Ph), 7.51 – 7.59 (m, br, 4H, *o*-Ph). ^{31}P NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –28.0 (s, br). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): –28.0 (s, br). ^{11}B NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –5.4 (s, br, $\mathrm{BH_2}$). ^{11}B{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –5.4 (s, br, $\mathrm{BH_2}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 25 °C): δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{\mathrm{F,F}}$ = 18 Hz, 1F), –154.5 (t, $J_{\mathrm{F,F}}$ = 22 Hz, 1F), –141.5 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 1F), –137.4 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –130.8 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –117.2 (d, $J_{\mathrm{F,F}}$ = 277 Hz, 2F), –112.7 (d, $J_{\mathrm{F,F}}$ = 283 Hz, 2F). ^{19}F{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 25 °C):

δ = –172.2 ppm (s, AlF), –165.2 (t, $J_{F,F}$ = 18 Hz, 1F), –154.5 (t, $J_{F,F}$ = 22 Hz, 1F), –141.5 (d, $J_{F,F}$ = 277 Hz, 1F), –137.4 (d, $J_{F,F}$ = 277 Hz, 2F), –130.8 (d, $J_{F,F}$ = 277 Hz, 2F), –128.1 (s, 2F), –122.1 (d, $J_{F,F}$ = 277 Hz, 2F), –117.2 (d, $J_{F,F}$ = 277 Hz, 2F), –112.7 (d, $J_{F,F}$ = 283 Hz, 2F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 54.6 (d, $^3J_{P,C}$ = 6 Hz, NMe_3), 129.2 (d, $^3J_{P,C}$ = 8 Hz, *m*-Ph), 129.6 (s, *p*-Ph), 133.6 (d, $^1J_{P,C}$ = 23 Hz, *i*-Ph), 134.4 (s, $^4J_{P,C}$ = 12 Hz, *o*-Ph). Several signals have been observed from 135-150 ppm for phenyl^F- and from 105 – 115 ppm for cyclohexyl^F-group of FAl-anion, cannot be exactly assigned. IR (KBr): $\tilde{\nu}$ = 3066 (w, CH), 3059 (w, CH), 3005 (w, CH), 2956 (w, CH), 2876 (vw, CH), 2424 (m, br, BH), 2405 (m, br, BH), 1652 (s), 1586 (w), 1533 (s), 1485 (vs), 1436 (s), 1409 (w), 1384 (w), 1332 (s), 1308 (s), 1267 (s), 1224 (s), 1205 (vs), 1186 (s), 1156 (s), 1124 (s), 1104 (s), 1067 (s), 1018 (vs), 955 (vs), 910 (s), 851 (s) , 811 (m), 767 (s), 749 (s), 729 (s), 696 (s), 666 (w), 645 (m), 635 (m), 624 (m), 600 (m), 527 (m), 511 (m), 469 (m). ESI-MS (MeCN, pos): *m/z* = 878 (0.2%, $[Ag(Ph_2PBH_2\cdot NMe_3)_3]^+$), 819 (100%, $[Ag(Ph_2PBH_2\cdot NMe_3)(Ph_2PBH_2)]^+$), 621 (100%, $[Ag(Ph_2PBH_2\cdot NMe_3)_2]^+$). ESI-MS (MeCN, neg): *m/z* = 1381 (100%, $[FAl]^-$). Elemental analysis (%) calculated for $C_{81}H_{63}AgAlB_3F_{46}N_3O_3P_3$ (**3**): C: 43.02, H: 2.81, N: 1.86; found: C: 43.64, H: 3.39, N: 1.69.

Synthesis of $[Ag(Ph_2PBH_2\cdot NMe_3)][BF_4]$ (4):

A solution of 54 mg (0.2 mmol) $Ph_2PBH_2\cdot NMe_3$ in 10 mL MeCN is added to a solution of 39 mg (0.2 mmol) $Ag[BF_4]$ in 10 ml MeCN. Upon addition the solution turns slightly red, the solution is stirred for 1 day. After removal of all volatiles under reduced pressure the remaining solid is dissolved in 5 mL of CH_2Cl_2 and filtrated. The clear solution is over layered by the 6 fold amount of *n*-hexane. Compound **4** crystallises at r.t. as colourless needles. The crystals are separated, washed with *n*-hexane (3×5 mL) and dried under vacuum. Yield: 32 mg (34 %).

