Supporting Information

Controlled Scrambling Reactions to Polyphosphanes *via* Bond Metathesis Reactions

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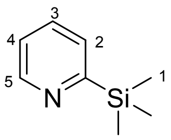
1. Experimental Section

1.1. Materials and Methods

All manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified argon or nitrogen. Dry, oxygen-free solvents were distilled either from CaH_2 (CH_2Cl_2, CH_3CN, C_6H_5F), from potassium/benzophenone (Et_2O) or from potassium (*n*-pentane). Anhydrous CD_3CN, $CDCl_3$ and CD_2Cl_2 were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored over molecular sieves (4 Å: CH_2Cl_2, C_6H_5F, *n*-pentane, Et_2O, CD_2Cl_2; 3 Å: CD_3CN, CH_3CN). All glassware was oven-dried at 160 °C prior to use. 2-Bromopyridine was purchased from TCI and distilled under inert conditions prior to use. Me_3SiCl (purified by redistillation, 99%) and *n*-butyl lithium (2.5 M in hexanes) were purchased by Sigma Aldrich and used as received. PCl_3 was purchased from Sigma Aldrich and distilled under inert conditions prior to use. MeOTf was purchased from Manchester Organics and distilled under inert conditions prior to use. Di-*tert*-butylphosphine was purchased from Cytec Solvay Group and used as received. Dicyclohexylphosphine was purchased from Strem Chemicals and used as received. 2-(Trimethylsilyl)benzo[*d*]thiazol[1] and 1,2-Bis(phenylphosphaneyl)ethane[2] were prepared as described in the literature. NMR spectra were measured on a Bruker AVANCE III HD Nanobay 400 MHz UltraShield (^1H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{31}P: 161.98 MHz, ^{19}F: 376.50 MHz, ^{77}Se: 76.31 Hz), or on a Bruker AVANCE III HDX, 500 MHz Ascend (^1H: 500.13 MHz, ^{13}C: 125.75 MHz, ^{31}P: 202.45 MHz, ^{19}F: 470.59 MHz). Reported numbers assigning atoms in the ^{13}C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts are referenced to $\delta(Me_4Si) = 0.00$ ppm (^1H, ^{13}C, externally), $\delta(CFCl_3) = 0.00$ ppm (externally) and $\delta(H_3PO_4, 85\%) = 0.00$ ppm (externally). Unless stated otherwise, all NMR spectra were measured at 300 K. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. The designation of the spin systems is performed by convention. The furthest downfield resonance is denoted by the latest letter in the alphabet and the furthest upfield by the earliest letter. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Nitrogen atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd: YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS modus.

2. Synthesis and spectroscopic data

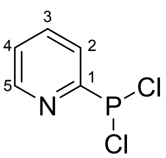
2.1. Preparation of 2-(Trimethylsilyl)pyridine



A solution of 2-Bromopyridine (24.4 ml, 250 mmol) in THF (300 ml) is cooled to -78°C. A solution of *n*-butyllithium in hexanes (100 ml, 250 mmol) is added dropwise and the reaction mixture is stirred for 15 min at -78°C to form a dark red suspension. To this suspension Trimethylsilylchloride (31.8 ml, 250 mmol) is added dropwise and the reaction mixture is allowed to rise to room temperature. After evaporating all volatile compounds the crude product is distilled (T = 75 °C; p = 30 mbar) to obtain the product as a clear, colourless oil. The spectral data are in accordance with the ones reported in the literature.[3]

Yield: 22.4 g (59 %); **^{1}H NMR (CD_3CN, 300 K, [ppm]):** δ = 0.39 (9H, s, C1–H), 7.05-7.10 (1H, m, C4–H), 7.47-7.48 (1H, m, C2–H), 7.48-7.49 (1H, m, C3–H), 8.77-8.78 (1H, m, C5–H). **^{29}Si{^{1}H} NMR (CD_3CN, 300 K, [ppm]):** δ = –5.8 (1Si, s).

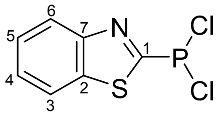
2.2. Preparation of 2-(Dichlorophosphaneyl)pyridine (5)



2-(Trimethylsilyl)pyridine (22.4 g, 148 mmol) and PCl_3 (38.8 ml, 444 mmol) are placed in a Schlenk flask and heated under reflux for 48 h. After evaporation of all volatiles the crude product is distilled (T = 48°C, p = 1.1 x 10^{-2} mbar) to afford the product as a clear, colourless oil that turns yellow upon standing at room temperature within 20-30 min. Hence, 2-(dichlorophosphaneyl)pyridine is stored at -30°C under inert conditions.

Yield: 21.5 g (81 %); **Raman (100 mW, 200 scans, 298 K, in cm^{-1})**: *ν* = 3128 (12), 3064 (58), 3052 (61), 2988 (9), 2972 (8), 2899 (10), 1572 (36), 1564 (38), 1447 (7), 1276 (11), 1243 (6), 1154 (21), 1126 (12), 1086 (8), 1044 (78), 989 (100), 723 (18), 617 (15), 503 (61), 462 (27), 420 (9), 285 (31), 243 (15), 188 (31), 149 (38); **IR (ATR, 298 K, in cm^{-1})**: *ν* = 2361 (vw), 1572 (vw), 1446 (vw), 1424 (vw), 1202 (vs), 1147 (vs), 1044 (vw), 988 (vw), 850 (vw), 764 (vw), 739 (vw), 722 (vw), 638 (m), 626 (m), 554 (m), 498 (vs), 422 (vw); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ = 7.42-7.45 (1H, m, C4–H), 7.88-7.93 (1H, m, C3–H), 8.10-8.12 (1H, m, C2–H), 8.73-8.74 (1H, m, C5–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 126.1 (1C, d, $^2J_{CP}$ = 15.0 Hz, C2), 126.3 (1C, d, $^4J_{CP}$ = 1.2 Hz, C4), 138.8 (1C, s, C3), 150.2 (1C, d, $^3J_{CP}$ = 18.4 Hz, C5), 163.4 (1C, d, $^1J_{CP}$ = 31.7 Hz, C1); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** δ = 138.7 (1P, s).

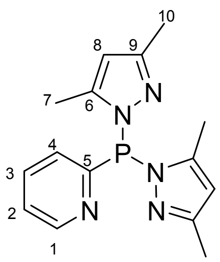
2.3. Preparation of 2-(Dichlorophosphaneyl)benzo[d]thiazole (6)



2-(Trimethylsilyl)benzo[*d*]thiazol (15.80 g, 76.21 mmol) and PCl_3 (20.0 ml, 228.6 mmol) are placed in a Schlenk flask and heated under reflux for 48 h. After evaporation of all volatiles the residue is sublimed (T = 55 °C, p = 9 x 10^{-3} mbar) to yield the product as colourless crystals. The spectral data are in accordance with the ones reported in the literature.[4]

Yield: 11.37 g (63 %); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ = 6.90-6.94 (1H, m, C4–H), 7.01-7.05 (1H, m, C5–H), 7.23-7.26 (1H, m, C6–H), 7.93-7.95 (1H, m, C3–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 122.0 (1C, s, C6), 125.1 (1C, s, C4), 127.0 (1C, s, C5), 127.1 (1C, s, C4), 137.7 (1C, d, $^3J_{CP}$ = 2.7 Hz, C7), 155.1 (1C, d, $^3J_{CP}$ = 15.8 Hz, C2), 173.1 (1C, d, $^1J_{CP}$ = 63.4 Hz, C1); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** δ = 132.0 (1P, s).

2.4. Preparation of 2-(bis(3,5-dimethyl-1H-pyrazol-1-yl)phosphaneyl)-pyridine (7)

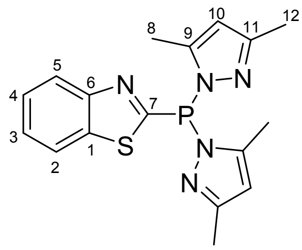


3,5-Dimethyl-1-(trimethylsilyl)-1*H*-pyrazole (50.10 mmol, 8.40 g) is added to 2-(dichlorophosphaneyl)pyridine **5** (24.40 mmol, 4.40 g) while cooling with an ice bath. The suspension is stirred for 16 h at room temperature. After evaporation of all volatiles *in vacuo* the product is obtained as an off white solid.

Yield: 7.080 g (97 %); **m.p.:** 109°C; **Raman (100 mW, 298 K, in cm^{-1})**: *ν* = 3132(18), 3101(22), 3071(26), 3054(29), 3039(37), 2988(31), 2921(100), 2860(16), 2729(8), 1572(62), 1464(33), 1439(43), 1380(17), 1274(9), 1158(19), 1139(24), 1088(11), 1046(43), 1020(26), 991(86), 960(9), 741(10), 721(18), 635(11), 618(16), 588(58), 558(10), 477(17), 463(15), 399(16), 374(14), 358(9), 305(10), 237(24), 220(17), 196(25), 156(25), 125(54); **IR (ATR, 298 K, in cm^{-1})**: *ν* = 3134(vw), 3038(vw), 2920(vw), 1564(m), 1446(w), 1425(w), 1406(w), 1366(vw), 1323(vw), 1309(w), 1291(m), 1155(w), 1131(m), 1087(vw), 1079(vw), 1043(vw), 1021(w), 990(w), 960(w), 895(vw), 847(vw), 806(m), 776(w), 761(w), 747(m), 720(vw), 659(vw), 633(vw), 617(vw), 600(vw), 588(w), 556(m), 491(s), 473(s), 446(m); **^{1}H NMR (CD_3Cl, 300 K, in ppm)**: δ = 2.20 (6H, s, C10–H), 2.41 (6H, s, C7–H), 5.89 (2H, s, C8–H), 7.20-7.23 (1H, m, C2–H), 7.40-7.42 (1H, m, C4–H), 7.63-7.68 (1H, m, C3–H), 8.68-8.70 (1H, m, C1–H); **^{13}C{^{1}H} NMR (CD_3Cl, 300 K, in ppm):** δ = 12.5 (2C, d, $^3J_{CP}$ = 13.8 Hz, C7), 13.9

(2C, s, C10), 108.6 (2C, s, C8), 132.2 (1C, s, C2), 127.5 (1C, d, $^2J_{CP}$ = 16.9 Hz, C4), 135.9 (1C, s, C3), 148.4 (2C, d, $^2J_{CP}$ = 17.2 Hz, C6), 150.0 (1C, d, $^3J_{CP}$ = 14.4 Hz, C1), 153.7 (2C, d, $^3J_{CP}$ = 5.8 Hz, C9), 159.6 (1C, d, $^1J_{CP}$ = 23.1 Hz, C5); **^{31}P NMR (CD_3Cl, 300 K, ppm):** δ = 44.8 (1P, s); **elemental analysis**: calcd. for $C_{15}H_{18}N_5P$: C: 60.19, H: 6.06, N: 23.40; found: C: 60.13, H: 6.34, N 22.91.

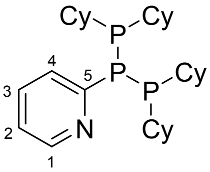
2.5. Preparation of 2-(bis(3,5-dimethyl-1H-pyrazol-1-yl)phosphaneyl)-benzo[d]thiazole (8)



To a suspension of 2-(dichlorophosphaneyl)benzo[d]thiazole **6** (2.50 g, 10.59 mmol) in Et_2O 3,5-Dimethyl-1-(trimethylsilyl)-1*H*-pyrazole (3.74 g, 22.24 mmol) is added. After stirring for 16 h, all volatiles are evaporated *in vacuo* to yield the product as a light yellow powder.

Yield: 3.620 g (96%); **m.p.:** 102°C ; **Raman (100 mW, 298 K, in cm^{-1}):** *ν* = 3097 (12), 3055 (33), 3009 (7), 2970 (15), 2928 (37), 1589 (7), 1571 (9), 1550 (32), 1467 (14), 1452 (28), 1441 (27), 1400 (100), 1384 (12), 1375 (8), 1314 (13), 1272 (23), 1232 (52), 1158 (7), 1125 (12), 1016 (15), 1006 (37), 853 (13), 762 (7), 707 (20), 631 (6), 590 (19), 579 (5), 516 (5), 507 (15), 459 (11), 419 (5), 366 (10), 219 (9), 203 (10), 175 (17); **IR (ATR, 298 K, in cm^{-1}):** *ν* = 3071 (w), 3053 (w), 2976 (w), 2926 (w), 1569 (s), 1455 (m), 1440 (m), 1398 (s), 1367 (m), 1305 (m), 1284 (s), 1230 (m), 1154 (m), 1129 (vs), 1085 (m), 1068 (m), 1035 (w), 1016 (s), 1005 (m), 956 (vs), 852 (m), 813 (s), 773 (vs), 759 (s), 738 (s), 706 (m), 675 (w), 659 (m), 604 (w), 577 (m), 534 (s), 516 (s), 486 (vs), 458 (vs), 431 (vs), 417 (vs); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ = 2.25 (6H, s, C12-H), 2.50 (6H, s, C8–H), 5.98 (2H, s, C10–H), 7.44-7.48 (1H, m, C3–H), 7.50-7.54 (1H, m, C4–H), 7.98-8.00 (1H, m, C5–H), 8.10-8.12 (1H, m, C2–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 12.8 (2C, d, $^3J_{CP}$ = 14.9 Hz, C8), 14.1 (2C, s, C12), 109.5 (2C, d, $^3J_{CP}$ = 1.8 Hz, C10), 122.1 (1C, s, C5), 124.3 (1C, s, C2), 126.5 (1C, s, C3), 126.7 (1C, s, C4), 138.5 (1C, d, $^3J_{CP}$ = 1.7 Hz, C1), 149.9 (2C, d, $^2J_{CP}$ = 20.8 Hz, C9), 154.7 (2C, d, $^3J_{CP}$ = 5.4 Hz, C11), 154.8 (1C, d, $^3J_{CP}$ = 19.1 Hz, C6), 168.6 (1C, d, $^1J_{CP}$ = 5.0 Hz, C7); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** δ = 38.0 (1P, s); **elemental analysis**: calcd. for $C_{17}H_{18}N_5PS$: C: 57.45, H: 5.11, N: 19.71, S: 9.02; found: C: 57.70, H: 5.11, N: 19.25, S: 9.33.

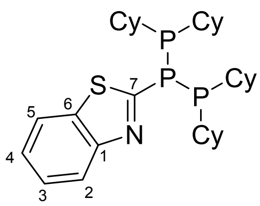
2.6. Preparation of 2-(1,1,3,3-tetracyclohexyltriphosphane-2-yl)pyridine (9a)



To a solution of Dipyrazolylphosphane **7** (2.00 g, 6.682 mmol) in 20 ml of MeCN dicyclohexylphosphane (2.9 ml, 13.364 mmol) is added while stirring vigorously. After a few moments a colorless precipitate forms. The reaction mixture is stirred for 16 h. After that the precipitate is filtered off and washed with MeCN (3 x 10 ml). Evaporation of all volatiles *in vacuo* yields the product as a colourless powder.

Yield: 3.239 g (96%); **m.p.:** 122 °C; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3057 (13), 3033 (18), 2928 (80), 2916 (79), 2890 (45), 2848 (100), 2649 (6), 1569 (30), 1460 (5), 1443 (30), 1420 (5), 1343 (8), 1328 (9), 1298 (10), 1274 (20), 1189 (8), 1179 (6), 1153 (5), 1122 (11), 1080 (5), 1043 (21), 1025 (21), 986 (22), 848 (9), 815 (17), 735 (8), 714 (10), 697 (6), 505 (6), 464 (10), 444 (5), 401 (5), 364 (5), 211 (11), 160 (9), 132 (16), 122 (19); **IR (ATR, 298 K, in cm^{-1}):** ν = 3056 (w), 3032 (w), 2916 (vs), 2847 (s), 1568 (m), 1558 (w), 1443 (vs), 1420 (m), 1339 (w), 1293 (w), 1262 (w), 1212 (vw), 1188 (w), 1177 (w), 1169 (w), 1153 (w), 1121 (w), 1080 (w), 1045 (w), 1028 (vw), 997 (m), 953 (vw), 914 (vw), 902 (vw), 884 (w), 849 (w), 814 (vw), 763 (s), 747 (w), 735 (vw), 714 (w), 621 (w), 504 (w), 484 (w), 464 (w), 454 (vw), 438 (vw); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =1.08-1.42 (20H, m, CH_2), 1.59-1.65 (4H, m, CH_2), 1.65-1.78 (12H, m, CH_2), 1.78-1.89 (8H, m, CH, CH_2), 7.07-7.11 (1H, m, C2–H), 7.51-7.55 (1H, m, C3–H), 7.81-7.83 (1H, m, C4–H), 8.57-8.59 (1H, m C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 27.0 (m, CH_2), 28.1 (m, CH_2), 31.8 (m, CH_2), 32.7 (m, CH_2), 33.9 (4C, m, CH), 121.9 (1C, s, C2), 130.3 (1C, dt, $^{2}J_{CP}$ = 18.5 Hz, $^{3}J_{CP}$ = 5.7 Hz, C4), 134.8 (1C, d, $^{3}J_{CP}$ = 3.8 Hz, C3), 150.0 (1C, d, $^{3}J_{CP}$ = 11.4 Hz, C1), 163.6 (1C, dt, $^{1}J_{CP}$ = 22.3 Hz, $^{2}J_{CP}$ = 8.1 Hz, C5); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AX_2 spin system: $\delta(P_A)$ = -57.3 (1P), $\delta(P_X)$ = -7.7 (2P); $^{1}J(P_AP_X)$ = -251.3 Hz; **elemental analysis**: calcd. for $C_{29}H_{48}NP_3$: C: 69.16, H: 9.61, N: 2.78; found: C: 68.85, H: 9.33, N: 2.80.

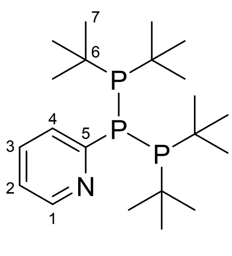
2.7. Preparation of 2-(1,1,3,3-tetracyclohexyltriphosphane-2-yl)-benzo[d]thiazole (9b)



To a solution of Dipyrazolylphosphane **8** (500 mg, 1.407 mmol) in 10 ml of MeCN dicyclohexylphosphane (0.57 ml, 2.814 mmol) is added while stirring vigorously. After a few moments a slightly yellow oil forms which solidifies over the course of approximately five minutes; this can be supported by means of ultrasonification. The suspension is then stirred for 16 h. After that the precipitate is filtered off and washed with MeCN (3 x 5 ml). Evaporation of all volatiles *in vacuo* yields the product as a pale yellow powder.