^1H NMR (CD_3CN, 25 °C): δ = 2.58 (q, BH_2), 2.71 (s, 9H, NMe_3), 7.34 – 7.41 (m, 6H, *m*- & *p*-Ph), 7.63 (s, br, 4H, *o*-Ph). ^{31}P NMR (CD_3CN, 25 °C): δ = –29.7 (d, br, $^1J_{P,Ag}$ = 610 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 25 °C): δ = –29.7 (d, br, $^1J_{P,Ag}$ = 610 Hz). ^{11}B NMR (CD_3CN, 25 °C): δ = –4.6 (m, BH_2), –0.6 (s, BF_4). $^{11}B\{^1H\}$ NMR (CD_3CN, 25 °C): δ = –4.6 (d, br, $^1J_{B,P}$ = 64 Hz, BH_2), –0.6 (s, BF_4). ^{19}F NMR (CD_3CN, 25 °C): δ = −150.64 (s, $^{11}BF_4$), −150.58 (s, $^{10}BF_4$). $^{19}F\{^1H\}$ NMR (CD_3CN, 25 °C): δ = −150.64 (s, $^{11}BF_4$), −150.58 (s, $^{10}BF_4$). $^{13}C\{^1H\}$ NMR (CD_3CN, 25 °C): δ = 54.5 (s, NMe_3), 129.5 (s, *p*-Ph), 129.9 (s, *m*-Ph), 135.2 (d, $^2J_{C,P}$ = 10 Hz, *o*-Ph), 136.5 (d, $^1J_{B,P}$ = 32 Hz, *i*-Ph). IR (KBr): $\tilde{\nu}$ = 3052 (vw, CH), 3009 (vw, CH), 2950 (vw, CH), 2423 (m, br, BH), 2389 (m, br, BH), 2300 (w), 1568 (vw), 1479 (s), 1466 (m), 1433 (m), 1412 (w), 1312 (vw), 1285 (vw), 1250 (w), 1180 (m), 1115 (s), 1079 (vs), 1073 (vs), 1010 (s), 862 (s), 766 (s), 775 (s), 750 (s), 711 (s), 519 (s), 486 (vw). ESI-MS (CH_2Cl_2): *m/z* = 562 (10%, $[Ag(Ph_2PBH_2\cdot NMe_3)(Ph_2PBH_2)]^+$, 621 (100%, $[Ag(Ph_2PBH_2\cdot NMe_3)_2]^+$). Elemental analysis (%) calculated for $C_{15}H_{21}AgB_2F_4NP$ (**4**): C: 39.88, H: 4.61, N: 3.10; found: C: 39.75, H: 4.61, N: 3.13.

1. Crystallographic details:

The single crystal X-Ray diffraction experiments were performed either on a Gemini Ultra diffractometer equipped with an Ruby CCD detector (**1**, **4**), a SuperNova diffractometer equipped with an Atlas CCD detector (**2**) or a SuperNova diffractometer equipped with an Eos CCD detector (**3**) from Agilent Technologies (formerly Oxford Diffraction) applying Cu-K_α radiation (λ = 1.54178 Å) or Mo-K_α radiation (λ = 0.71073 Å). The measurements were performed at 123 K. Data collection and reduction were performed with **CrysAlisPro** (Version 1.171.36.21 (2012) (**1**, **4**), 1.171.37.33 (2014) (**2**), 1.171.38.37b (2015) (**3**)).[3] For the compounds (**1**, **2**) an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.(Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. For the compounds (**3**) a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. For the compound (**4**) a multi-scan absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was applied. Using **Olex2**,[4] all structures were solved by **ShelXT**[5] and a least-square refinement on F^2 was carried out with **ShelXL**[6] or **Olex2.refine**.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. The figures were created with **Olex2**.[4]

Compound **1**: The asymmetric unit contains one molecule $Ph_2PBH_2NMe_3$, an Ag atom, a $[FAl\{O(C_6F_{10})(C_6F_5)\}_3]$ anion, one CH_3CN molecule and three CH_2Cl_2 solvent molecules.

Compound **2**: The asymmetric unit contains the complex $[Ag\{Ph_2PBH_2NMe_3\}_2]$ and one $[FAl\{O(C_6F_{10})(C_6F_5)\}_3]$ anion. The complex fragment $[Ag\{Ph_2PBH_2NMe_3\}]$ shows a disorder over two positions (90:10). To describe this disorder the SADI, ISOR and SIMU restraints were applied.

Compound **3**: The asymmetric unit contains the complex $[Ag\{Ph_2PBH_2NMe_3\}_3]$ and one $[FAl\{O(C_6F_{10})(C_6F_5)\}_3]$ anion. It further contains one CH_2Cl_2 solvent molecule, which is heavily disordered over several positions. Therefore, a solvent mask was calculated and 180 electrons were found in a volume of 1018 Å^3 in 4 voids per unit cell. This is consistent with the presence of one CH_2Cl_2 molecule per asymmetric unit, which account for 168 electrons per unit cell."

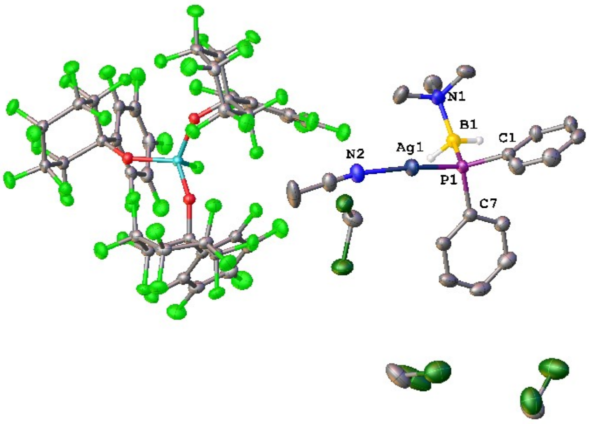
Compound **4**: The asymmetric unit contains one molecule $Ph_2PBH_2NMe_3$, an Ag atom and a BF_4 anion. Two of the four F atoms at the BF_4 molecule are disordered over two positions (62:38). To model this disorder the restraints SADI and SIMU were applied. Additionally compound **4** was treated as an inversion twin (BASF 0.424).

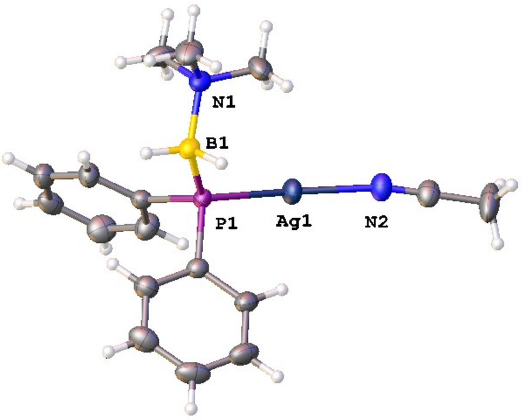
CCDC-1994656 (**1**), CCDC-1994657 (**2**), CCDC-1994658 (**3**) and CCDC-1994659 (**4**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1: Crystallographic data for the compounds **1-4**.

Compound	**1**	**2**	**3**	**4**
CCDC	1994656	1994657	1994658	1994659
Exp. Name	CM300	CM429	Hulk218	CM279
Formula	$C_{56}H_{30}AgAlBCl_6F_{46}N_2O_3P$	$C_{66}H_{42}AgAlB_2F_{46}N_2O_3P_2$	$AgAlB_3C_{82}Cl_2F_{46}H_{65}N_3O_3P_3$	$C_{15}H_{21}AgB_2F_4NP$
$D_{calc.}$/ g cm^{-3}	1.928	1.765	1.624	1.697
μ/mm^{-1}	6.310	4.158	0.463	10.335
Formula Weight	2042.163	2003.42	2345.46	451.825
Colour	clear colourless	clear colourless	clear colourless	colourless
Shape	block	block	needle	needle
Size/mm^3	0.41×0.29×0.27	0.21×0.12×0.10	0.58×0.12×0.07	0.23×0.04×0.04
T/K	123.05(10)	123.01(10)	123(1)	123.05(10)
Crystal System	monoclinic	triclinic	monoclinic	orthorhombic
Space Group	$P2_1/n$	P-1	$P2_1/c$	$P2_12_12_1$
a/Å	11.3947(1)	11.3066(2)	11.41518(14)	11.1197(2)
b/Å	19.7346(1)	17.6908(3)	19.8618(3)	12.5198(2)
c/Å	31.3137(1)	21.6344(3)	42.3218(5)	12.7040(2)
α/°	90	66.0358(15)	90	90
β/°	92.186(1)	88.8395(14)	90.4893(11)	90
γ/°	90	73.5586(17)	90	90
V/Å^3	7036.38(8)	3770.45(12)	9595.1(2)	1768.61(5)
Z	4	2	4	4
Z'	1	1	1	1
Wavelength/Å	1.54178	1.54184	0.71073	1.54178
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Mo K$_\alpha$	Cu K$_\alpha$
Θ_{min}/°	2.82	4.101	2.808	4.96
Θ_{max}/°	66.61	72.962	27.154	66.45
Measured Refl.	63686	27960	146206	5953
Independent Refl.	12388	14497	21220	2926
Reflections with I > 2(I)	11322	13677	15636	2768
R_{int}	0.0276	0.0212	0.0638	0.0342
Parameters	1066	1251	1303	247
Restraints	0	81	0	3
Largest Peak	1.0999	0.327	0.504	1.2089
Deepest Hole	-1.0723	-0.525	-0.737	-0.6691
GooF	1.0400	1.055	0.977	1.0323
wR_2 (all data)	0.0912	0.0724	0.0888	0.0906
wR_2	0.0897	0.0697	0.0860	0.0895
R_1 (all data)	0.0360	0.0317	0.0493	0.0371
R_1	0.0334	0.0289	0.0346	0.0352