Yield: 731 mg (93%); **m.p.:** 99°C; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3058 (29), 2931 (100), 2882 (7), 2848 (61), 1557 (7), 1448 (18), 1408 (61), 1268 (11), 1231 (18), 1022 (11), 961 (11), 501 (7); **IR (ATR, 298 K, in cm^{-1}):** ν = 2919 (vs), 2846 (s), 1446 (m), 1413 (m), 1314 (w), 1301 (w), 1265 (w), 1241 (w), 1192 (w), 1181 (w), 1158 (w), 1015 (w), 997 (m), 964 (s), 884 (w), 847 (m), 757 (vs), 726 (s), 652 (w), 599 (w), 510 (w), 453 (w), 433 (w); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ = 1.11-1.30 (12H, m, CH_2), 1.34-1.47 (8H, m, CH_2), 1.60-1.66 (4H, m, CH_2), 1.68-1.76 (8H, m, CH_2), 1.76-1.82 (4H, m, CH_2), 1.88-1.95 (4H, m, CH_2), 1.98-2.07 (4H, m, CH), 7.32-7.36 (1H, m, C4–H), 7.42-7.46 (1H, m, C3–H), 7.86-7.89 (1H, m, C2–H), 7.98-8.00 (1H, m, C5–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 26.9 (m, CH_2), 28.0 (m, CH_2), 31.7 (m, CH_2), 32.6 (m, CH_2), 34.2 (4C, m, CH), 121.6 (1C, s, C2), 123.0 (1C, s, C5), 125.1 (1C, s, C4), 126.2 (1C, s, C3),137.8 (1C, dt, $^3J_{CP}$ = 5.1 Hz, $^4J_{CP}$ = 2.1 Hz, C6), 155.9 (1C, d, $^3J_{CP}$ = 11.7 Hz, C1), 173.6 (1C, dt, $^1J_{CP}$ = 50.2 Hz, $^2J_{CP}$ = 15.2 Hz, C7); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AX_2 spin system: δ(P_A) = -58.1 (1P), δ(P_X) = -0.7 (2P); $^1J(P_AP_x)$ = -268.8 Hz; **elemental analysis**: calcd. for $C_{31}H_{48}NP_3S$: C: 66.52, H: 8.64, N: 2.50. S: 5.73; found: C: 66.16, H: 8.20, N: 2.45, S: 5.36.

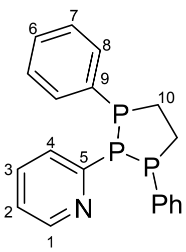
2.8. Preparation of 2-(1,1,3,3-tetra-tert-butyltriphosphane-2-yl)pyridine (9c)



To a solution of Dipyrazolylphosphane **7** (485 mg, 1.62 mmol) in 3 ml of MeCN di-*tert*-butylphosphane (0.6 ml, 3.24 mmol) is added while stirring. After stirring for 5 h the solution is stored at -30C°C for five days. During this time large colourless crystals of **9c** are growing. These crystals are isolated by decantation, washed with MeCN (2 x 1 ml) and dried *in vacuo* to afford **9c**. The mother liquor is again stored at -30°C for a second crop of crystals to grow which are isolated as described.

Yield: 501 mg (77%); **m.p.:** 142 °C; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3114 (5), 3081 (6), 3056 (20), 3044 (24), 2986 (31), 2941 (59), 2892 (100), 2861 (70), 2766 (9), 2701 (12), 1569 (51), 1557 (19), 1472 (28), 1459 (31), 1445 (30), 1413 (10), 1389 (7), 1362 (7), 1278 (10), 1202 (22), 1190 (22), 1172 (33), 1145 (18), 1114 (17), 1079 (7), 1046 (36), 1015 (10), 989 (50), 932 (25), 808 (59), 707 (10), 620 (9), 569 (43), 509 (13), 481 (16), 395 (15), 379 (10), 361 (9), 257 (27), 237 (23), 190 (20); **IR (ATR, 298 K, in cm^{-1}):** ν = 2992 (m), 2940 (s), 2889 (s), 2857 (s), 2703 (w), 1567 (s), 1556 (m), 1466 (s), 1450 (s), 1412 (s), 1384 (s), 1360 (vs), 1272 (w), 1201 (w), 1169 (vs), 1144 (m), 1111 (m), 1079 (w), 1044 (m), 1015 (m), 987 (m), 930 (m), 806 (s), 760 (vs), 742 (s), 705 (m), 621 (m); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =1.26 (36H, d, $^3J_{HP}$ = 11.1 Hz, C7–H), 7.07-7.10 (1H, m, C2–H), 7.46-7.51 (1H, m, C3–H), 8.17-8.20 (1H, m, C4–H), 8.53-8.55 (1H, m C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 32.2 (12C, m, C7), 36.5 (4C, m, CH_2), 122.4 (1C, s, C2), 132.6 (1C, dt, $^2J_{CP}$ = 20.8 Hz, $^3J_{CP}$ = 5.8 Hz, C4), 135.0 (1C, d, $^3J_{CP}$ = 4.7 Hz, C3), 149.7 (1C, dt, $^3J_{CP}$ = 12.6 Hz, $^4J_{CP}$ = 0.9 Hz, C1), 164.9 (1C, dt, $^1J_{CP}$ = 22.5 Hz, $^2J_{CP}$ = 9.3 Hz, C5); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AX_2 spin system: δ(P_A) = -44.1 (1P), δ(P_X) = 37.0 (2P); $^1J(P_AP_X)$ = -307.4 Hz; **elemental analysis**: calcd. for $C_{21}H_{48}NP_3$: C: 63.14, H: 10.09, N: 3.51; found: C: 62.98, H: 10.13, N: 3.56.

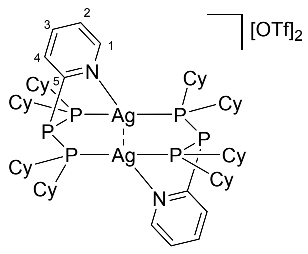
2.9. Preparation of 2-(1,3-diphenyl-1,2,3-triphospholane-2-yl)pyridine (9d)



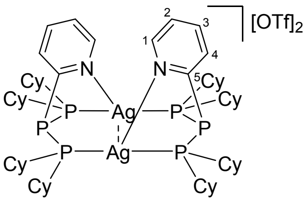
To a solution of Dipyrazolylphosphane **7** (599 mg, 0.2 mmol) in 3 ml of MeCN 1,2-bis(phenylphosphaneyl)ethane (492 mg, 0.2 mmol) is added while stirring. After stirring for 5 min the solution is stored at -30C°C for 24 h. During this time colourless crystals of **9d** are growing. These crystals are isolated by decantation, washed with MeCN (2 x 1 ml) and dried *in vacuo* to afford **9d**. The mother liquor is again stored at -30°C for a second crop of crystals to grow which are isolated as described.

Yield: 489 mg (69%); **m.p.:** 101°C; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3054 (68), 3037 (29), 3001 (5), 2955 (11), 2941 (17), 2896 (77), 1584 (71), 1570 (40), 1407 (12), 1276 (7), 1185 (8), 1152 (13), 1116 (17), 1099 (36), 1045 (26), 1027 (44), 1000 (100), 874 (5), 714 (8), 690 (7), 650 (15), 639 (18), 619 (17), 509 (8), 488 (20), 459 (39), 423 (46), 398 (8), 381 (10), 303 (8), 282 (17), 244 (11), 225 (33), 205 (35), 179 (28); **IR (ATR, 298 K, in cm^{-1}):** ν = 3063 (w), 3045 (w), 3035 (w), 3014 (w), 2982 (w), 2953 (w), 2940 (w), 2895 (w), 1984 (w), 1952 (w), 1892 (w), 1821 (w), 1757 (w), 1657 (w), 1583 (w), 1567 (m), 1558 (w), 1473 (w), 1444 (w), 1429 (m), 1413 (m), 1326 (w), 1304 (w), 1273 (w), 1224 (w), 1181 (w), 1146 (w), 1110 (w), 1096 (w), 1080 (w), 1069 (w), 1044 (w), 1023 (w), 998 (w), 987 (w), 974 (w), 921 (w), 910 (w), 893 (w), 873 (w), 854 (w), 781 (m), 759 (m), 740 (s), 694 (s); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =2.69-2.79 (4H, m, C10–H), 7.15-7.18 (1H, m, C2–H), 7.19-7.22 (6H, m, C6/C7–H), 7.34-7.38 (4H, m, C8–H), 7.59-7.63 (1H, m, C3–H), 7.86-7.89 (1H, m, C4–H), 8.63-8.65 (1H, m C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 33.0 (2C, m, C10), 122.5 (1C, bs, C2), 128.2 (2C, m, C6), 128.8 (4C, m, C7), 129.3 (1C, dt, $^2J_{CP}$ = 27.9 Hz, $^3J_{CP}$ = 7.7 Hz, C4), 132.5 (4C, m, C8), 135.9 (1C, d, $^3J_{CP}$ = 6.2 Hz, C3), 137.5 (2C, m, C9), 150.8 (1C, d, $^3J_{CP}$ = 7.2 Hz, C1), 163.6 (1C, dt, $^1J_{CP}$ = 8.8 Hz, $^2J_{CP}$ = 14.7 Hz, C5); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AX_2 spin system: δ(P_A) = -12.1 (1P), δ(P_X) = 14.5 (2P); $^1J(P_AP_X)$ = -260.7 Hz; **elemental analysis**: calcd. for $C_{19}H_{18}NP_3$: C: 64.60, H: 5.14, N: 3.96; found: C: 64.47, H: 5.05, N: 4.02.

2.10. Preparation of [(9a*Ag)$_2$][OTf]$_2$



anti-[(**9a***Ag)$_2$][OTf]$_2$



syn-[(**9a***Ag)$_2$][OTf]$_2$

To Triphosphane **9a** (1007 mg, 2.00 mmol) in PhF (5 ml) Ag[OTf] (513.9 mg, 2 mmol) is added. After stirring for 16 h the colourless suspension is filtered and the residue is washed with PhF (1 x 2 ml) and *n*-pentane (2 x 2 ml). The precipitate is subsequently dried *in vacuo* to afford the product as a colourless powder.

Yield: 1504 mg (99%); **m.p.:** 263°C (dec.); **Raman (100 mW, 50 scans, 298 K, in cm^{-1}):** ν = 3073 (25), 3058 (24), 3046 (19), 2955 (80), 2935 (91), 2923 (94), 2893 (51), 2881 (56), 2854 (78), 1603 (17), 1592 (15), 1574 (32), 1560 (33), 1445 (65), 1350 (26), 1329 (24), 1294 (31), 1266 (38), 1213 (29), 1200 (26), 1176 (21), 1159 (19), 1110 (24), 1085 (23), 1050 (42), 1030 (100), 999 (76), 851 (40), 816 (41), 752 (28), 734 (19), 710 (31), 573 (18), 512 (31), 457 (15), 437 (16), 426 (15), 388 (16), 348 (26), 315 (26), 233 (36), 192 (22), 168 (62); **IR (ATR, 298 K, in cm^{-1}):** ν = 3069 (vw), 2920 (m), 2847 (w), 1590 (vw), 1573 (w), 1486 (vw), 1446 (w), 1424 (vw), 1348 (vw), 1327 (vw), 1292 (w), 1282 (m), 1258 (vs), 1219 (m), 1196 (w), 1177 (vw), 1147 (s), 1122 (vw), 1084 (vw), 1070 (vw), 1045 (vw), 1029 (vs), 997 (w), 916 (vw), 888 (vw), 853 (vw), 806 (w), 778 (w), 762 (m), 752 (w), 734 (vw), 705 (vw), 690 (vw), 633 (vs), 572 (w), 516 (m), 466 (m), 438 (vw), 419 (vw), 409 (vw); **^{1}H NMR (CD_3CN, 263 K, in ppm):** δ = 0.85-1.16 (m, CH/CH_2), 1.18-1.36 (m, CH/CH_2), 1.36-1.46 (m, CH/CH_2), 1.46-1.56 (m, CH/CH_2), 1.58-1.66 (m, CH/CH_2), 1.66-1.88 (m, CH/CH_2), 2.00-2.07 (m, CH/CH_2), 2.07-2.17 (m, CH/CH_2), 7.09-7.14 (m, C2–H), 7.17-7.21 (m, C2–H), 7.37-7.43 (m, C3–H), 7.60-7.64 (m, C3–H), 7.73-7.78 (m, C3–H), 8.01-8.08 (m, C4–H), 8.11-8.16 (m, C4/C1–H), 8.83-8.87 (m, C1–H); **^{13}C{^{1}H} NMR (CD_3CN, 263 K,**

in ppm): δ = 25.9 (m, CH/CH_2), 26.1 (m, CH/CH_2), 27.9 (m, CH/CH_2), 28.2 (m, CH/CH_2), 28.4 (m, CH/CH_2), 28.8 (m, CH/CH_2), 32.6 (m, CH/CH_2), 32.8 (m, CH/CH_2), 33.5 (m, CH/CH_2), 33.7 (m, CH/CH_2), 34.6 (m, CH/CH_2), 34.9 (m, CH/CH_2), 36.2 (m, CH/CH_2), 36.9 (m, CH/CH_2), 116.2 (d, $^4J_{CP}$ = 21 Hz, C2), 122.1 (2C, q, $^1J_{CF}$ = 320 Hz, CF_3), 125.5 (d, $^4J_{CP}$ = 3 Hz, C2), 128.2 (d, $^3J_{CP}$ = 40 Hz, C3), 131.4 (d, $^3J_{CP}$ = 8 Hz, C3), 137.0 (dd, $^2J_{CP}$ = 51 Hz, $^3J_{CP}$ = 17 Hz, C4), 140.7 (dd, $^2J_{CP}$ = 64 Hz, $^3J_{CP}$ = 13 Hz, C4), 153.9 (s, C1), 154.8 (s, C1), 155.8 (dt, $^1J_{CP}$ = 98 Hz, $^2J_{CP}$ = 30 Hz, C5); **^{19}F NMR (CD_3CN, 263 K, in ppm):** δ = –78.5 (3F, s); **^{31}P NMR (CD_3CN, 263 K, in ppm):** isomer 1: AA'XX'X''X''' spin system: δ(P_A) = -48.5 (2P), δ(P_X) = 29.3 (4P); isomer 2 AA'XX'X''X''' spin system: δ(P_A) = -51.5 (2P), δ(P_X) = 36.1 (4P); coupling constants could not be determined; **elemental analysis**: calcd. for $C_{60}H_{96}Ag_2F_6N_2O_6P_6S_2$: C: 47.38, H: 6.36, N: 1.84, S: 4.22; found: C: 47.59, H: 6.14, N: 1.96, S: 3.75.

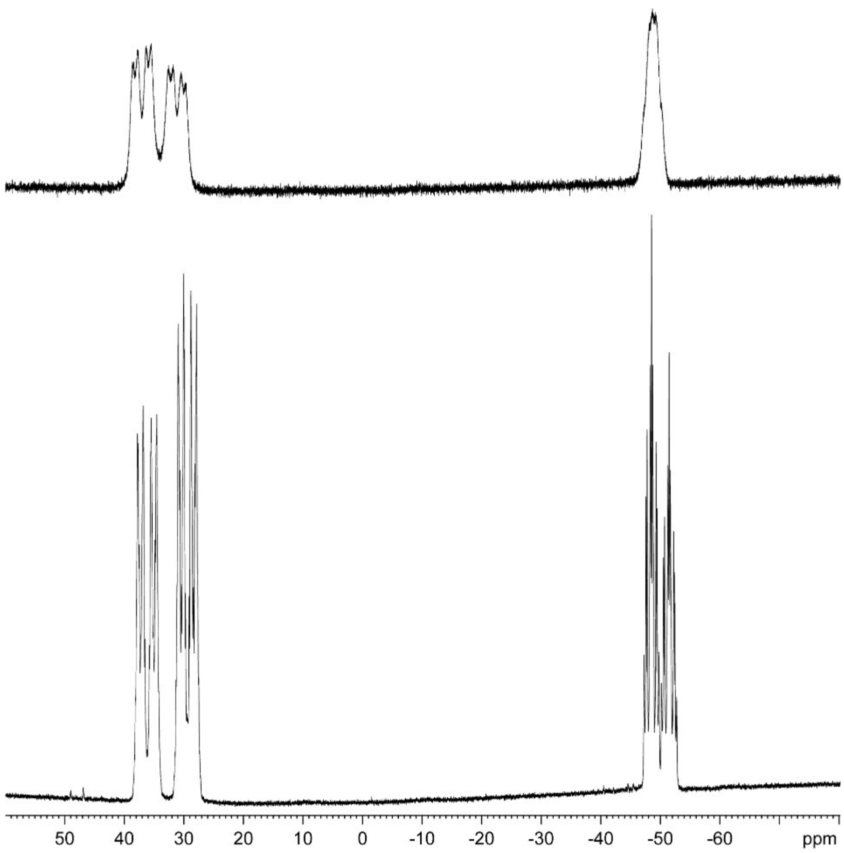
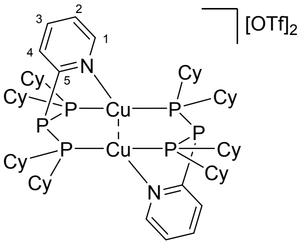


Figure 1: ^{31}P NMR spectrum of [(**9a***Ag)$_2$][OTf]$_2$ at 300 K (top) and 263 K bottom.

2.11. Preparation of [(9a*Cu)$_2$][OTf]$_2$



To Triphosphane **9a** (100 mg, 0.199 mmol) in CH_2Cl_2 (2 ml) [(MeCN)$_4$Cu][OTf] (75 mg, 0.199 mmol) is added to form a yellow solution. After stirring for 1 h all volatiles are evaporated *in vacuo*. The yellow residue is recrystallized by slow vapour diffusion of *n*-pentane in a CH_2Cl_2 solution at -30°C. This yields the product as light yellow crystals which are isolated by filtration, washing with *n*-pentane (2 x 1 ml) and subsequent evaporation of all volatiles.

Yield: 134 mg (94%); **m.p.:** 266°C (dec.); **Raman (100 mW, 50 scans, 298 K, in cm^{-1}):** v = 3127 (5), 3063 (17), 2933 (100), 2857 (98), 2660 (6), 1579 (14), 1560 (13), 1446 (37), 1356 (10), 1343 (10), 1292 (13), 1267 (25), 1224 (10), 1200 (14), 1174 (11), 1111 (7), 1083 (8), 1045 (16), 1031 (43), 1005 (52), 850 (15), 815 (19), 754 (12), 707 (20), 640 (7), 572 (7), 520 (19), 462 (6), 437 (7), 372 (6), 347 (10), 311 (9), 286 (5), 235 (10), 216 (10), 192 (16); **IR (ATR, 298 K, in cm^{-1}):** v = 2926 (w), 2853 (w), 1578 (w), 1448 (w), 1420 (vw), 1355 (vw), 1326 (vw), 1257 (vs), 1221 (m), 1154 (s), 1088 (vw), 1053 (vw), 1028 (s), 1002 (m), 917 (vw), 891 (w), 850 (vw), 816 (vw), 782 (w), 753 (vw), 733 (w), 703 (vw), 635 (vs); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =0.96-1.14 (16H, m, CH_2), 1.28-1.49 (8H, m, CH_2), 1.53-1.57 (2H, m, CH_2), 1.62-1.69 (4H, m, CH_2), 1.73-1.82 (6H, m, CH_2), 1.90-2.02 (8H, m, CH_2), 2.03-2.25 (8H, m, CH), 8.17-8.27 (2H, m, C2–H), 8.29-8.40 (4H, m, C3/C4–H), 8.93-8.96 (2H, m C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 25.2 (m, CH/CH_2), 27.6 (m, CH/CH_2), 32.7 (m, CH/CH_2), 36.1 (m, CH/CH_2), 120.9 (2C, d, $^1J_{CF}$ = 321 Hz, CF_3), 128.8 (2C, d, $^4J_{CP}$ = 13 Hz, C2), 135.6 (2C, m, C4), 141.7 (2C, m, C3), 153.1 (2C, s, C1), 158.1 (2C, d, $^1J_{CP}$ = 39 Hz, C5); **^{19}F NMR (CD_2Cl_2, 300 K, in ppm):** δ = –78.8 (6F, s); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AA'XX'X''X''' spin system: δ(P_A) = -39.1 (2P), δ(P_X) = 15.4 (4P); coupling constants could not be determined; **elemental analysis**: calcd. for $C_{60}H_{96}Cu_2F_6N_2O_6P_6S_2$ * 0.5 CH_2Cl_2 : C: 49.27, H: 6.63, N: 1.90, S: 4.35; found: C: 49.09, H: 6.76, N: 1.98, S: 4.26.

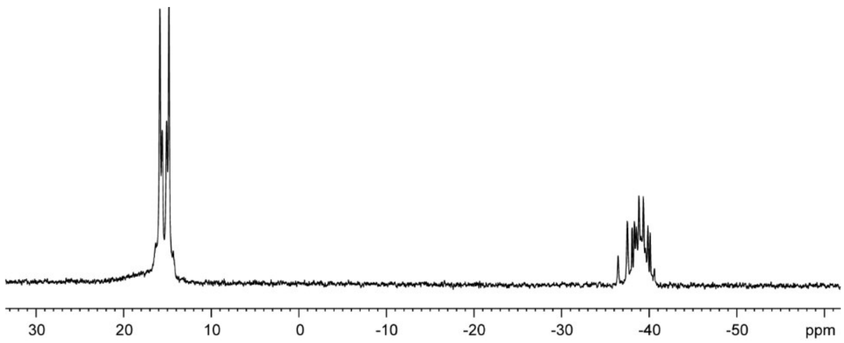
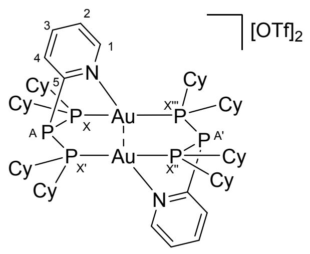
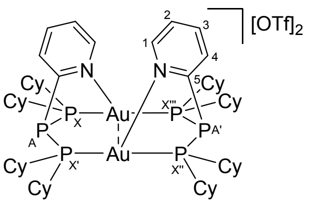


Figure 2: ^{31}P NMR spectrum of [(**9a***Cu)$_2$][OTf]$_2$ at 300 K.

2.12. Preparation of $[(\mathbf{9aAu})_2][OTf]_2$



anti-[(**9a***Ag)$_2$][OTf]$_2$



syn-[(**9a***Ag)$_2$][OTf]$_2$

To silver complex [(**9a***Ag)$_2$][OTf]$_2$ (456 mg, 0.30 mmol) in MeCN (3 ml) (tht)AuCl (192 mg, 0.60 mmol) is added. The occurring precipitate is filtered off. To the filtrate Et_2O is added until the formation of a faint mist. The mixture is stored at -30°C. After 16 h colourless crystals of the product are formed which are isolated by filtration and subsequent washing with Et_2O (2 x 2 ml). After evaporation of all volatiles *in vacuo* the product is obtained as a colourless, crystalline solid.

Yield: 327 mg (64%); **m.p.:** 266°C (dec.); **Raman (100 mW, 50 scans, 298 K, in cm^{-1}):** ν = 3076 (9), 3045 (17), 2944 (100), 2918 (67), 2851 (74), 2666 (6), 1560 (22), 1444 (35), 1351 (14), 1328 (12), 1293 (22), 1270 (31), 1224 (11), 1209 (16), 1178 (14), 1160 (6), 1110 (21), 1080 (10), 1044 (40), 1030 (62), 1003 (21), 986 (38), 851 (21), 816 (30), 754 (16), 742 (12), 707 (22), 620 (7), 572 (8), 542 (15), 519 (9), 437 (9), 396 (11), 373 (5), 348 (14), 334 (12), 313 (15), 220 (19); **IR (ATR, 298 K, in cm^{-1}):** ν = 3043 (vw), 2921 (w), 2848 (w), 1565 (w), 1444 (w), 1422 (w), 1352 (vw), 1326 (vw), 1260 (vs), 1221 (m), 1177 (w), 1148 (vs), 1076 (w), 1043 (w), 1028 (s), 1000 (w), 985 (w), 918 (w), 891 (w), 851 (w), 820 (vw), 777 (m), 752 (w), 635 (vs), 571 (w), 516 (m), 466 (m), 420 (vw); **^{1}H NMR (CD_2Cl_2, 243 K, in ppm):** δ = 0.90-1.05 (m, CH/CH$_2$), 1.08-1.19 (m, CH/CH$_2$), 1.22-1.42 (m, CH/CH$_2$), 1.49-1.56 (m, CH/CH$_2$), 1.56-1.65 (m, CH/CH$_2$), 1.65-1.73 (m, CH/CH$_2$), 1.76-1.86 (m, CH/CH$_2$), 1.94-2.02 (m, CH/CH$_2$), 2.04-2.14 (m, CH/CH$_2$), 2.14-2.22 (m, CH/CH$_2$), 2.28-2.37 (m, CH/CH$_2$), 7.60-7.64 (m, C2–H), 7.65-7.69 (m, C2–H), 7.90-7.95 (m, C3–H), 7.97-8.02 (m, C4–H), 8.02-8.07 (m, C3/C4-H), 8.47-8.50 (m, C1–H), 8.74-8.77 (m, C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 243 K, in ppm):** δ = 25.2 (m, CH/CH$_2$), 25.5 (m, CH/CH$_2$), 27.1 (m, CH/CH$_2$), 27.7 (m, CH/CH$_2$), 31.1 (m, CH/CH$_2$), 31.5 (m, CH/CH$_2$), 32.7 (m, CH/CH$_2$), 33.1 (m, CH/CH$_2$), 33.6 (m, CH/CH$_2$), 36.9 (m, CH/CH$_2$), 37.1 (m, CH/CH$_2$), 121.0 (2C, q, $^1J_{CF}$ = 321 Hz, CF$_3$), 126.9 (d, $^4J_{CP}$ = 8 Hz, C2), 127.4 (d, $^4J_{CP}$ = 9 Hz, C2), 134.0 (m, C3), 135.1 (m, C3), 138.8 (m, C4), 139.2 (m, C4), 151.8 (bs, C1), 152.1 (d, $^1J_{CP}$ = 22 Hz); **^{19}F NMR (CD_2Cl_2, 243 K, in ppm):** δ = –79.0 (6F, s); **^{31}P NMR (CD_2Cl_2, 243 K, in ppm):** Isomer 1: AA'XX'X''X''' spin system: δ(P_A) = δ($P_{A'}$) = -34.2, δ(P_X) = δ($P_{X'}$) = 52.5, δ($P_{X''}$) = δ($P_{X'''}$) = 52.6, $^4J(P_AP_{A'})$ = -5.9 Hz, $^1J(P_AP_X)$ = -232.0 Hz, $^1J(P_AP_{X'})$ = -188.3 Hz, $^3J(P_AP_{X''})$ = -23.8 Hz, $^3J(P_AP_{X'''})$ = -23.9 Hz, $^3J(P_{A'}P_X)$ = -3.0 Hz, $^3J(P_{A'}P_{X'})$ = 50.7 Hz, $^1J(P_{A'}P_{X''})$ = -270.6 Hz,

$^{1}J(P_{A'}P_{X'''})$ = -245.2 Hz, $^{2}J(P_{X}P_{X'})$ = 40.4 Hz, $^{4}J(P_{X}P_{X''})$ = -11.7 Hz, $^{2}J(P_{X}P_{X'''})$ = 244.5 Hz, $^{2}J(P_{X'}P_{X''})$ = 261.5 Hz, $^{4}J(P_{X'}P_{X'''})$ = 33.4 Hz, $^{2}J(P_{X''}P_{X'''})$ = 7.5 Hz; isomer 2: AA'XX'X''X''' spin system: $\delta(P_{A}) = \delta(P_{A'})$ = -37.8, $\delta(P_{X}) = \delta(P_{X'}) = \delta(P_{X''}) = \delta(P_{X'''})$ = 50.3, $^{4}J(P_{A}P_{A'})$ = 0.1 Hz, $^{1}J(P_{A}P_{X})$ = -250.4 Hz, $^{1}J(P_{A}P_{X'})$ = -262.3 Hz, $^{3}J(P_{A}P_{X''})$ = 12.4 Hz, $^{3}J(P_{A}P_{X'''})$ = -8.0 Hz, $^{3}J(P_{A'}P_{X})$ = 29.5 Hz, $^{3}J(P_{A'}P_{X'})$ = -22.7 Hz, $^{1}J(P_{A'}P_{X''})$ = -241.2 Hz, $^{1}J(P_{A'}P_{X'''})$ = -283.2 Hz, $^{2}J(P_{X}P_{X'})$ = 26.2 Hz, $^{4}J(P_{X}P_{X''})$ = 1.5 Hz, $^{2}J(P_{X}P_{X'''})$ = 261.0 Hz, $^{2}J(P_{X'}P_{X''})$ = 251.8 Hz, $^{4}J(P_{X'}P_{X'''})$ = 16.1 Hz, $^{2}J(P_{X''}P_{X'''})$ = 23.7 Hz; **elemental analysis**: calcd. for $C_{60}H_{96}Au_{2}F_{6}N_{2}O_{6}P_{6}S_{2}$: C: 42.41, H: 5.69, N: 1.65, S: 3.77; found: C: 42.51, H: 5.67, N: 1.70, S: 3.76.

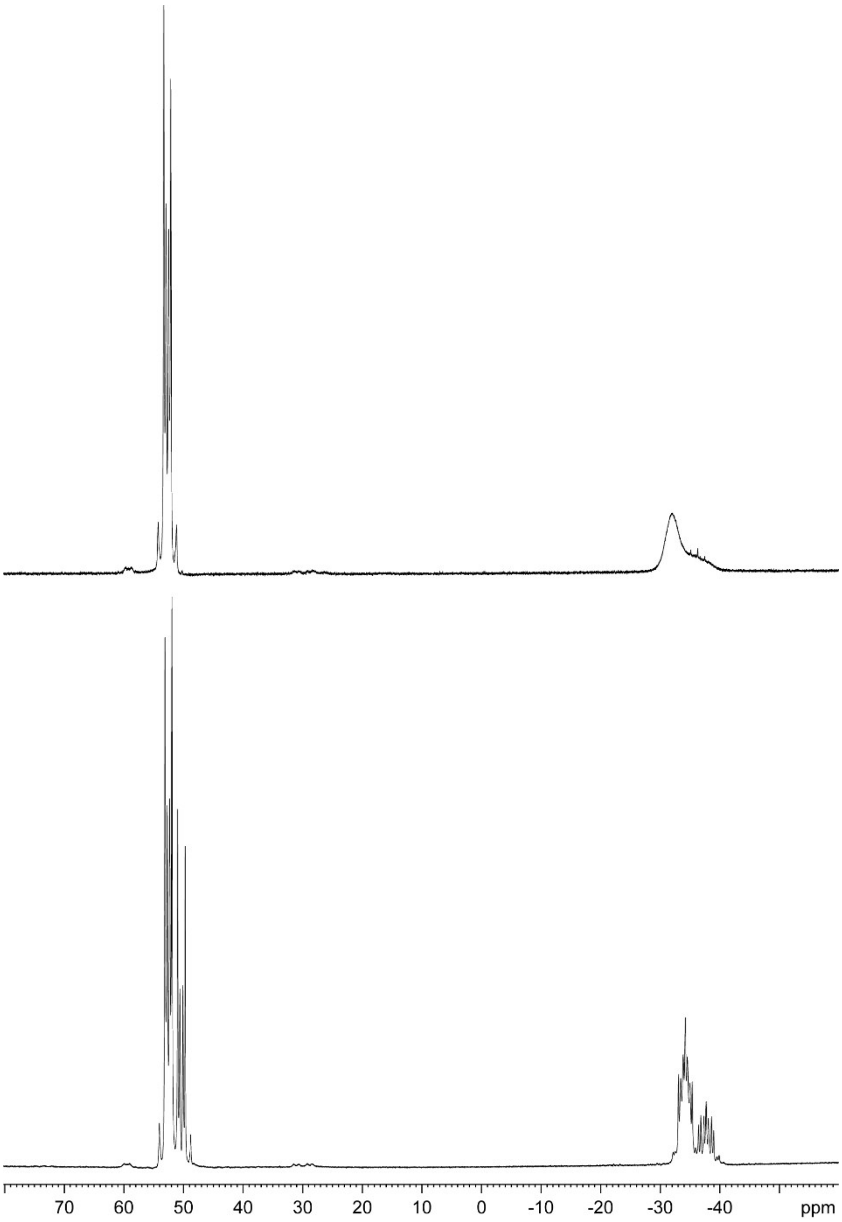
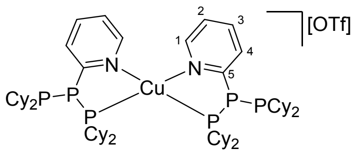


Figure 3: ^{31}P NMR spectrum of [(**9a***Au)$_2$][OTf]$_2$ at 300 K (top) and 243 K (bottom).

2.13. Preparation of $[(9a)_2Cu][OTf]$



To Triphosphane **9a** (200 mg, 0.397 mmol) in CH_2Cl_2 (0.5 ml) $[(MeCN)_4Cu][OTf]$ (75 mg, 0.199 mmol) is added to form a yellow solution. Slow vapour diffusion of *n*-pentane into the reaction mixture at -30°C over the course of three days leads to the formation of colourless crystals. These are isolated by filtration, washing with *n*-pentane (2 x 1 ml) and evaporation of all volatiles.

Yield: 225 mg (93%); **m.p.:** 189°C (dec.); **Raman (100 mW, 50 scans, 298 K, in cm^{-1}):** ν = 3112 (7), 3068 (13), 3044 (9), 2934 (99), 2891 (45), 2850 (100), 2659 (7), 1580 (44), 1551 (34), 1443 (44), 1416 (8), 1338 (12), 1293 (18), 1271 (23), 1201 (11), 1169 (6), 1156 (7), 1121 (33), 1087 (10), 1048 (27), 1027 (35), 1000 (46), 850 (15), 817 (20), 751 (6), 736 (10), 722 (11), 710 (15), 633 (6), 510 (5), 470 (11), 433 (9), 379 (6), 347 (6), 313 (8), 227 (13), 207 (13), 179 (12); **IR (ATR, 298 K, in cm^{-1}):** ν = 2920 (s), 2848 (m), 1579 (m), 1551 (w), 1446 (s), 1414 (m), 1340 (w), 1265 (vs), 1221 (m), 1198 (w), 1179 (w), 1143 (s), 1119 (m), 1086 (w), 1048 (w), 1030 (vs), 998 (m), 915 (w), 887 (w), 849 (m), 815 (w), 760 (m), 735 (w), 722 (w), 710 (w), 636 (vs); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =1.06-1.53 (44H, m, CH_2), 1.62-1.73 (20H, m, CH_2), 1.77-1.90 (16H, m, CH_2), 2.00-2.11 (8H, m, CH), 7.11-7.15 (2H, m, C2–H), 7.65-7.70 (2H, m, C3–H), 7.72-7.78 (2H, m, C4–H), 8.35-8.38 (2H, m C1–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 26.6 (m, CH_2), 27.7 (m, CH_2), 31.2 (m, CH_2), 32.3 (m, CH_2), 34.0 (8C, m, CH), 121.7 (1C, q, $^1J_{CF}$ = 321 Hz, CF_3), 123.1 (2C, s, C2), 130.9 (2C, d, $^2J_{CP}$ = 38 Hz, C4), 137.0 (2C, d, $^3J_{CP}$ = 9 Hz, C3), 151.8 (2C, bs, C1), 161.4 (2C, d, $^1J_{CP}$ = 32 Hz, C5); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AX_2 spin system: $\delta(P_A)$ = -44.8 ppm (2P), $\delta(P_X)$ = -8.9 ppm (4P); $^1J(P_AP_X)$ = -275 Hz; **^{19}F NMR (CD_3CN, 300 K, in ppm):** δ = –78.9 (3F, s); **elemental analysis**: calcd. for $C_{59}H_{96}CuF_3N_2O_3P_6S$: C: 58.09, H: 7.93, N: 2.30, S: 2.63; found: C: 57.67, H: 7.55, N: 2.61, S: 2.54.

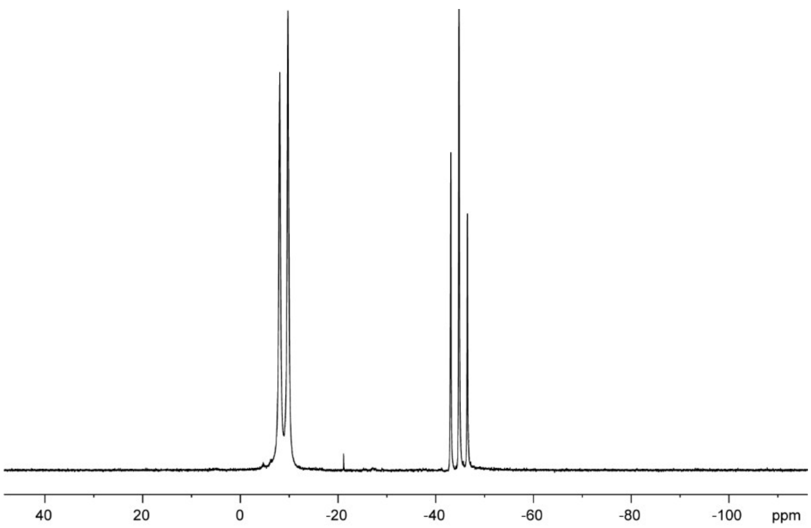
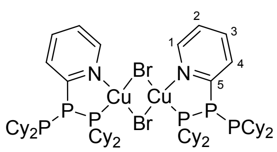


Figure 4: ^{31}P NMR spectrum of [(**9a**)$_2$Cu][OTf] at 300 K.

2.14. Preparation of (9a*CuBr)$_2$



To Triphosphane **9a** (100 mg, 0.199 mmol) in THF (0.5 ml) (tht)CuBr (46 mg, 0.199 mmol) is added to form a yellow solution. Slow vapour diffusion of *n*-pentane into the reaction mixture at -30°C over the course of three days leads to the formation of colourless crystals. These are isolated by filtration, washing with *n*-pentane (2 x 1 ml) and evaporation of all volatiles.

Yield: 120 mg (93%); **m.p.:** 154°C (dec.); **Raman (100 mW, 50 scans, 298 K, in cm^{-1}):** *v* = 3051 (17), 2934 (100), 2894 (39), 2850 (95), 2657 (6), 1575 (23), 1556 (14), 1462 (6), 1443 (27), 1343 (7), 1330 (8), 1298 (9), 1268 (12), 1206 (6), 1187 (8), 1175 (7), 1153 (6), 1118 (9), 1086 (6), 1047 (19), 1027 (18), 1000 (42), 850 (10), 815 (15), 742 (6), 705 (10), 634 (5), 516 (5), 477 (6), 437 (5), 423 (7), 358 (5), 329 (5), 229 (6), 182 (11); **IR (ATR, 298 K, in cm^{-1}):** *v* = 2919 (vs), 2846 (vs), 1574 (m), 1555 (w), 1460 (w), 1445 (s), 1416 (m), 1339 (w), 1290 (w), 1267 (w), 1222 (w), 1174 (w), 1152 (w), 1116 (w), 1069 (w), 1046 (w), 1029 (w), 998 (m), 914 (w), 886 (w), 850 (m), 815 (w), 755 (vs), 711 (w), 633 (w); **^{1}H NMR (CD$_2$Cl$_2$, 300 K, in ppm):** δ =1.10-1.44 (44H, m, CH$_2$), 1.60-1.78 (36H, m, CH$_2$), 1.93-2.05 (8H, m, CH), 7.23-7.35 (2H, m, C2–H), 7.66-7.40 (2H, m, C3–H), 7.74-7.76 (2H, m, C4–H), 8.80-9.00 (2H, m C1–H); **^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 300 K, in ppm):** δ = 26.6 (s, CH$_2$), 27.7 (m, CH$_2$), 31.4 (m, CH$_2$), 32.5 (m, CH$_2$), 33.9 (8C, m, CH), 123.7 (2C, s, C2), 131.4 (2C, d, $^{2}J_{CP}$ = 43 Hz, C4), 137.3 (2C, d, $^{3}J_{CP}$ = 10.4 Hz, C3), 151.3 (2C, bs, C1), 160.3 (2C, bs, C5); **^{31}P NMR (CD$_2$Cl$_2$, 300 K, in**

ppm): AX_2 spin system: $\delta(P_A)$ = -46.6 ppm (2 P), $\delta(P_X)$ = -6.2 ppm (4P); $^1J(P_AP_X)$ = -253 Hz; **elemental analysis**: calcd. for $C_{58}H_{96}Cu_2Br_2N_2P_6$: C: 53.83, H: 7.48, N: 2.16; found: C: 54.12, H: 7.65, N: 1.98.