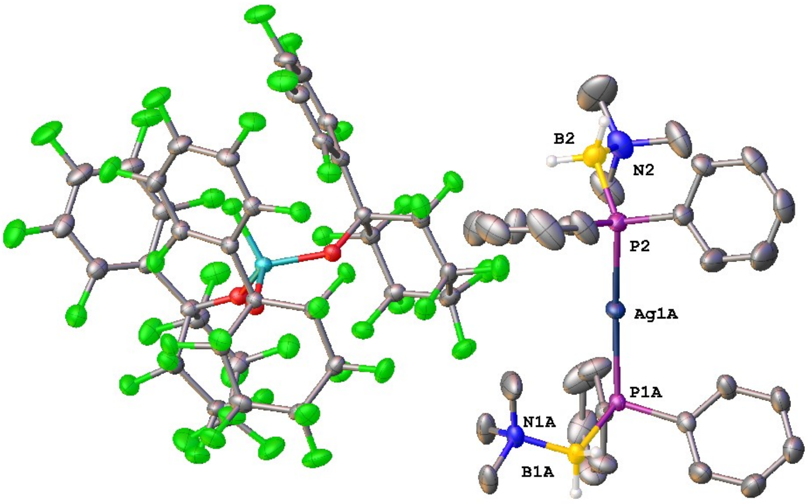
1.1. Compound 1

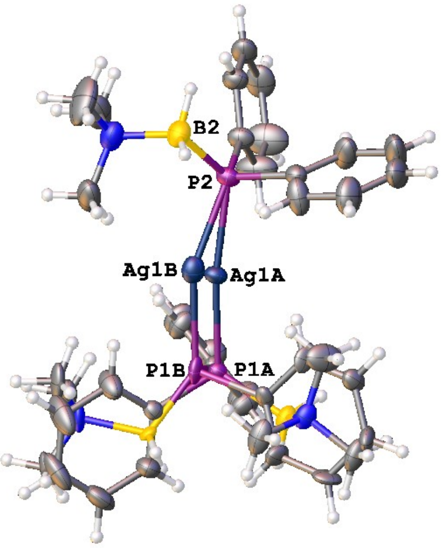




Bond Lengths [Å]		Bond Angles [°]	
Ag1–P1	2.3633(6)	P1–Ag1–N2	163.85(6)
P1–B1	1.972(3)	Ag1–P1–B1	117.70(9)
B1–N1	1.603(4)	P1–B1–N1	116.47(19)
Ag–N2	2.129(2)		