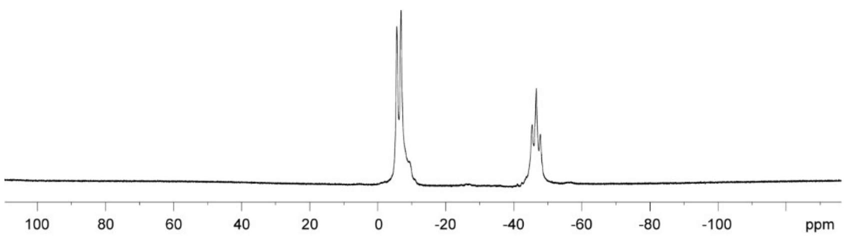
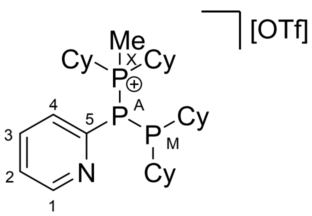


Figure 5: ^{31}P NMR spectrum of (**9a***CuBr)$_2$ at 300 K.

2.15. Preparation of 1,1,3,3-tetracyclohexyl-1-methyl-2-pyridyl-triphosphan-1-ium trifluoromethanesulfonate (10[OTf])

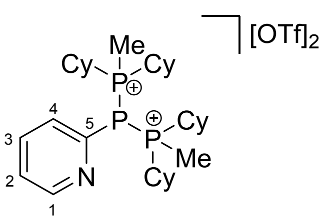


To a solution of **9a** (504 mg, 1 mmol) in 3 ml of Et_2O MeOTf (164 mg, 1 mmol) is added while stirring. After 16 h a colourless suspension is formed. The precipitate is filtered off and washed with Et_2O (3 x 3 ml). Evaporation of all volatiles *in vacuo* yields the product as a colourless powder.

Yield: 658 mg (99%); **m.p.:** 127°C dec.; **Raman (100 mW, 298 K, in cm^{-1}):** v = 3058 (23), 3019 (6), 2987 (20), 2942 (85), 2923 (77), 2875 (50), 2853 (100), 2680 (5), 2658 (6), 1571 (30), 1561 (21), 1445 (33), 1419 (7), 1330 (9), 1302 (14), 1293 (12), 1274 (22), 1220 (11), 1205 (7), 1191 (7), 1181 (8), 1155 (9), 1122 (19), 1085 (10), 1047 (34), 1029 (45), 991 (33), 973 (5), 849 (13), 819 (23), 752 (13), 734 (8), 715 (15), 700 (11), 623 (6), 572 (8), 517 (6), 481 (12), 468 (13), 455 (10), 433 (8), 401 (11); **IR (ATR, 298 K, in cm^{-1}):** v = 3056 (w), 3032 (w), 2916 (vs), 2847 (s), 1568 (m), 1558 (w), 1443 (vs), 1420 (m), 1339 (w), 1293 (w), 1262 (w), 1212 (vw), 1188 (w), 1177 (w), 1169 (w), 1153 (w), 1121 (w), 1080 (w), 1045 (w), 1028 (vw), 997 (m), 953 (vw), 914 (vw), 902 (vw), 884 (w), 849 (w), 814 (vw), 763 (s), 747 (w), 735 (vw), 714 (w), 621 (w), 504 (w), 484 (w), 464 (w), 454 (vw), 438 (vw); **^{1}H NMR (CD_3CN, 300 K, in ppm):** δ =1.10-1.40 (14H, m, CH_2), 1.43-1.56 (6H, m, CH_2), 1.61-1.75 (9H, m, CH_2), 1.80-1.88 (7H, m, CH_2), 1.99-2.09 (6H, m, CH, CH_2), 2.59-2.81 (2H, m, CH), 7.41-7.45 (1H, m, C2–H), 7.65-7.69 (1H, m, C4–H), 7.85-7.90 (1H, m, C3–H), 8.63-8.65 (1H, m C1–H); **^{13}C{^{1}H} NMR**

(CD$_3$CN, 300 K, in ppm): δ = 4.7 (1C, ddd, $^1J_{CP}$ = 39.2 Hz, $^2J_{CP}$ = 7.1 Hz, $^3J_{CP}$ = 5.6 Hz, CH$_3$), 26.5 (m, CH$_2$), 27.1 (m, CH$_2$), 27.8 (m, CH$_2$), 28.1 (m, CH$_2$), 28.8 (m, CH$_2$), 32.5 (m, CH$_2$), 33.2 (2C, m, CH), 35.4 (2C, m, CH), 122.6 (1C, q, $^1J_{CF3}$ = 321.1 Hz, CF$_3$), 125.6 (1C, s, C2), 131.9 (1C, dd, $^2J_{CP}$ = 46.1 Hz, $^3J_{CP}$ = 9.2 Hz, C4), 138.6 (1C, dd, $^3J_{CP}$ = 11.9 Hz, $^4J_{CP}$ = 2.2, C3), 152.0 (1C, d, $^3J_{CP}$ = 3.2 Hz, C1), 155.3 (1C, dd, $^1J_{CP}$ = 19.1 Hz, $^2J_{CP}$ = 2.9 Hz, C5); **^{19}F NMR (CD$_3$CN, 300 K, in ppm):** δ = –79.3 (3F, s); **^{31}P NMR (CD$_3$CN, 300 K, in ppm):** AMX spin system: δ(P$_A$) = -46.2 (1P), δ(P$_M$) = -12.9 (1P), δ(P$_X$) = 34.2 (1P); ^1J(P$_A$P$_M$) = -290.3 Hz, ^1J(P$_A$P$_X$) = -281.0 Hz, ^2J(P$_M$P$_X$) = 58.5 Hz; **elemental analysis**: calcd. for $C_{31}H_{51}F_3NO_3P_3S$: C: 55.76, H: 7.70, N: 2.10, S: 4.80; found: C: 55.83, H: 7.83, N: 2.16, S: 4.96.

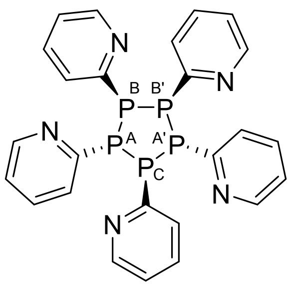
2.16. Preparation of 1,1,3,3-tetracyclohexyl-1,3-dimethyl-2-pyridyltriphosphane-1,3-diium bis(trifluoromethanesulfonate) (11[OTf]$_2$)



To **9a** (250 mg, 0.496 mmol) an excess of MeOTf (407 mg, 2.482 mmol) is added. After stirring for 16 h all volatiles are removed *in vacuo*. Recrystallization from MeCN/Et$_2$O and subsequent removal of all volatiles *in vacuo* yields the product as colourless crystals.

Yield: 401 mg (97%); **m.p.:** 161°C dec.; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3068 (34), 3009 (21), 2940 (100), 2910 (76), 2864 (96), 1614 (23), 1562 (31), 1449 (40), 1356 (27), 1328 (23), 1301 (28), 1278 (33), 1250 (24), 1222 (27), 1180 (24), 1083 (21), 1044 (28), 1030 (56), 992 (27), 849 (24), 816 (29), 757 (27), 702 (24), 574 (21), 520 (19), 444 (20), 431 (20), 348 (19), 313 (17), 212 (21), 136 (19); **IR (ATR, 298 K, in cm^{-1}):** ν = 3010 (vw), 2935 (w), 2861 (w), 1571 (vw), 1561 (vw), 1447 (w), 1424 (vw), 1308 (w), 1260 (vs), 1246 (vs), 1223 (m), 1152 (vs), 1085 (vw), 1029 (vs), 1005 (w), 991 (w), 923 (w), 909 (w), 923 (w), 909 (w), 893 (w), 884 (w), 869 (m), 850 (w), 816 (vw), 774 (w), 757 (w), 701 (vw), 636 (vs), 573 (m), 517 (s), 466 (w), 443 (vw), 432 (vw), 407(vw); **^{1}H NMR (CD$_3$CN, 300 K, in ppm):** δ = 0.86-0.96 (2H, m, CH$_2$), 0.98-1.14 (4H, m, CH$_2$), 1.20-1.31 (2H, m, CH$_2$), 1.34-1.43 (4H, m, CH$_2$), 1.47-1.55 (4H, m, CH$_2$), 1.57-1.62 (2H, m, CH$_2$), 1.62-1.69 (4H, m, CH$_2$), 1.71-1.82 (10H, m, CH$_2$), 1.90-2.06 (4H, m, CH$_2$), 2.07-2.15 (4H, m, CH$_2$), 2.30-2.37 (2H, m, CH), 2.39-2.42 (6H, m, CH$_3$), 2.57-2.67 (2H, m, CH), 7.75-7.79 (1H, m, C2–H), 8.06-8.11 (1H, m, C3–H), 8.23-8.27 (1H, m, C4–H), 8.93-8.95 (1H, m C1–H); **^{13}C{^{1}H} NMR (CD$_3$CN, 300 K, in ppm):** δ = 6.23 (2C, m, CH$_3$), 25.9 (m, CH$_2$), 26.0 (m, CH$_2$), 27.4 (m, CH$_2$), 27.6 (m, CH$_2$), 27.9 (m, CH$_2$), 28.2 (m, CH$_2$), 28.4 (m, CH$_2$), 29.1 (m, CH$_2$), 29.3 (m, CH$_2$), 37.0 (2C, m, CH), 38.0 (2C, m, CH), 122.5 (1C, q, $^{1}J_{CF3}$ = 321.2 Hz, CF_3), 129.7 (1C, bs, C2), 137.6 (1C, dd, $^{2}J_{CP}$ = 54.5 Hz, $^{3}J_{CP}$ = 5.7 Hz, C4), 141.1 (1C, d, $^{3}J_{CP}$ = 15.5 Hz, C3), 145.9 (1C, dd, $^{1}J_{CP}$ = 10.7 Hz, $^{2}J_{CP}$ = 4.3 Hz, C5), 154.9 (1C, d, $^{3}J_{CP}$ = 4.3 Hz, C1); **^{19}F NMR (CD_3CN, 300 K, in ppm):** δ = –79.2 (3F, s); **^{31}P NMR (CD_3CN, 300 K, in ppm):** AX_2 spin system: δ(P_A) = -67.9 (1P), δ(P_X) = 44.0 (2P); $^{1}J(P_AP_X)$ = -315.4 Hz; **elemental analysis**: calcd. for $C_{33}H_{54}F_6NO_6P_3S_2$: C: 47.65, H: 6.54, N: 1.68, S: 7.71; found: C: 47.13, H: 6.28, N: 1.69, S: 8.23.

2.17. Preparation of 1,2,3,4,5-penta(pyridine-2-yl)pentaphospholane (13)

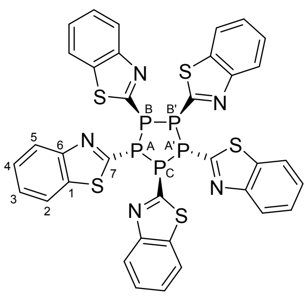


To a solution of Dipyrazolylphosphane **7** (2.275 g, 7.600 mmol) in 20 ml of Et_2O dicyclohexylphosphane (1.5 ml, 7.600 mmol) is added while stirring. After a few moments a colourless precipitate forms. The reaction mixture is stirred for 16 h. After that the precipitate is filtered off and washed with Et_2O (3 x 10 ml). Evaporation of all volatiles *in vacuo* yields the product as a colourless powder.

Yield: 810 mg (98%); **m.p.:** 197°C; **Raman (100 mW, 298 K, in cm^{-1}):** *ν* = 3133 (7), 3114 (10), 3042 (76), 2977 (11), 2954 (7), 1571 (69), 1555 (27), 1446 (8), 1417 (15), 1271 (11), 1151 (13), 1129 (31), 1083 (8), 1052 (31), 1044 (41), 986 (100), 712 (14), 619 (13), 517 (8), 493 (7), 439 (42), 417 (15), 408 (15), 399 (15), 383 (20), 290 (7), 271 (14), 243 (11), 230 (13), 203 (25), 161 (35), 133 (41); **IR (ATR, 298 K, in cm^{-1}):** *ν* = 3035 (w), 2919 (s), 2844 (s), 1569 (s), 1553 (m), 1444 (s), 1413 (s), 1333 (w), 1267 (m), 1191 (w), 1179 (w), 1147 (m), 1120 (w), 1043 (w), 1000 (w), 987 (m), 885 (m), 851 (w), 755 (vs), 739 (s), 711 (m), 618 (m), 514 (w), 483 (s), 463 (w); **^{1}H NMR (CD_3CN, 300 K, in ppm):** δ = 6.98-7.02 (2H, m, C2–H), 7.14-7.17 (1H, m, C2–H), 7.17-7.21 (2H, m, C2–H), 7.25-7.29 (2H, m, C4–H), 7.33-7.37 (2H, m, C3–H), 7.58-7.67 (3H, m, C3–H), 7.99-8.03 (3H, m, C4–H), 8.04-8.07 (2H, m, C1–H), 8.44-8.46 (2H, m, C1–H), 8.46-8.49 (1H, m, C1–H); **^{13}C{^{1}H} NMR (CD_3CN, 300 K, in ppm):** δ = 123.0 (1C, s, C2), 123.6 (2C, s, C2), 123.7 (2C, s, C2), 127.8 (1C, m, C4), 129.5 (4C, m, C4), 136.5 (1C, s, C3), 136.6 (2C, s, C3), 137.0 (2C, s, C3), 150.3 (2C, m, C1), 150.6 (1C, m, C1), 150.9 (2C, m, C1), 162.0 (2C, m, C5), 164.5 (2C, m, C5), 165.2 (1C, m, C5); **^{31}P NMR (CD_3CN, 300 K, in ppm):** AA'BB'C spin system: δ(P_A) = δ($P_{A'}$) = 14.1 (2P), δ(P_B) = δ($P_{B'}$) = 20.3 (2P), δ(P_C) = 25.1 (1P); $^{2}J(P_AP_{A'})$ = -2.59 Hz, $^{1}J(P_AP_B)$ = $^{1}J(P_{A'}P_{B'})$ = -242.59 Hz, $^{2}J(P_AP_{B'})$ = $^{2}J(P_{A'}P_B)$ = -6.74 Hz, $^{1}J(P_AP_C)$ = $^{1}J(P_{A'}P_C)$ = -275.37 Hz, $^{1}J(P_BP_{B'})$ = -327.59 Hz, $^{2}J(P_BP_C)$ = $^{2}J(P_{B'}P_C)$ = 28.00

Hz; **elemental analysis**: calcd. for $C_{25}H_{20}N_5P_5$: C: 55.06, H: 3.70, N: 12.84; found: C: 54.87, H: 3.67, N: 12.60.

2.18. Preparation of 1,2,3,4,5-pentakis(benzo[d]thiazole-2-yl)-pentaphospholane (18)



To a solution of Dipyrazolylphosphane **8** (2.00 g, 5.627 mmol) in 20 ml of CH_2Cl_2 dicyclohexylphosphane (1.14 ml, 5.627 mmol) is added while stirring. After stirring for 16 h the reaction mixture is reduced to half of its volume *in vacuo*. Et_2O (10 ml) is added and the reaction mixture is stored at -30°C for 16 h to form a colourless precipitate. The precipitate is filtered off, washed with *n*-pentane (2 x 5 ml) and dried *in vacuo* to yield the product as a colourless solid.

Yield: 669 mg (72%); **m.p.:** 188 °C; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3059 (15), 3026 (5), 1589 (15), 1555 (22), 1454 (45), 1447 (40), 1412 (100), 1312 (8), 1272 (27), 1236 (54), 1124 (20), 1015 (10), 986 (28), 849 (16), 708 (18), 504 (17), 485 (7), 467 (6), 440 (9), 412 (37), 396 (12), 371 (16), 354 (7), 280 (6), 248 (6), 229 (5), 194 (12), 160 (12), 136 (20), 126 (24); **IR (ATR, 298 K, in cm^{-1}):** ν = 3058 (w), 2920 (w), 1555 (vw), 1447 (w), 1412 (m), 1311 (w), 1272 (w), 1234 (w), 1157 (w), 1122 (w), 1073 (w), 1014 (w), 979 (m), 940 (w), 848 (w), 757 (vs), 727 (s), 706 (w), 668 (m), 594 (w), 579 (w), 532 (w), 523 (w), 504 (vw), 458 (vw), 430 (m); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ =7.12-7.16 (2H, m, C2–H), 7.17-7.21 (2H, m, C5–H), 7.27-7.31 (1H, m, C5–H), 7.35-7.38 (2H, m, C4–H), 7.39-7.41 (2H, m, C5–H), 7.41-7.42 (1H, m, C2–H), 7.43-7.47 (2H, m, C2–H), 7.63-7.69 (3H, m, C3–H), 7.83-7.86 (1H, m, C4–H), 7.86-7.89 (2H, m, C3–H), 7.90-7.93 (2H, m, C4–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 121.6 (2C, s, C3), 121.7 (1C, s, C3), 122.1 (2C, s, C3), 123.1 (1C, s, C4), 123.3 (2C, s, C4), 123.6 (2C, s, C4), 125.7 (1C, s, C5), 126.1 (2C, s, C5), 126.3 (2C, s, C5), 126.6 (2C, s, C2), 126.8 (1C, s, C2), 127.0 (2C, s, C2), 137.8 (1C, m, C1), 138.4 (2C, m, C1), 138.5 (2C, m, C1), 154.5 (2C, m, C6), 155.6 (3C, m, C6), 169.9 (2C, m, C7), 168.5 (2C, m, C7), 165.4 (1C, m, C7); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AA'BB'C spin system: $\delta(P_A) = \delta(P_{A'})$ = 24.8 (2P), $\delta(P_B) = \delta(P_{B'})$ = 31.6 (2P), $\delta(P_C)$ = 38.3 (1P); $^2J(P_AP_{A'})$ = 2.35 Hz, $^1J(P_AP_B) = {}^1J(P_{A'}P_{B'})$ = -240.58 Hz, $^2J(P_AP_{B'}) = {}^2J(P_{A'}P_B)$ = -2.59 Hz, $^1J(P_AP_C) = {}^1J(P_{A'}P_C)$ = -274.52 Hz, $^1J(P_BP_{B'})$ = -335.67 Hz, $^2J(P_BP_C) = {}^2J(P_{B'}P_C)$ = 32.07 Hz; **elemental analysis**: calcd. for $C_{35}H_{20}N_5P_5S_5$: C: 50.91, H: 2.44, N: 8.48. S: 19.41; found: C: 50.99, H: 2.62, N: 8.30, S: 18.98.

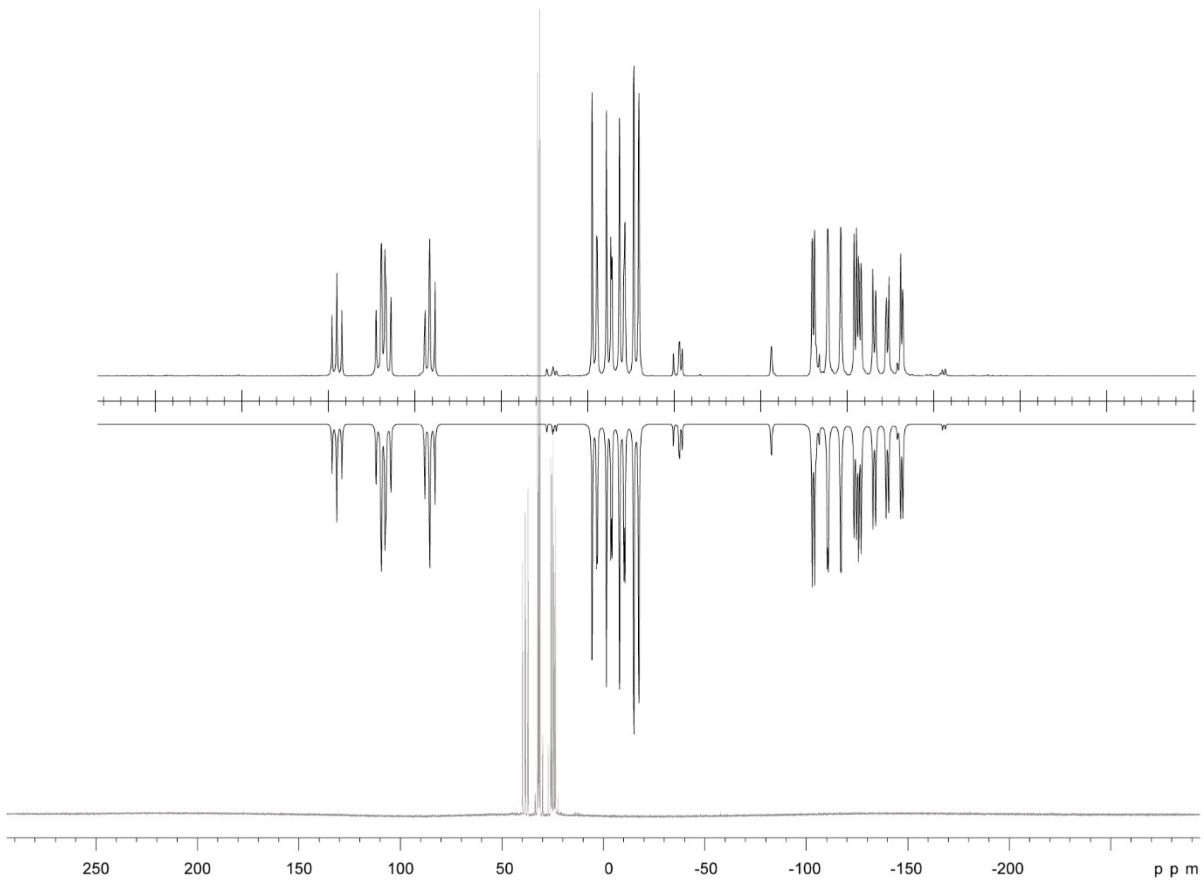
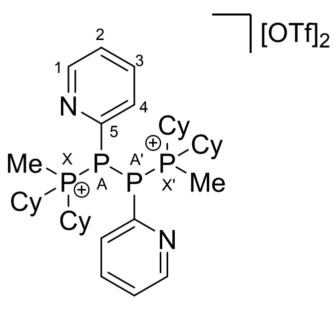


Figure 6: ^{31}P NMR spectrum of pentaphospholane **18** (CD_2Cl_2, 300 K, inset is showing the AA'BB'C spin system of the experimental (upwards) and fitted spectra (downwards)).

2.19. 1,1,4,4-tetracyclohexyl-1,4-dimethyl-2,3-dipyridyltetraphosphane-1,4-diium bis(trifluoromethanesulfonate) (19[OTf]$_2$)



To **11**[OTf]$_2$ (500 mg, 0.60 mmol) in MeCN (3 ml) pentaphospholane **13** (66 mg, 0.12 mmol) is added. After stirring for 24 h the solvent is evaporated *in vacuo*. The residue is washed with PhF (3 x 4 ml) and recrystallized from MeCN/Et_2O to yield the product as colourless crystals after filtration and evaporation of all volatiles *in vacuo*.

Yield: 287 mg (51%); **m.p.:** 181°C dec.; **Raman (100 mW, 298 K, in cm^{-1}):** ν = 3063 (43), 2982 (24), 2946 (89), 2915 (75), 2895 (57), 2856 (75), 1620 (21), 1573 (53), 1562 (35), 1522 (19), 1451 (52), 1350 (25), 1334 (25), 1308 (58), 1299 (39), 1283 (39), 1255 (21), 1223 (22), 1209 (25), 1185 (19), 1176 (20), 1120 (27), 1093 (20), 1080 (27), 1048 (61), 1032 (100), 991 (66), 851 (25), 821 (42), 770 (25), 753 (39), 724 (20), 706 (39), 625 (25), 572 (29), 530 (25), 518 (26), 500 (48), 479 (31), 436 (27), 426 (43), 410 (35), 356 (38), 347 (44); **IR (ATR, 298 K, in cm^{-1}):** v = 3063 (vw), 2981 (vw), 2936 (w), 2858 (w), 1572 (w), 1558 (vw), 1449 (w), 1426 (vw), 1351 (vw), 1307 (vw), 1299 (w), 1268 (s), 1253 (vs), 1222 (m), 1184 (vw), 1176 (w), 1139 (s), 1079 (vw), 1030 (vs), 1007 (w), 989 (w), 930 (w), 918 (w), 906 (m), 886 (w), 869 (vw), 849 (vw), 820 (vw), 776 (m), 752 (w), 703 (vw), 635 (vs), 571 (w), 516 (s), 492 (w), 466 (w), 441 (vw), 427 (vw), 405 (vw); **^{1}H NMR (CD_2Cl_2, 300 K, in ppm):** δ = 0.94-1.14 (4H, m, CH_2), 1.17-1.24 (4H, m, CH_2), 1.31-1.44 (6H, m, CH_2), 1.54-1.75 (12H, m, CH_2), 1.80-1.88 (6H, m, CH_2), 2.00-2.08 (4H, m, CH_2), 2.09-2.23 (4H, m, CH_2), 2.23-2.32 (2H, m, CH), 2.40-2.44 (6H, m, CH_3), 2.81-2.89 (2H, m, CH), 7.28-7.32 (1H, m, C2–H), 7.82-7.87 (1H, m, C3–H), 7.97-7.99 (1H, m, C1–H), 8.20-8.24 (1H, m, C4–H); **^{13}C{^{1}H} NMR (CD_2Cl_2, 300 K, in ppm):** δ = 4.5 (2C, m, CH_3), 25.6 (m, CH_2), 25.9 (m, CH_2), 26.8 (m, CH_2), 27.1 (m, CH_2), 27.9 (m, CH_2), 28.1 (m, CH_2), 28.5 (m, CH_2), 28.7 (m, CH_2), 35.2 (2C, m, CH), 35.7 (2C, m, CH), 121.6 (1C, q, $^{1}J_{CF3}$ = 322.2 Hz, CF_3), 126.3 (1C, s, C2), 135.9 (1C, m, C4), 138.6 (1C, m, C3), 150.3 (1C, m, C5), 151.3 (1C, bs, C1); **^{19}F NMR (CD_2Cl_2, 300 K, in ppm):** δ = –79.2 (3F, s); **^{31}P NMR (CD_2Cl_2, 300 K, in ppm):** AA'XX' spin system: δ(P_A) = -55.1 (2P), δ(P_X) = 40.7 (2P); $^{1}J(P_AP_{A'})$ = -298.7 Hz, $^{1}J(P_AP_X)$ = -287.0 Hz, $^{2}J(P_AP_{X'})$ = 58.6 Hz, $^{3}J(P_XP_{X'})$ = 38.9 Hz; **elemental analysis**: calcd. for $C_{38}H_{58}F_6N_2O_6P_4S_2$: C: 48.51, H: 6.21, N: 2.98, S: 6.81; found: C: 48.50, H: 5.83, N: 3.13, S: 6.99.

3. Additional information

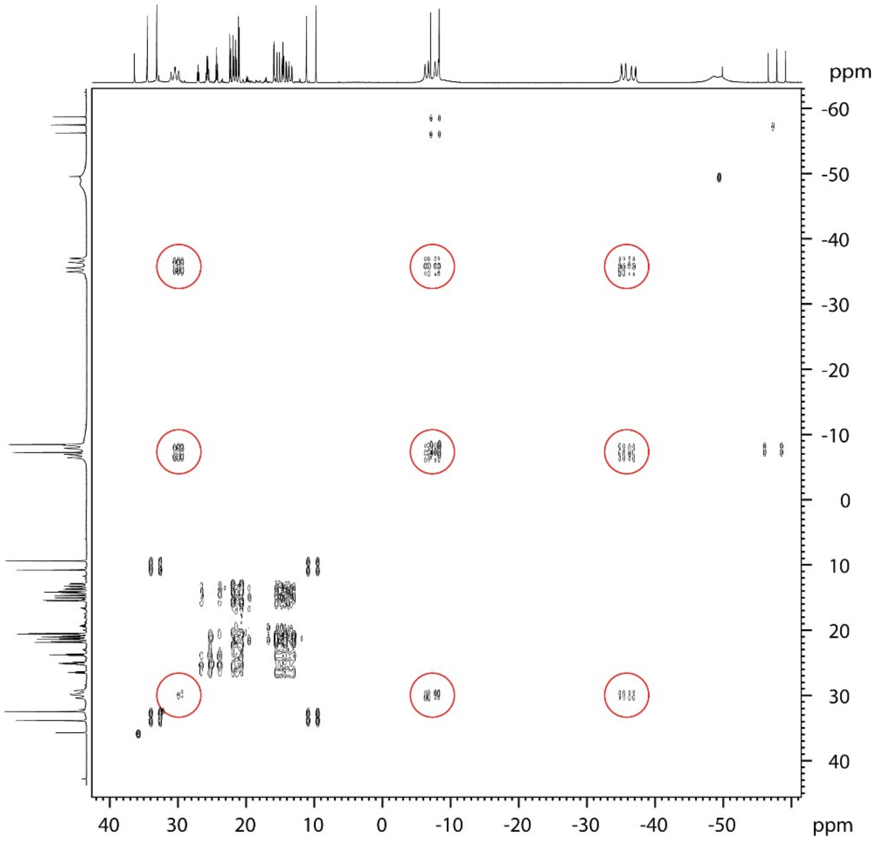


Figure 7: ^{31}P-^{31}P COSY NMR spectrum of the reaction of **Type II** phosphane **7** with Cy_2PH in a 1 : 1 ration in CD_2Cl_2 (cross peaks of **16** are circled in red).

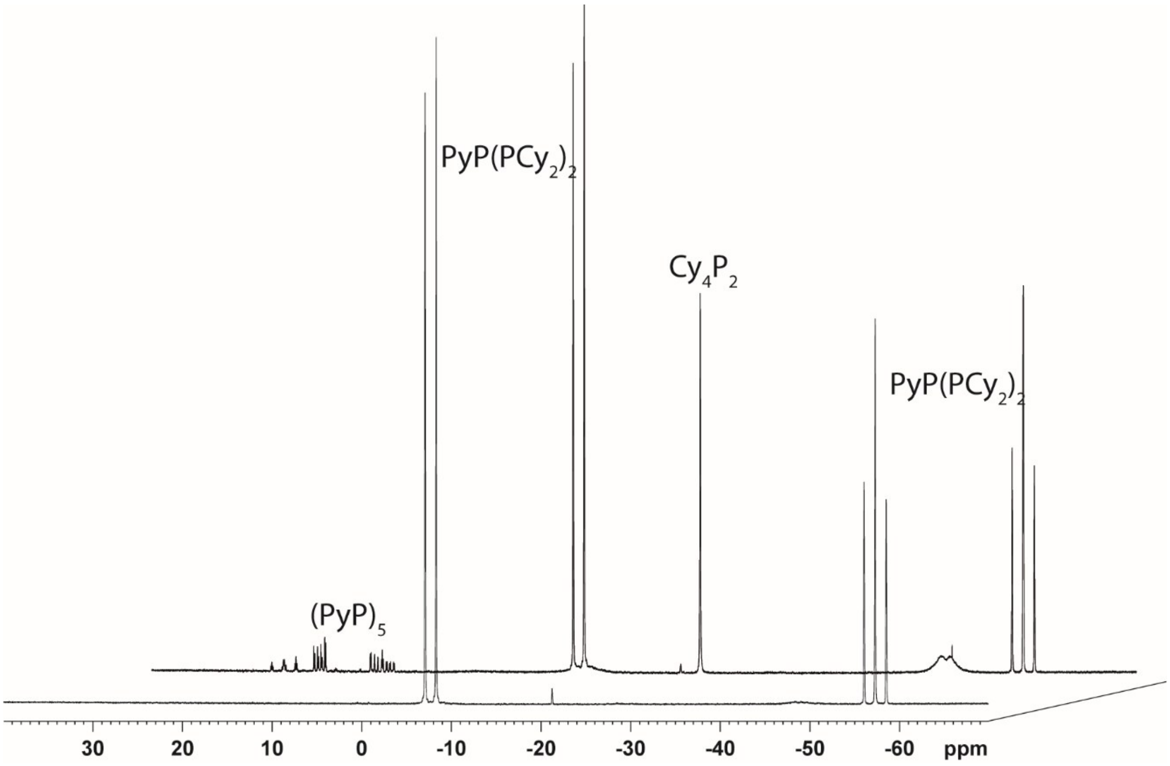


Figure 8: ^{31}P NMR spectra of $PyP(PCy_2)_2$ in CD_2Cl_2 after 30 min (front) and 24 h (back).

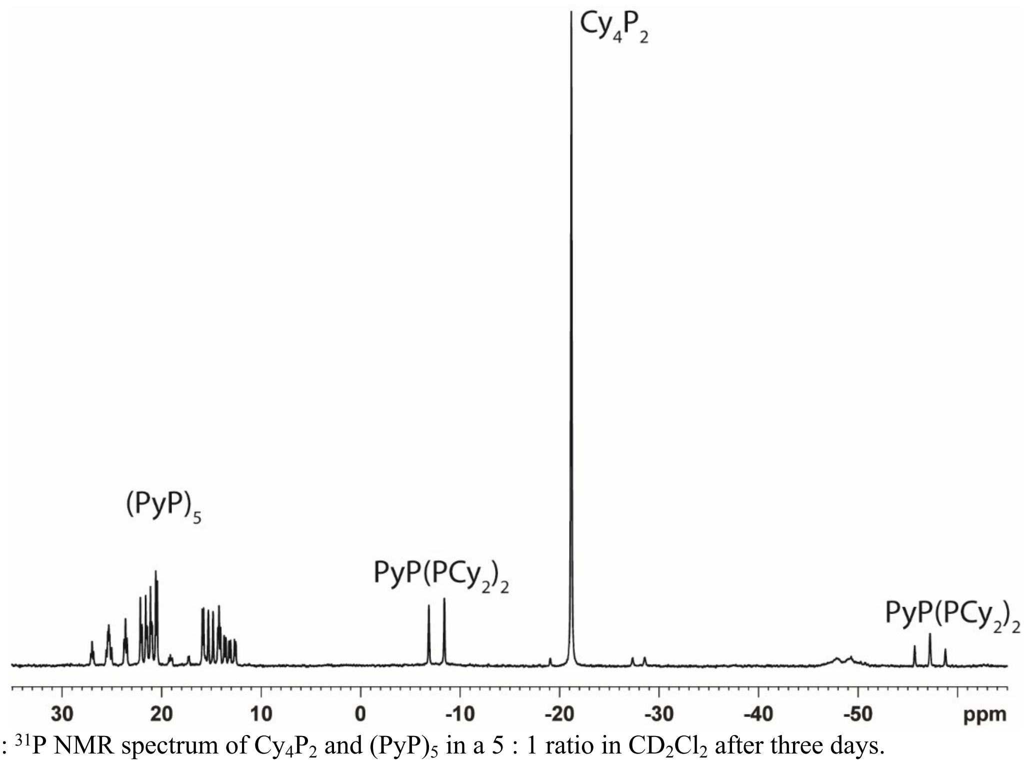


Figure 9: ^{31}P NMR spectrum of Cy_4P_2 and $(PyP)_5$ in a 5 : 1 ratio in CD_2Cl_2 after three days.

4. Details on the theoretical calculations

We have computed the two possible isomers (*syn* and *anti*) for the three metal complexes. The optimized geometries and relative energies are given in Figure 10. The geometries are similar to the experimental X-ray structures thus giving reliability to the level of theory (BP86-D3/def2-TZVP). Figure 10 shows that the largest difference between both isomers corresponds to the Cu atom (5 kcal/mol more stable the *anti*-isomer). As we go down in the group the behavior changes. For Ag the difference is reduced and both isomers are isoenergetic (only 0.1 kcal/mol more stable the *anti*-isomer) and for Au the *syn*-isomer is 1.7 kcal/mol more stable. This result is in good agreement with the solid state X-ray structures since the *syn*-isomer is observed for the Au complex. This behavior could be related to the type of coordination of the pyridine to the metal centers. In Figure 11 we have represented on-top views of the M_2P_6 core and the coordination mode with the Py rings. It can be observed that the N-atoms of the pyridine rings are pointing to the metal centers in the Ag and Cu complexes. In contrast, for the Au complex the N-atoms of Py are pointing to the middle of the Au–Au bond. This different binding mode likely explains the different behavior of the Au complex.

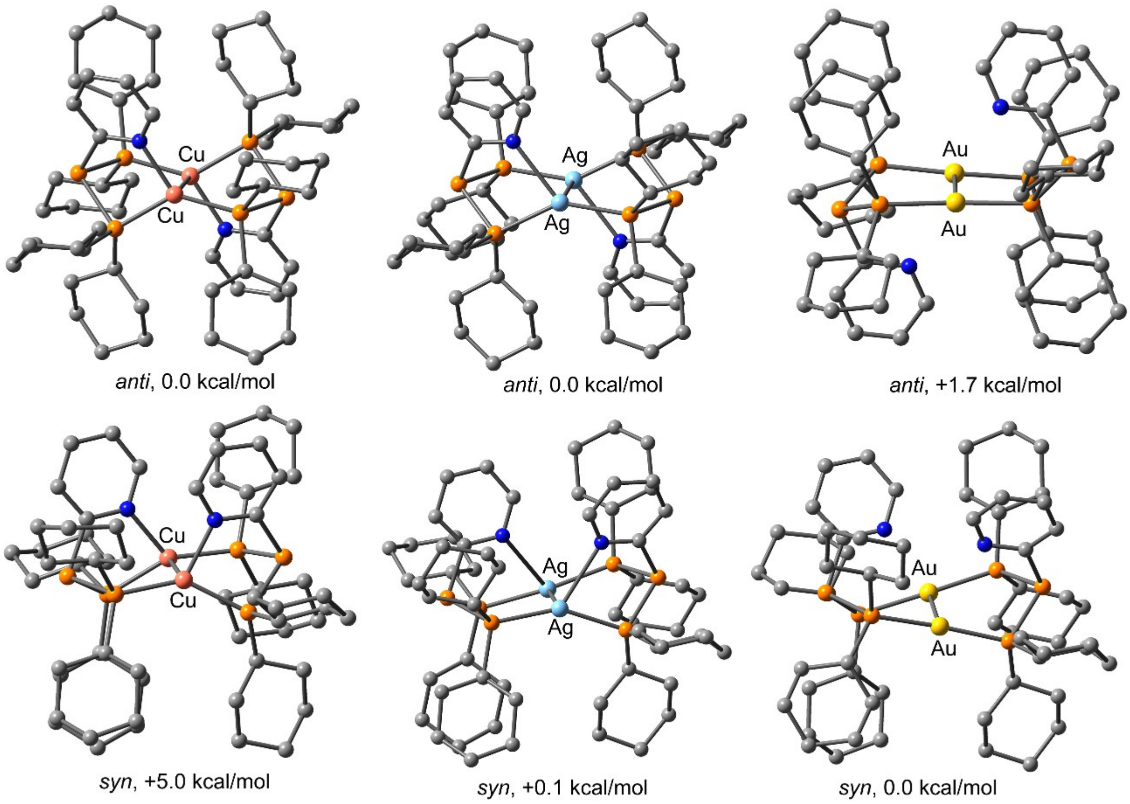


Figure 10. Optimized structures of the two isomers of Cu, Ag and Au complexes and the relative energy of the isomers at the BP86-D3/def2-TZVP.