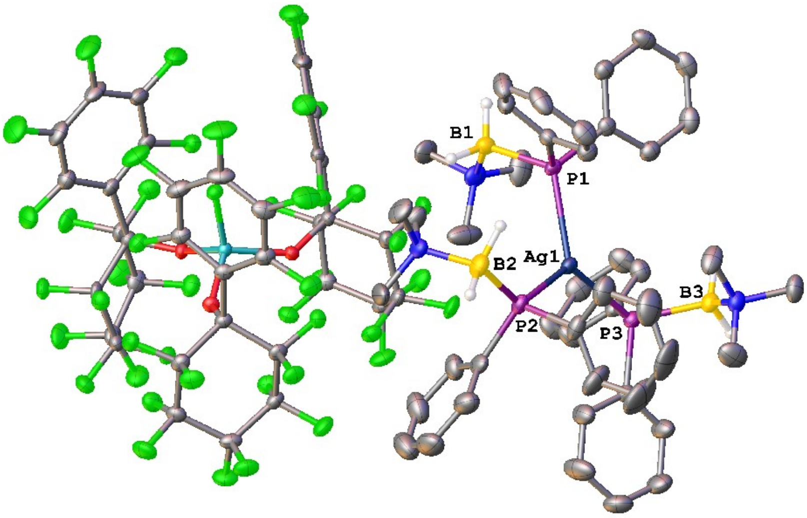
1.2. Compound 2

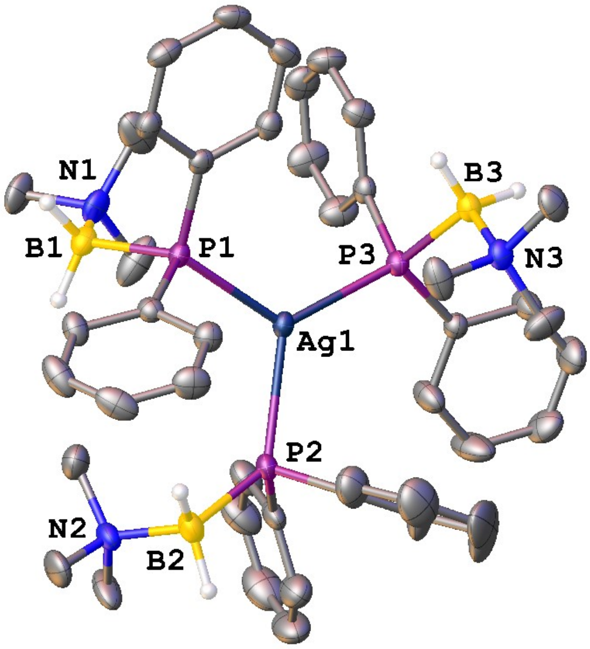




Bond Lengths [Å]		Bond Angles [°]	
P1A–Ag1A	2.3859(6)	P1A–Ag1A–P2	170.72(3)
P1B–Ag1B	2.462(9)	P1B–Ag1B–P2	157.0(3)
P2–Ag1A	2.3937(5)		
P2–Ag1B	2.352(3)		

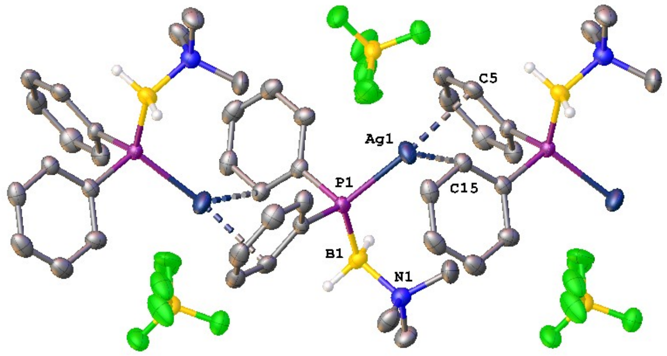
1.3. Compound 3

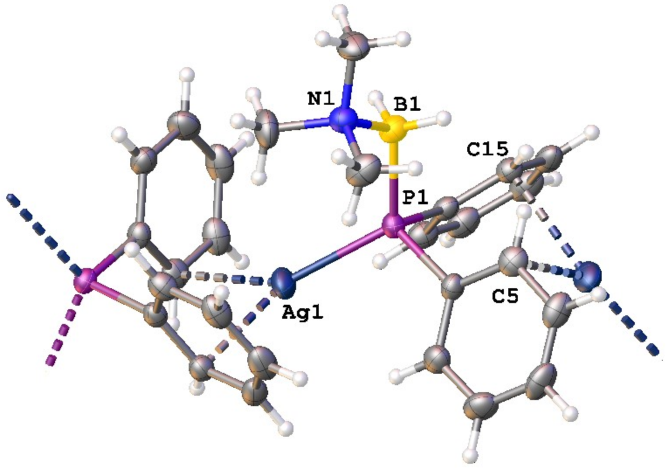




Bond Lengths [Å]		Bond Angles [°]	
Ag1–P1	2.4785(6)	P1–Ag1–P2	112.477(19)
Ag1–P2	2.5113(6)	P2–Ag1–P3	122.941(19)
Ag1–P3	2.4805(6)	P3–Ag1–P1	124.406(19)

1.4. Compound 4





Bond Lengths [Å]		Bond Angles [°]	
Ag1–P1	2.4059(10)	C15–Ag1–P1	129.96(11)
P1–B1	1.984(6)	C5–Ag1–P1	142.91(13)
B1–N1	1.608(6)	C5–Ag1–C15	84.36(16)
Ag1–C5	2.535(5)	Ag1–P1–B1	120.57(17)
Ag1–C15	2.657(5)	P1–B1–N1	115.4(3)

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