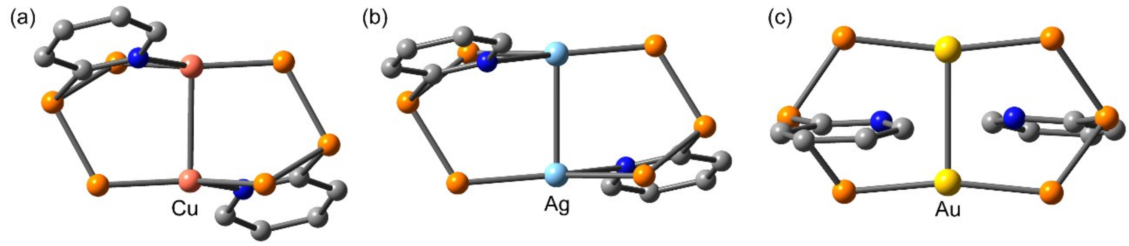


Figure 11. On-top views of the *anti*-isomers of Cu (a), Ag (b) and Au (c) complexes.

Figure 12 shows the structure of the transition states that connects *iso*-$\mathbf{22}^{2+}$ to $\mathbf{20}^{+}$ and $\mathbf{21}^{+}$, see scheme 10 of the main text for further details.

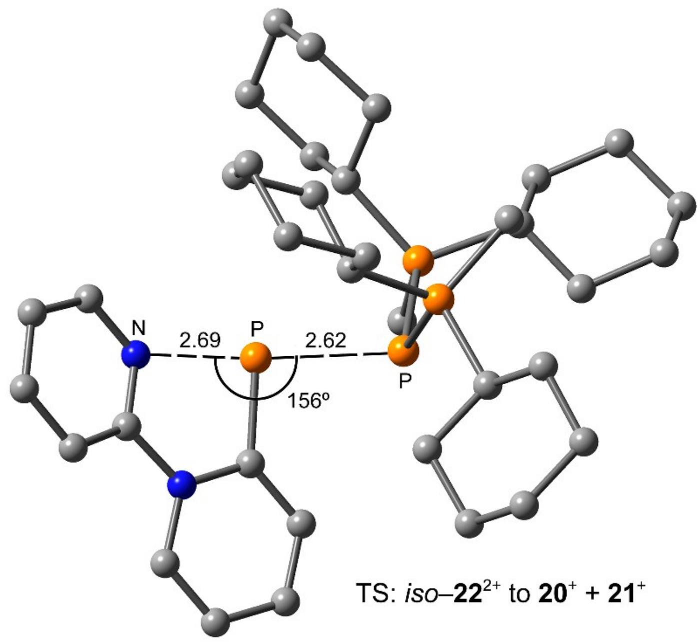
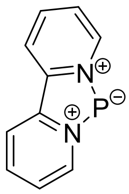


Figure 12. Optimized structure of the TS with indication of some geometrical features.

4.1. NMR chemical shifts

To further understand possible side reactions in the decomposition reaction of **19**[OTf]$_2$ we calculated possible chemical shifts for compounds we assumed in the ^{31}P NMR spectra (figure 12 in the article). Regarding these theoretical ^{31}P NMR spectra, the theoretical values can differ from the experimental ones to a large extend due to different factors. In any case, for compound $\mathbf{21}^{+}$ the theoretical ^{31}P NMR is: 159 ppm and for compound $\mathbf{23}^{+}$ the ^{31}P NMR is: 255 ppm. Whilst the one for $\mathbf{21}^{+}$ is in quite good agreement with the signal marked in Figure 12 in the article, for compound $\mathbf{23}^{+}$ it seems that the theoretical value is largely overestimated.



23^{+}

Figure13: Compound **23**$^{+}$.

4.2. Computational methods

The geometry optimization has been performed at the BP86-D3/def2-TZVP level of theory without symmetry constrains by means of the Turbomole version 7.2 program.[5] The minimum nature or transition state condition of the compounds has been checked by using frequency analysis. In addition, IRC calculations by using the DRC module of Turbomole 7.2 were carried out to validate the transition state geometries. Solvent effects have been taken into consideration by using Conductor-like Screening Model (COSMO).[6]

We used the DFT/GIAO (Gauge Including Atomic Orbitals) approach as implemented in the Gaussian 09 program to estimate the ^{31}P-NMR chemical shifts.[7] The level of theory used was BP86/def2-TZVP and the molecular systems were completely optimized in acetonitrile. The primary result of a quantum chemical calculation of NMR shifts is the absolute magnetic shielding (σ) (i.e., with respect to a naked nucleus). The chemical shift of a substance S with respect to a reference compound is then given as: $\delta(S) = \sigma(ref)–\sigma(S)$. We have used phosphoric acid as reference to estimate the chemical shift. At our level of theory, the absolute shielding of phosphoric acid in acetonitrile is 260 ppm.

4.3. Cartesian Coordinates

Complex *anti*-**[9a*Ag]**$_2^{2+}$

Ag	5.0152332	6.8761024	9.4646703
P	5.4721521	8.5298342	7.8303260
P	4.1558625	10.3667170	7.8577562
P	3.6615408	10.3423923	10.0370978
N	2.0109961	8.5276687	8.0534539
C	7.2480830	9.1150325	7.6971040
H	7.6394345	8.5021863	6.8641504

C	8.0527821	8.7510693	8.9593112
H	7.6444590	9.3102687	9.8196412
H	7.9352878	7.6795023	9.1905093
C	9.5370678	9.1055266	8.7918178
H	10.0815793	8.8670944	9.7178570
H	9.9710782	8.4700708	8.0012472
C	9.7213371	10.5810380	8.4194857
H	9.3837905	11.2153749	9.2579481
H	10.7870166	10.8045043	8.2693223
C	8.9200345	10.9381638	7.1630744
H	9.3238620	10.3837982	6.2986197
H	9.0264806	12.0066518	6.9258434
C	7.4321203	10.5969038	7.3292968
H	6.8752029	10.8445640	6.4141913
H	7.0086611	11.2224619	8.1344744
C	5.0583815	7.7947115	6.1636227
H	3.9707799	7.6143338	6.2287444
C	5.7364119	6.4216810	5.9902169
H	6.8321330	6.5454753	5.9521452
H	5.5167025	5.7767921	6.8566540
C	5.2521035	5.7538041	4.6945992
H	5.7585666	4.7858261	4.5656875
H	4.1733688	5.5372025	4.7907051
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H	5.0972972	6.1718031	2.5662734
H	6.5743037	6.7745014	3.3195630
C	4.8478203	8.0324304	3.6631148
H	3.7495401	7.9264098	3.7089347
H	5.0668320	8.6809132	2.8026051
C	5.3345201	8.7043228	4.9559346
H	6.4177994	8.8981785	4.8813316
H	4.8501202	9.6846817	5.0828671
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C	2.0750670	9.8743893	6.0630013

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H	0.5238543	9.5108849	4.5994872
C	0.3453430	8.2313486	6.3380711
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C	0.9108769	7.9234976	7.5760106
H	0.4704277	7.1613308	8.2208782
C	2.5082659	11.7920274	10.2887076
H	2.7824551	12.1548889	11.2975059
C	1.0444680	11.3061647	10.3347108
H	0.7757483	10.8794538	9.3523868
H	0.9357114	10.4934324	11.0724763
C	0.0908951	12.4601895	10.6730615
H	-0.9467119	12.0948461	10.6720659
H	0.2999699	12.8086305	11.6993974
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H	-0.4087151	14.4590349	9.9821389
H	-0.0624680	13.3097781	8.6875180
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H	1.8258964	14.9150181	8.9057537
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H	2.4203323	12.5865949	8.2755675
H	3.7004970	13.3102169	9.2521739
C	5.2451923	10.7166135	10.9294192
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C	5.0661263	10.3827788	12.4266487
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H	6.1956677	10.4172675	14.2759152
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C	6.9248148	12.0253674	12.9930292

H	7.8732669	12.1460529	13.5354957
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C	7.1214670	12.3132262	11.5007262
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C	5.8086745	12.1315939	10.7262617
H	5.9593807	12.3384351	9.6557600
H	5.0768406	12.8716634	11.0892747
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P	2.1932436	6.5265564	12.0964945
P	3.5092401	4.6895553	12.0688106
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C	0.4172295	5.9418236	12.2300308
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H	0.0199094	5.7451598	10.1077769
H	-0.2695003	7.3766724	10.7356890
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H	-2.4169996	6.1904483	10.2105003
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C	-2.0572521	4.4769785	11.5096106
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H	-3.1230130	4.2544656	11.6606445
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H	0.6553908	3.8341237	11.7933717
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C	1.9295854	8.6346143	13.9367798
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H	2.1488086	9.2793608	13.0701195
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H	1.9091042	10.2707917	15.3609679
H	3.4937159	9.5183170	15.1354818
C	2.1782133	8.4042763	16.4525662
H	2.5702643	8.8846519	17.3603379
H	1.0924850	8.2830222	16.6077733
C	2.8178171	7.0236186	16.2638371
H	3.9161990	7.1286936	16.2185014
H	2.5979414	6.3753352	17.1242808
C	2.3311446	6.3519255	14.9708995
H	1.2478581	6.1581539	15.0454440
H	2.8154839	5.3715338	14.8439503
C	5.0703476	5.5628210	12.6195637
C	5.5908140	5.1807720	13.8629280
H	5.1058821	4.3880155	14.4330070
C	6.7270635	5.8247190	14.3580606
H	7.1427127	5.5433471	15.3259525
C	7.3202972	6.8241177	13.5881809
H	8.2088422	7.3534333	13.9306958
C	6.7541737	7.1327758	12.3507077
H	7.1943630	7.8953203	11.7061147
C	5.1564457	3.2642674	9.6374584
H	4.8820659	2.9016627	8.6286191
C	6.6203180	3.7498631	9.5912924
H	6.8891811	4.1765929	10.5735768
H	6.7290961	4.5625697	8.8534994
C	7.5738042	2.5957770	9.2529156
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H	7.3650923	2.2477879	8.2263496
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H	5.8379914	0.1405413	11.0189577
C	5.0023866	2.1025381	10.6367089
H	5.2446224	2.4690216	11.6503467
H	3.9639646	1.7461485	10.6738041
C	2.4195220	4.3402755	8.9974074
H	1.7049670	5.0736562	9.4140656
C	2.5983425	4.6735169	7.5000396
H	3.3939748	4.0389415	7.0715055
H	2.9345060	5.7174189	7.3909615
C	1.2955239	4.4428900	6.7202857
H	1.4678152	4.6394657	5.6513159
H	0.5430873	5.1767087	7.0559419
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H	-0.2192326	3.4306593	8.8385524
H	0.1599649	1.7248298	8.5797812
C	1.8554806	2.9255881	9.2011289
H	1.7050439	2.7190426	10.2717237
H	2.5869185	2.1851478	8.8380557

Complex *syn*-**[9a*Ag]**$_2^{2+}$

Ag	1.0476628	6.9646987	10.4462307
P	-0.4874512	7.9585899	8.9098954
P	-0.3793304	7.2892851	6.7572110
P	0.6438899	5.3429240	7.1475946
N	2.3472876	8.0072077	6.9326606
C	-2.2801257	7.8276492	9.4443641
H	-2.4533234	8.8080617	9.9263824
C	-2.4792749	6.7409217	10.5176500
H	-2.2567614	5.7518141	10.0817135
H	-1.7666970	6.8853175	11.3459749

C	-3.9217796	6.7437928	11.0435273
H	-4.0457172	5.9385148	11.7826883
H	-4.1082033	7.6911429	11.5780382
C	-4.9355062	6.5932665	9.9035926
H	-4.8172404	5.5993802	9.4373525
H	-5.9605317	6.6324441	10.2986748
C	-4.7327320	7.6769427	8.8397860
H	-4.9513154	8.6670110	9.2758774
H	-5.4371015	7.5406166	8.0063601
C	-3.2954843	7.6707202	8.2994753
H	-3.1630744	8.4613313	7.5471267
H	-3.1099624	6.7128788	7.7837201
C	-0.1260822	9.7850494	8.7883723
H	0.8604324	9.8193790	8.2947741
C	0.0358985	10.3982194	10.1942724
H	-0.9185582	10.3324899	10.7432099
H	0.7771578	9.8270896	10.7782102
C	0.4625616	11.8709701	10.0906373
H	0.5391255	12.3046241	11.0985758
H	1.4740239	11.9183038	9.6493172
C	-0.5072803	12.6835345	9.2245105
H	-0.1563433	13.7214874	9.1341066
H	-1.4899631	12.7279661	9.7236183
C	-0.6750952	12.0554958	7.8358813
H	0.2839504	12.1005769	7.2901901
H	-1.4034915	12.6241336	7.2400964
C	-1.1214297	10.5890923	7.9364732
H	-2.1217993	10.5452151	8.3978167
H	-1.2180742	10.1495975	6.9318789
C	1.1720765	8.2301708	6.3046259
C	1.0401483	9.1954084	5.2972577
H	0.0775295	9.3411624	4.8062381
C	2.1519790	9.9596412	4.9354777

H	2.0717963	10.7150294	4.1533349
C	3.3620660	9.7327271	5.5899955
H	4.2569363	10.3021799	5.3404914
C	3.4107775	8.7449563	6.5765063
H	4.3366065	8.5341603	7.1143689
C	0.9030675	4.5811921	5.4616200
H	0.7572397	3.5004156	5.6496033
C	2.3595180	4.7982006	5.0006200
H	2.5417460	5.8805640	4.8812674
H	3.0595823	4.4436310	5.7757139
C	2.6304533	4.0798004	3.6714036
H	3.6637418	4.2762944	3.3493613
H	2.5527923	2.9905587	3.8306863
C	1.6353631	4.5073027	2.5863006
H	1.8240584	3.9502983	1.6574851
H	1.7896876	5.5743861	2.3493112
C	0.1896634	4.2966825	3.0486164
H	-0.0019526	3.2187027	3.1852968
H	-0.5178321	4.6450947	2.2819431
C	-0.0878207	5.0283584	4.3703433
H	0.0265894	6.1148931	4.2069470
H	-1.1267217	4.8673961	4.6895569
C	-0.6008618	4.3143788	8.0575880
H	-0.8688291	4.9477032	8.9239699
C	0.0850569	3.0528480	8.6200939
H	0.4348144	2.4158512	7.7889896
H	0.9776728	3.3395953	9.1984057
C	-0.8911783	2.2584542	9.4977806
H	-0.3961374	1.3501730	9.8724600
H	-1.1462091	2.8688640	10.3813764
C	-2.1762191	1.9053727	8.7408242
H	-2.8708927	1.3666144	9.4010752
H	-1.9354136	1.2176887	7.9123448
C	-2.8462262	3.1634814	8.1765171

H	-3.1821601	3.8060383	9.0096568
H	-3.7464788	2.8996594	7.6029772
C	-1.8808946	3.9594987	7.2859867
H	-2.3705366	4.8685831	6.9047173
H	-1.6175705	3.3500348	6.4057500
Ag	2.6778112	5.8083755	8.3652433
P	4.4589291	5.1276911	9.7933309
P	4.5446185	6.1405230	11.7950639
P	2.3568460	6.2285643	12.3055628
N	3.6253247	8.3133724	10.2795481
C	6.1661305	5.3869348	9.0702364
H	6.3178373	4.4560922	8.4914372
C	6.1536274	6.5687726	8.0804064
H	5.9261974	7.4970304	8.6345348
H	5.3474409	6.4278140	7.3414099
C	7.5045674	6.7130779	7.3666388
H	7.4769110	7.5839023	6.6941892
H	7.6682528	5.8288841	6.7273456
C	8.6596002	6.8371559	8.3665835
H	8.5529189	7.7789826	8.9330414
H	9.6190592	6.8993206	7.8336384
C	8.6679597	5.6577793	9.3445492
H	8.8730994	4.7229975	8.7950633
H	9.4763332	5.7708102	10.0814382
C	7.3236177	5.5289678	10.0764057
H	7.3475052	4.6846170	10.7778164
H	7.1629289	6.4367317	10.6821049
C	4.2960303	3.3173443	10.1904520
H	3.3806468	3.2845618	10.8092041
C	4.0012656	2.5070235	8.9124867
H	4.8879039	2.5154881	8.2552480
H	3.1781215	2.9697476	8.3442915
C	3.6473189	1.0581473	9.2794637

H	3.4477837	0.4814672	8.3641121
H	2.7089603	1.0609156	9.8626314
C	4.7620288	0.3987464	10.1002636
H	4.4698387	-0.6208945	10.3894266
H	5.6626673	0.2982358	9.4706256
C	5.1050129	1.2247927	11.3447511
H	4.2450261	1.2211892	12.0372486
H	5.9457298	0.7716879	11.8894868
C	5.4474808	2.6787248	10.9837155
H	6.3609055	2.6926601	10.3669429
H	5.6710465	3.2569216	11.8935841
C	4.5903742	7.8823621	11.1174556
C	5.6484840	8.7057791	11.5244926
H	6.4033911	8.3268044	12.2144823
C	5.7150967	10.0133044	11.0363728
H	6.5294706	10.6735415	11.3359928
C	4.7176702	10.4571671	10.1681284
H	4.7249904	11.4711083	9.7687508
C	3.6920034	9.5721006	9.8256663
H	2.8869847	9.8792291	9.1555129
C	1.8601355	4.6590671	13.1811552
H	1.2660059	5.0419845	14.0320013
C	0.9188122	3.8125778	12.3027762
H	1.4602155	3.4731062	11.4025837
H	0.0807449	4.4309034	11.9407833
C	0.3995170	2.5928227	13.0753520
H	-0.2472398	1.9882648	12.4236859
H	-0.2327036	2.9393406	13.9108916
C	1.5536266	1.7474427	13.6244977
H	1.1633783	0.8917223	14.1935514
H	2.1256170	1.3263980	12.7786416
C	2.4869193	2.5881526	14.5027197
H	1.9419325	2.9214112	15.4021039
H	3.3351522	1.9841649	14.8571546

C	3.0175145	3.8168248	13.7489826
H	3.6577504	3.4748912	12.9204959
H	3.6566311	4.4248962	14.4042496
C	2.3585304	7.5771907	13.5990905
H	2.8214011	8.4357137	13.0793306
C	0.9065783	7.9691640	13.9432588
H	0.3885537	7.1112857	14.4056429
H	0.3494273	8.2167797	13.0238918
C	0.8843869	9.1575470	14.9168726
H	-0.1568121	9.4007644	15.1752955
H	1.2995339	10.0444956	14.4073983
C	1.7009524	8.8650692	16.1802332
H	1.6985199	9.7409117	16.8445604
H	1.2216280	8.0451000	16.7424657
C	3.1389754	8.4666999	15.8308098
H	3.6548116	9.3218988	15.3607230
H	3.7048358	8.2205373	16.7410678
C	3.1705087	7.2697229	14.8674954
H	4.2098210	7.0110337	14.6123072
H	2.7386094	6.3901359	15.3738931

Intermediate **[9a*Ag]**$_2^{2+}$

P	3.8653462	-0.2666298	4.9743548
P	3.7542444	0.1934478	7.1626945
P	2.3665264	-1.4597320	7.7496299
N	5.5331801	-1.9706803	7.2697274
C	2.1857093	0.1273740	4.2883399
H	1.5595436	-0.6683717	4.7353338
C	2.1656715	-0.1003811	2.7624815
H	2.7977050	0.6561069	2.2685588
H	2.5911291	-1.0869182	2.5140488
C	0.7287770	0.0142116	2.2304115
H	0.7291881	-0.1198725	1.1389156
H	0.1252209	-0.8101057	2.6487234

C	0.0932329	1.3576549	2.6075809
H	-0.9465586	1.3972148	2.2531929
H	0.6298689	2.1727240	2.0927978
C	0.1475779	1.5967817	4.1209910
H	-0.4799577	0.8461418	4.6347663
H	-0.2719303	2.5811077	4.3745236
C	1.5846617	1.4943749	4.6521163
H	2.1969743	2.2915330	4.2008415
H	1.6067275	1.6624340	5.7407394
C	5.1107822	0.9588168	4.3154993
H	4.7818202	1.1089803	3.2706390
C	5.1409536	2.3265343	5.0241790
H	4.1441510	2.7884421	5.0355457
H	5.4274664	2.1777865	6.0801932
C	6.1624240	3.2620986	4.3605182
H	5.8388311	3.4793672	3.3282377
H	6.1764091	4.2239746	4.8930110
C	7.5607661	2.6350032	4.3391602
H	8.2726947	3.3054454	3.8373104
H	7.9209820	2.5136494	5.3758625
C	7.5409011	1.2679187	3.6455010
H	8.5382907	0.8041605	3.6715203
H	7.2841690	1.4019252	2.5808029
C	6.5176198	0.3219338	4.2890440
H	6.8291746	0.0865093	5.3218300
H	6.4912051	-0.6347736	3.7416169
C	6.6559646	-2.5808548	7.6708456
H	6.7737200	-3.6198613	7.3539659
C	7.6348607	-1.9536004	8.4445767
H	8.5332829	-2.4951356	8.7394837
C	7.4296431	-0.6273924	8.8242369
H	8.1681339	-0.0985594	9.4272980
C	6.2549110	0.0143965	8.4221154
H	6.0553943	1.0477631	8.7087508

C	5.3293166	-0.6910974	7.6427411
C	0.6688347	-0.7341820	7.5488682
H	0.7055614	-0.3316625	6.5211379
C	-0.4183183	-1.8287790	7.5553648
H	-0.4920477	-2.2725398	8.5612561
H	-0.1449107	-2.6445116	6.8663121
C	-1.7736921	-1.2239745	7.1573167
H	-1.7177790	-0.8852056	6.1077271
H	-2.5501077	-2.0022239	7.1941326
C	-2.1515450	-0.0404165	8.0556774
H	-2.3190707	-0.4034721	9.0842833
H	-3.1025083	0.3987857	7.7223763
C	-1.0503670	1.0265950	8.0710017
H	-1.3158856	1.8464525	8.7539086
H	-0.9528709	1.4733716	7.0659289
C	0.3020311	0.4273642	8.4866486
H	1.0866320	1.1997287	8.4826093
H	0.2282260	0.0492853	9.5184434
C	2.8369993	-1.7369380	9.5351046
H	3.8279037	-2.2147589	9.4171381
C	1.9097660	-2.7754207	10.1964281
H	0.9128448	-2.3309312	10.3490215
H	1.7732149	-3.6499120	9.5390770
C	2.4901184	-3.2064875	11.5517313
H	1.8126978	-3.9276408	12.0323694
H	3.4443018	-3.7350062	11.3779763
C	2.7312383	-1.9999050	12.4673451
H	1.7606380	-1.5451559	12.7297022
H	3.1865187	-2.3261271	13.4133240
C	3.6142061	-0.9448416	11.7879872
H	4.6248081	-1.3588040	11.6226254
H	3.7362014	-0.0678398	12.4399308
C	3.0257063	-0.5063074	10.4377939

H	3.6830572	0.2367884	9.9602725
H	2.0592172	-0.0086130	10.6024310
P	3.4847353	-5.8432751	6.4006260
P	3.9941416	-6.3007740	4.2955365
P	5.3543757	-4.6268705	3.7687757
N	4.4540044	-8.7562266	3.4228804
C	4.8207851	-6.2000992	7.6718938
H	5.7555959	-5.8962724	7.1640517
C	4.6340023	-5.2814413	8.8991910
H	3.6788386	-5.5268077	9.3955763
H	4.5606005	-4.2286162	8.5813932
C	5.7893850	-5.4467541	9.8956239
H	5.6169644	-4.8011575	10.7703246
H	6.7208481	-5.0876418	9.4228614
C	5.9657918	-6.9074143	10.3238332
H	6.8316166	-7.0069285	10.9936696
H	5.0825467	-7.2249902	10.9038181
C	6.1231967	-7.8228157	9.1048346
H	7.0657009	-7.5826579	8.5803669
H	6.1993126	-8.8737061	9.4189725
C	4.9494034	-7.6636177	8.1267775
H	4.0174942	-7.9657251	8.6322802
H	5.0765985	-8.3370996	7.2703687
C	2.0425097	-6.9807044	6.7396044
H	2.0300247	-7.0361577	7.8444853
C	2.1790246	-8.4041023	6.1654663
H	3.1139708	-8.8784605	6.4920318
H	2.2236095	-8.3432882	5.0643764
C	0.9741488	-9.2685816	6.5663261
H	0.9651235	-9.3951577	7.6628062
H	1.0890976	-10.2739685	6.1358263
C	-0.3428220	-8.6329695	6.1099922
H	-1.1959253	-9.2467874	6.4327317
H	-0.3717517	-8.6085936	5.0072778

C	-0.4825290	-7.2066109	6.6532264
H	-1.4058930	-6.7390028	6.2808818
H	-0.5672966	-7.2399295	7.7533505
C	0.7227995	-6.3337767	6.2731550
H	0.7551196	-6.1997044	5.1781309
H	0.6150417	-5.3279597	6.7144593
C	5.0479195	-9.9514719	3.2938242
H	4.5815741	-10.6449901	2.5904683
C	6.1961530	-10.3143939	4.0055460
H	6.6399068	-11.3001966	3.8678924
C	6.7544318	-9.3866713	4.8849440
H	7.6531922	-9.6275591	5.4537411
C	6.1453373	-8.1386221	5.0242033
H	6.5688264	-7.3936402	5.6956912
C	4.9927361	-7.8687382	4.2750179
C	7.1190012	-4.8547309	4.3544151
H	6.9779448	-5.2638463	5.3731605
C	7.8417102	-3.4984380	4.5083441
H	8.0054102	-3.0560752	3.5125472
H	7.2179013	-2.7830887	5.0669227
C	9.1897524	-3.6918792	5.2176748
H	9.0031678	-4.0480354	6.2474091
H	9.7017335	-2.7225263	5.3096808
C	10.0761703	-4.7065875	4.4851404
H	10.3644269	-4.2927002	3.5042683
H	11.0105722	-4.8678930	5.0417995
C	9.3429091	-6.0362088	4.2724831
H	9.9674628	-6.7320014	3.6938467
H	9.1589883	-6.5186801	5.2497345
C	8.0005970	-5.8297208	3.5550966
H	7.4969481	-6.7918535	3.4014862
H	8.1869127	-5.4049066	2.5560297
C	5.2363684	-4.6407409	1.9070254

H	4.1785409	-4.3513481	1.7603478
C	6.1133835	-3.5301801	1.2942559
H	7.1771478	-3.7693355	1.4551034
H	5.9234177	-2.5664757	1.7968661
C	5.8495300	-3.4098040	-0.2146372
H	6.5063537	-2.6374477	-0.6416875
H	4.8125086	-3.0668858	-0.3720746
C	6.0580652	-4.7518585	-0.9259229
H	7.1206311	-5.0418889	-0.8528435
H	5.8359233	-4.6504008	-1.9977589
C	5.1876916	-5.8501933	-0.3045243
H	4.1222774	-5.6118091	-0.4650351
H	5.3696365	-6.8151992	-0.7993091
C	5.4495842	-5.9932568	1.2035708
H	4.7825608	-6.7610732	1.6257621
H	6.4806381	-6.3417127	1.3613169
Ag	2.8297320	-3.5490505	6.6843231
Ag	4.5340279	-2.5288410	4.5722221

Complex *anti*-**[9a*Au]**$_2^{2+}$

Au	7.3266393	12.7224622	5.9247610
P	5.8875698	10.9632047	5.3970732
P	6.1207999	9.1281049	6.6574148
P	6.3280543	10.0742599	8.6838566
N	8.7942187	9.9446478	6.6180464
C	4.1067619	11.4567092	5.5853267
H	3.9783202	11.5111782	6.6811880
C	3.0757753	10.4648890	5.0207689
H	3.2021644	10.3957512	3.9280749
H	3.2392814	9.4540378	5.4257763
C	1.6468866	10.9375656	5.3283608
H	1.4882176	10.9167846	6.4202348
H	0.9252756	10.2305222	4.8946909
C	1.3984533	12.3547209	4.8007023
H	1.4460845	12.3475784	3.6984152

H	0.3853263	12.6878071	5.0669402
C	2.4416525	13.3381569	5.3432310
H	2.2795994	14.3453251	4.9313018
H	2.3249001	13.4218495	6.4391476
C	3.8736025	12.8777751	5.0327341
H	4.6049521	13.5795244	5.4632616
H	4.0341076	12.8827968	3.9409371
C	6.1521978	10.3731172	3.6423907
H	5.4935087	11.0545216	3.0701911
C	5.7225854	8.9202478	3.3583284
H	6.3613480	8.2384034	3.9444856
H	4.6893896	8.7348820	3.6776509
C	5.8879734	8.5882870	1.8672130
H	5.5869665	7.5455355	1.6903084
H	5.1994061	9.2175383	1.2772864
C	7.3278661	8.8232612	1.3998546
H	7.9988552	8.1189126	1.9219810
H	7.4219181	8.6082383	0.3258783
C	7.7727906	10.2598497	1.6955450
H	7.1726550	10.9605497	1.0896807
H	8.8218871	10.4106851	1.4006890
C	7.6049117	10.6116201	3.1801377
H	8.2860303	9.9912943	3.7874602
H	7.8914242	11.6595231	3.3592531
C	10.0961114	9.7702433	6.3623341
H	10.7452867	10.6184620	6.5898722
C	10.6224521	8.5870442	5.8345817
H	11.6903067	8.5011157	5.6346047
C	9.7518268	7.5268424	5.5837835
H	10.1219684	6.5825073	5.1837125
C	8.3915547	7.6939778	5.8578002
H	7.6812434	6.8857801	5.6805000
C	7.9525608	8.9260535	6.3611652

C	4.6246061	10.2522683	9.4306378
H	4.7752927	9.8772344	10.4596058
C	4.2162111	11.7355891	9.5274168
H	4.9965740	12.3125830	10.0473764
H	4.1583369	12.1595765	8.5095385
C	2.8642241	11.8996067	10.2308921
H	2.9685396	11.5898762	11.2845179
H	2.5833450	12.9636700	10.2454613
C	1.7737505	11.0594310	9.5586893
H	1.6017253	11.4404939	8.5362941
H	0.8210916	11.1679124	10.0960515
C	2.1800769	9.5834093	9.4878828
H	1.4085468	8.9926215	8.9728993
H	2.2572000	9.1741223	10.5094080
C	3.5242379	9.4030866	8.7674567
H	3.8104502	8.3421027	8.7454125
H	3.4052482	9.7145981	7.7172269
C	7.1947337	8.7215928	9.6276261
H	8.1353389	8.5809753	9.0656578
C	6.4340860	7.3851784	9.6756523
H	5.4743960	7.5290144	10.2004672
H	6.1911543	7.0357085	8.6598857
C	7.2583061	6.3235073	10.4205916
H	8.1765289	6.1113877	9.8455830
H	6.6907753	5.3827922	10.4644089
C	7.6332768	6.7951959	11.8299129
H	8.2491532	6.0366125	12.3337716
H	6.7159650	6.9048248	12.4333828
C	8.3753151	8.1358938	11.7862123
H	8.6020331	8.4869084	12.8036675
H	9.3444629	8.0039212	11.2744274
C	7.5631167	9.2092332	11.0445080
H	8.1299834	10.1520392	10.9877125
H	6.6431100	9.4260955	11.6149840

Au	7.5814515	12.0387520	8.7885835
P	8.8194996	13.9179625	9.3907437
P	8.7570717	15.6624920	7.9762441
P	8.7542963	14.5668451	6.0254014
N	6.0757466	14.8672583	7.9347637
C	8.0791445	14.6710439	10.9262620
H	7.0656988	14.9649565	10.6001927
C	8.8179882	15.9147500	11.4502617
H	9.8461414	15.6363446	11.7368374
H	8.9053897	16.6801055	10.6628086
C	8.0937651	16.4937218	12.6761978
H	7.0992033	16.8585058	12.3666408
H	8.6470880	17.3669445	13.0508606
C	7.9338045	15.4413548	13.7791132
H	8.9301976	15.1546789	14.1571696
H	7.3863818	15.8651930	14.6329845
C	7.2130542	14.1941988	13.2541522
H	7.1403050	13.4282204	14.0403308
H	6.1787635	14.4575688	12.9729516
C	7.9272669	13.6023826	12.0285045
H	7.3736658	12.7320640	11.6410449
H	8.9229299	13.2360645	12.3331893
C	10.6082983	13.5449085	9.7845716
H	10.5917834	13.4538789	10.8864269
C	11.6102398	14.6531130	9.4135897
H	11.6030129	14.8012736	8.3212507
H	11.3143689	15.6135947	9.8588071
C	13.0331454	14.2732416	9.8495418
H	13.7316298	15.0660105	9.5443408
H	13.0752153	14.2260147	10.9511070
C	13.4593884	12.9222614	9.2644443
H	13.5151939	13.0023503	8.1639259
H	14.4696108	12.6588768	9.6082640

C	12.4638727	11.8193476	9.6375692
H	12.4816047	11.6629299	10.7296647
H	12.7546097	10.8609838	9.1814597
C	11.0360479	12.1803854	9.2092416
H	10.9799220	12.2208400	8.1073830
H	10.3281379	11.3962994	9.5203577
C	4.7584383	15.1036693	7.9468640
H	4.1143218	14.2264611	7.8535177
C	4.2084536	16.3836791	8.0676354
H	3.1273145	16.5207254	8.0596418
C	5.0743263	17.4678513	8.2067681
H	4.6880034	18.4815536	8.3159439
C	6.4518072	17.2323469	8.2050764
H	7.1604462	18.0538087	8.3157224
C	6.9103334	15.9171300	8.0502112
C	8.2949537	15.8571821	4.7523693
H	8.8587630	15.5163256	3.8625528
C	6.7893851	15.8008718	4.4172513
H	6.4989420	14.7731986	4.1491775
H	6.2073400	16.0668503	5.3162457
C	6.4448684	16.7660284	3.2747473
H	6.9449010	16.4242347	2.3522135
H	5.3632855	16.7279066	3.0767639
C	6.8868294	18.1991511	3.5908053
H	6.3066277	18.5790034	4.4499447
H	6.6637473	18.8629675	2.7434875
C	8.3803012	18.2499511	3.9287243
H	8.6849029	19.2726555	4.1946056
H	8.9713483	17.9683944	3.0400895
C	8.7244710	17.2994620	5.0855648
H	9.7947883	17.3562062	5.3210514
H	8.1841004	17.6333500	5.9875757
C	10.5245224	14.0760194	5.7531466
H	10.7841345	13.5560699	6.6932717

C	11.5091268	15.2382645	5.5441757
H	11.2455139	15.7725487	4.6165161
H	11.4344772	15.9693637	6.3640483
C	12.9475572	14.7139728	5.4259903
H	13.2442898	14.2602071	6.3877183
H	13.6334983	15.5557492	5.2537511
C	13.0762039	13.6738675	4.3082122
H	14.1031150	13.2837853	4.2666144
H	12.8859823	14.1582410	3.3350921
C	12.0789168	12.5266737	4.5040440
H	12.1506187	11.8020495	3.6795914
H	12.3355295	11.9783882	5.4293494
C	10.6358825	13.0397393	4.6163298
H	9.9422178	12.2032470	4.7935820
H	10.3349824	13.5039039	3.6611281

Complex *syn*-**[9a*Au]$_2$**$^{2+}$

Au	8.6803315	10.8324272	7.4241823
P	6.7519941	10.2579485	8.6038906
P	4.8344145	10.1494082	7.4210976
P	5.4331504	11.4669045	5.7134390
N	6.3463643	8.3171009	5.9625021
C	6.9004725	8.5342811	9.2936023
H	6.9454682	7.9058379	8.3894383
C	5.7035354	8.0861023	10.1482461
H	5.6136343	8.7404769	11.0309666
H	4.7625336	8.1830583	9.5837948
C	5.8922771	6.6346100	10.6152917
H	5.8840355	5.9696278	9.7342817
H	5.0403631	6.3363623	11.2430445
C	7.2113292	6.4610131	11.3767704
H	7.1763363	7.0531208	12.3066761
H	7.3412405	5.4121375	11.6796852

C	8.4031079	6.9203860	10.5295720
H	9.3421175	6.8281767	11.0947656
H	8.4989309	6.2602592	9.6493001
C	8.2345422	8.3702205	10.0499881
H	9.0767760	8.6607009	9.4016889
H	8.2575451	9.0445612	10.9224287
C	6.4220240	11.3719490	10.0742895
H	6.8290335	10.7708659	10.9089228
C	4.9375308	11.6511169	10.3684261
H	4.5108698	12.2360589	9.5357919
H	4.3621658	10.7161554	10.4221975
C	4.7844065	12.4510396	11.6706880
H	3.7189953	12.6550425	11.8512992
H	5.1330306	11.8339749	12.5167552
C	5.5854133	13.7569133	11.6236566
H	5.1586623	14.4159959	10.8478413
H	5.4917901	14.2967149	12.5765528
C	7.0615845	13.4895697	11.3086577
H	7.5179453	12.9277506	12.1417275
H	7.6187679	14.4344161	11.2277595
C	7.2296900	12.6830282	10.0126835
H	6.8810302	13.2880263	9.1576825
H	8.2934807	12.4679431	9.8268179
C	6.5114660	7.1876930	5.2633921
H	7.5073982	7.0326165	4.8429801
C	5.4931109	6.2494684	5.0692367
H	5.6768355	5.3521059	4.4786522
C	4.2502528	6.4872460	5.6557930
H	3.4325594	5.7752138	5.5401324
C	4.0695124	7.6571721	6.3992566
H	3.1139763	7.8745117	6.8779441
C	5.1403218	8.5533497	6.5116073
C	4.0127450	11.3731584	4.5057670
H	4.0153799	12.3816626	4.0495668

C	4.3083697	10.3401501	3.3971064
H	5.2832833	10.5532686	2.9300446
H	4.3890660	9.3369667	3.8506959
C	3.2007006	10.3405329	2.3346281
H	3.2069491	11.3117215	1.8109134
H	3.4206777	9.5743233	1.5766354
C	1.8189345	10.1069898	2.9551744
H	1.7782635	9.0904251	3.3839722
H	1.0408892	10.1510758	2.1796796
C	1.5323530	11.1313944	4.0573155
H	0.5579199	10.9349133	4.5279150
H	1.4702256	12.1412614	3.6172638
C	2.6287622	11.1166916	5.1333853
H	2.4042735	11.8488805	5.9191816
H	2.6354359	10.1251339	5.6180125
C	5.5020506	13.1614387	6.4584095
H	6.1966252	13.0235763	7.3091258
C	4.1606674	13.6948506	6.9881037
H	3.4638498	13.8215476	6.1430905
H	3.6955446	12.9736359	7.6774307
C	4.3557423	15.0504655	7.6801054
H	4.9964967	14.9123770	8.5689283
H	3.3878974	15.4220078	8.0457880
C	5.0047557	16.0640080	6.7327409
H	5.1684986	17.0208394	7.2490332
H	4.3164036	16.2736101	5.8965377
C	6.3304053	15.5297383	6.1807148
H	6.7725317	16.2465204	5.4737756
H	7.0513214	15.4204240	7.0097723
C	6.1638405	14.1654017	5.4940905
H	7.1413298	13.7805577	5.1602962
H	5.5402824	14.2781016	4.5907488
Au	7.4715285	10.8324753	4.7381670

P	9.3998845	10.2580164	3.5584556
P	11.3174411	10.1495706	4.7412893
P	10.7186914	11.4669932	6.4489952
N	9.8056344	8.3171762	6.1999482
C	9.2513601	8.5342914	2.8688405
H	9.2063855	7.9059841	3.7731011
C	10.4483137	8.0859467	2.0143087
H	10.5383055	8.7402661	1.1315530
H	11.3892935	8.1828823	2.5788016
C	10.2595339	6.6344409	1.5473215
H	10.2677340	5.9695036	2.4283693
H	11.1114566	6.3361347	0.9196086
C	8.9404957	6.4608308	0.7858142
H	8.9755571	7.0528637	-0.1441394
H	8.8105643	5.4119389	0.4829658
C	7.7486707	6.9203105	1.6328904
H	6.8097200	6.8281909	1.0675827
H	7.6526797	6.2601510	2.5131222
C	7.9172302	8.3701024	2.1126027
H	7.0750422	8.6604467	2.7610299
H	7.8940469	9.0445277	1.2402294
C	9.7298301	11.3719625	2.0880186
H	9.3224543	10.7709681	1.2534924
C	11.2143441	11.6506645	1.7935279
H	11.6414247	12.2352949	2.6261645
H	11.7893638	10.7155081	1.7394569
C	11.3674753	12.4507884	0.4913887
H	12.4329228	12.6544464	0.3105976
H	11.0184523	11.8340217	-0.3547310
C	10.5669437	13.7569356	0.5388727
H	10.9940146	14.4156566	1.3148187
H	10.6606323	14.2969629	-0.4138908
C	9.0907205	13.4899821	0.8539649
H	8.6341016	12.9284763	0.0208271

H	8.5338340	14.4349847	0.9351186
C	8.9224930	12.6832369	2.1497984
H	9.2713381	13.2880223	3.0048740
H	7.8586570	12.4683784	2.3356885
C	9.6407172	7.1879110	6.8993280
H	8.6449529	7.0329965	7.3201918
C	10.6590981	6.2496705	7.0932883
H	10.4754802	5.3523272	7.6839340
C	11.9018273	6.4873942	6.5064402
H	12.7195219	5.7753349	6.6219253
C	12.0824363	7.6572935	5.7629007
H	13.0378953	7.8746284	5.2840591
C	11.0115952	8.5534504	5.6506823
C	12.1391251	11.3731170	7.6566007
H	12.1365065	12.3815443	8.1129646
C	11.8436105	10.3398759	8.7650721
H	10.8685868	10.5526601	9.2320450
H	11.7632734	9.3367289	8.3113467
C	12.9511860	10.3404870	9.8276487
H	12.9446755	11.3116612	10.3513819
H	12.7313169	9.5742127	10.5856050
C	14.3330576	10.1072595	9.2072174
H	14.3740325	9.0906604	8.7785378
H	15.1110298	10.1516291	9.9827690
C	14.6194927	11.1316074	8.1049851
H	15.5939515	10.9352147	7.6344024
H	14.6814876	12.1415192	8.5449488
C	13.5230857	11.1166756	7.0289174
H	13.7474934	11.8487885	6.2430267
H	13.5164604	10.1250509	6.5444224
C	10.6497525	13.1615912	5.7042008
H	9.9549038	13.0238838	4.8536804
C	11.9910276	13.6949781	5.1742057

H	12.6880224	13.8217034	6.0190654
H	12.4560045	12.9737486	4.4847958
C	11.7957743	15.0505719	4.4822128
H	11.1548386	14.9124373	3.5935269
H	12.7635342	15.4221121	4.1163013
C	11.1469497	16.0641870	5.4296311
H	10.9828303	17.0208705	4.9131829
H	11.8356395	16.2741159	6.2654704
C	9.8216200	15.5299186	5.9824219
H	9.3799370	16.2466834	6.6896559
H	9.1002207	15.4207153	5.1537702
C	9.9883988	14.1655164	6.6688641
H	9.0110258	13.7807011	7.0030240
H	10.6123263	14.2781217	7.5719579

Intermediate **[9a*Au]$_2^{2+}$**

P	3.8976256	-0.3307303	4.9976096
P	3.7125286	0.2115717	7.1603049
P	2.4278454	-1.5060477	7.7964996
N	5.6440089	-1.7768967	7.5113054
C	2.2086166	-0.0649594	4.2759325
H	1.6371123	-0.8928772	4.7389604
C	2.2162031	-0.3254018	2.7555687
H	2.7913561	0.4677130	2.2500777
H	2.7176668	-1.2812083	2.5310257
C	0.7770954	-0.3321736	2.2172292
H	0.7926781	-0.4888330	1.1288530
H	0.2372431	-1.1912833	2.6520335
C	0.0384463	0.9667043	2.5624344
H	-1.0003127	0.9175740	2.2064353
H	0.5121162	1.8083465	2.0288776
C	0.0706058	1.2460162	4.0695743
H	-0.4999726	0.4637993	4.6019527
H	-0.4219331	2.2023722	4.2980123

C	1.5102512	1.2652018	4.6032961
H	2.0617455	2.0923761	4.1286469
H	1.5178911	1.4671121	5.6863628
C	5.1036661	0.9022509	4.2948897
H	4.8132165	0.9403113	3.2284483
C	5.0076962	2.3211983	4.8854185
H	3.9837049	2.7127663	4.8146835
H	5.2524743	2.2801505	5.9607744
C	5.9943603	3.2689086	4.1867016
H	5.7025675	3.3794430	3.1282749
H	5.9206002	4.2692129	4.6374219
C	7.4300504	2.7406344	4.2714075
H	8.1174788	3.4171461	3.7441087
H	7.7511191	2.7268499	5.3276538
C	7.5299295	1.3250527	3.6928136
H	8.5539063	0.9353264	3.7924134
H	7.3089522	1.3551913	2.6121548
C	6.5487578	0.3638147	4.3779822
H	6.8324332	0.2402436	5.4366162
H	6.6089043	-0.6358621	3.9186232
C	6.8480135	-2.2217263	7.8950247
H	7.0336708	-3.2880566	7.7470422
C	7.8289961	-1.3975923	8.4540357
H	8.7957487	-1.8108702	8.7403308
C	7.5336328	-0.0475626	8.6420874
H	8.2663474	0.6288295	9.0829788
C	6.2751568	0.4251635	8.2602155
H	6.0038468	1.4720513	8.4009403
C	5.3637741	-0.4723306	7.6873509
C	0.7002389	-0.8648329	7.5783833
H	0.7171949	-0.4950089	6.5379261
C	-0.3472118	-1.9962342	7.6276191
H	-0.3936977	-2.4151817	8.6452452

H	-0.0506221	-2.8186904	6.9577491
C	-1.7268090	-1.4504782	7.2286534
H	-1.6948093	-1.1414228	6.1689850
H	-2.4744420	-2.2543083	7.2977539
C	-2.1376382	-0.2547101	8.0958386
H	-2.2807565	-0.5919598	9.1368279
H	-3.1070840	0.1404514	7.7607309
C	-1.0747066	0.8499902	8.0658281
H	-1.3617909	1.6814610	8.7256527
H	-1.0026110	1.2674408	7.0461440
C	0.3017020	0.3111770	8.4850301
H	1.0576613	1.1108277	8.4497787
H	0.2513751	-0.0384500	9.5283442
C	2.9156322	-1.7409353	9.5782758
H	3.9106220	-2.2066754	9.4545953
C	2.0093158	-2.7759217	10.2738852
H	1.0085238	-2.3412193	10.4301389
H	1.8785230	-3.6659021	9.6375915
C	2.6152020	-3.1644597	11.6307971
H	1.9579118	-3.8875084	12.1358772
H	3.5776608	-3.6780927	11.4569383
C	2.8413558	-1.9321726	12.5152556
H	1.8643769	-1.4908890	12.7769703
H	3.3129741	-2.2261628	13.4638970
C	3.6965178	-0.8765318	11.8023749
H	4.7139745	-1.2734707	11.6394521
H	3.8048966	0.0193737	12.4305351
C	3.0904281	-0.4832166	10.4455928
H	3.7353122	0.2567023	9.9465083
H	2.1171005	0.0038657	10.6038426
P	3.4260898	-5.8105475	6.4211220
P	3.9155642	-6.2299498	4.2897510
P	5.3596992	-4.5973473	3.8219377
N	5.9829517	-7.8549578	5.2115734

C	4.7989660	-6.2452260	7.6285466
H	5.7134013	-6.1342123	7.0238588
C	4.8429690	-5.2331988	8.7930161
H	3.9113364	-5.3054664	9.3811933
H	4.8888999	-4.2044797	8.4029394
C	6.0490019	-5.5035815	9.7040321
H	6.0485444	-4.7835666	10.5367674
H	6.9760702	-5.3222761	9.1309456
C	6.0542578	-6.9436291	10.2266918
H	6.9492071	-7.1254623	10.8387859
H	5.1847981	-7.0934381	10.8889852
C	5.9850230	-7.9436838	9.0678236
H	6.9019143	-7.8658514	8.4576397
H	5.9456390	-8.9746879	9.4484107
C	4.7682702	-7.6856720	8.1653438
H	3.8457928	-7.8464890	8.7466754
H	4.7663882	-8.4060577	7.3392164
C	1.9431380	-6.9022062	6.7305761
H	1.9235618	-6.9724119	7.8339993
C	2.0429243	-8.3209186	6.1383671
H	2.9628036	-8.8263648	6.4586645
H	2.0889432	-8.2400117	5.0383036
C	0.8130559	-9.1582755	6.5206126
H	0.7966936	-9.2975024	7.6151455
H	0.9037532	-10.1614081	6.0791487
C	-0.4842971	-8.4819453	6.0668942
H	-1.3547581	-9.0766308	6.3788780
H	-0.5088537	-8.4436505	4.9642296
C	-0.5856904	-7.0589784	6.6262463
H	-1.4934678	-6.5606196	6.2552309
H	-0.6778360	-7.1032396	7.7252265
C	0.6447551	-6.2138801	6.2643373
H	0.6876295	-6.0651076	5.1714312

H	0.5634055	-5.2133930	6.7178440
C	6.7084078	-8.9828967	5.2144355
H	7.5262534	-9.0237435	5.9377911
C	6.4602010	-10.0584896	4.3564453
H	7.0840433	-10.9509734	4.3993510
C	5.3996470	-9.9599636	3.4555230
H	5.1695837	-10.7778537	2.7720735
C	4.6314170	-8.7940182	3.4472818
H	3.7880832	-8.6843406	2.7646540
C	4.9624612	-7.7652890	4.3408892
C	7.0763541	-4.9497395	4.4579419
H	6.8702750	-5.4558663	5.4182518
C	7.8485557	-3.6463046	4.7516292
H	8.0728863	-3.1276059	3.8047121
H	7.2317415	-2.9548275	5.3455615
C	9.1543977	-3.9650941	5.4924688
H	8.9068960	-4.3953248	6.4799929
H	9.7079009	-3.0334666	5.6841534
C	10.0214261	-4.9596067	4.7105347
H	10.3678324	-4.4814706	3.7786395
H	10.9240031	-5.2128499	5.2853039
C	9.2359519	-6.2298204	4.3633032
H	9.8523824	-6.9097218	3.7574699
H	8.9796745	-6.7741063	5.2891958
C	7.9384220	-5.9017902	3.6102919
H	7.3962782	-6.8242224	3.3704510
H	8.1885975	-5.4148629	2.6541843
C	5.2849950	-4.5212330	1.9616106
H	4.2464088	-4.1740305	1.8031994
C	6.2305851	-3.4255582	1.4269514
H	7.2765311	-3.7205095	1.6087936
H	6.0661012	-2.4803930	1.9701873
C	6.0171964	-3.2248436	-0.0810596
H	6.7221706	-2.4669031	-0.4532499

H	5.0027207	-2.8244851	-0.2504377
C	6.1831942	-4.5409355	-0.8499681
H	7.2279014	-4.8860574	-0.7613765
H	5.9979582	-4.3803251	-1.9215904
C	5.2433727	-5.6232279	-0.3059015
H	4.1958788	-5.3246593	-0.4829897
H	5.3943001	-6.5716423	-0.8417147
C	5.4574179	-5.8464921	1.1998943
H	4.7436490	-6.5978635	1.5718417
H	6.4653710	-6.2520691	1.3677520
Au	4.5780080	-2.5316134	4.5966264
Au	2.8706426	-3.5581768	6.7787816

Complex *anti*-**[9a*Cu]$_2$**$^{2+}$

Cu	5.0783554	-2.4863462	5.4324478
P	4.1402884	-0.4720951	5.0300064
P	3.6946896	0.1166259	7.1488737
P	2.2964602	-1.6050962	7.5329377
N	5.7906357	-1.7912798	7.2445177
C	2.5460339	-0.3049524	4.1012274
H	1.9146781	-1.0704106	4.5886306
C	2.7622604	-0.7705763	2.6475723
H	3.4889701	-0.1085215	2.1475945
H	3.2022467	-1.7795846	2.6519895
C	1.4462947	-0.7593582	1.8549291
H	1.6477238	-1.0284445	0.8071315
H	0.7818345	-1.5428257	2.2553827
C	0.7320072	0.5942212	1.9418474
H	-0.2246215	0.5530542	1.4019567
H	1.3408306	1.3651246	1.4397293
C	0.5058516	1.0046357	3.4020713
H	-0.1693422	0.2777738	3.8904367
H	0.0055886	1.9821120	3.4584818

C	1.8337142	1.0533951	4.1709265
H	2.4783612	1.8256873	3.7215758
H	1.6668078	1.3542605	5.2174572
C	5.3368507	0.8231133	4.4184771
H	5.1456966	0.8428661	3.3287559
C	5.1644217	2.2474818	4.9745894
H	4.1389618	2.6120737	4.8252197
H	5.3313907	2.2283451	6.0663323
C	6.1763155	3.2068613	4.3287074
H	5.9551002	3.2916104	3.2508459
H	6.0504669	4.2135794	4.7532287
C	7.6166127	2.7180093	4.5195908
H	8.3193018	3.3970920	4.0161746
H	7.8695213	2.7449435	5.5937168
C	7.7936243	1.2879710	3.9950060
H	8.8169050	0.9305654	4.1826992
H	7.6515797	1.2760926	2.9006821
C	6.7830508	0.3299717	4.6390473
H	6.9790463	0.2654585	5.7233392
H	6.9044551	-0.6912836	4.2392176
C	6.9422441	-2.2756357	7.7504757
H	7.3546024	-3.1462301	7.2395989
C	7.5886185	-1.7146605	8.8498115
H	8.5242873	-2.1430348	9.2068865
C	7.0102352	-0.6089176	9.4701498
H	7.4818730	-0.1427686	10.3354325
C	5.8199078	-0.0948982	8.9506566
H	5.3496706	0.7803244	9.3985591
C	5.2328441	-0.6939363	7.8309272
C	0.6182533	-0.8804756	7.1800390
H	0.7081830	-0.6789281	6.0955333
C	-0.4796736	-1.9515758	7.3342506
H	-0.6427512	-2.1581135	8.4043272
H	-0.1590245	-2.9040301	6.8767158

C	-1.7877856	-1.4489298	6.7055401
H	-1.6379656	-1.3262576	5.6169084
H	-2.5789213	-2.2024543	6.8323302
C	-2.2183492	-0.1070870	7.3142444
H	-2.4813324	-0.2621867	8.3744896
H	-3.1293005	0.2580934	6.8189878
C	-1.1047122	0.9442298	7.2201062
H	-1.4160830	1.8776599	7.7106424
H	-0.9199950	1.1933219	6.1601990
C	0.2034423	0.4381829	7.8500065
H	0.9965246	1.1955813	7.7570623
H	0.0477221	0.2721736	8.9268299
C	2.5828029	-1.9275604	9.3458543
H	3.6637973	-2.1685747	9.3439573
C	1.8491898	-3.1967193	9.8204445
H	0.7620593	-3.0191863	9.8226342
H	2.0371572	-4.0226818	9.1153371
C	2.3073234	-3.5776071	11.2363619
H	1.7509581	-4.4624939	11.5795632
H	3.3715478	-3.8670307	11.2022276
C	2.1304152	-2.4143266	12.2204210
H	1.0547624	-2.2001459	12.3422213
H	2.5052711	-2.6978466	13.2142984
C	2.8411830	-1.1485133	11.7238738
H	3.9317646	-1.3227383	11.6967653
H	2.6718606	-0.3137237	12.4192274
C	2.3604134	-0.7594458	10.3178612
H	2.8710300	0.1509822	9.9676742
H	1.2873841	-0.5185215	10.3583900
Cu	2.6937145	-3.4219903	6.3476656
P	3.6317586	-5.4361416	6.7499048
P	4.0772410	-6.0248209	4.6310504
P	5.4755314	-4.3031961	4.2469925

N	1.9813454	-4.1169297	4.5356735
C	5.2260036	-5.6035375	7.6786805
H	5.8575626	-4.8383098	7.1911616
C	5.0099230	-5.1376261	9.1322757
H	4.2830766	-5.7994410	9.6323785
H	4.5701386	-4.1285248	9.1277121
C	6.3259199	-5.1490158	9.9248840
H	6.1245959	-4.8797211	10.9726520
H	6.9905169	-4.3657365	9.5242730
C	7.0399046	-6.5027699	9.8381181
H	7.9965618	-6.4617309	10.3779643
H	6.4309278	-7.2734707	10.3403670
C	7.2659285	-6.9134339	8.3779420
H	7.9412435	-6.1867805	7.8894290
H	7.7659802	-7.8910250	8.3216609
C	5.9380160	-6.9620500	7.6091538
H	5.2932240	-7.7341412	8.0586425
H	6.1048147	-7.2630930	6.5626605
C	2.4351496	-6.7313327	7.3614018
H	2.6265421	-6.7513636	8.4510724
C	2.6072614	-8.1556159	6.8049823
H	3.6327214	-8.5203552	6.9539716
H	2.4399542	-8.1362849	5.7133085
C	1.5954528	-9.1149762	7.4510253
H	1.8169790	-9.1999080	8.5288073
H	1.7210593	-10.1216438	7.0263224
C	0.1551565	-8.6259332	7.2606350
H	-0.5474594	-9.3050083	7.7641587
H	-0.0980660	-8.6526848	6.1865847
C	-0.0215431	-7.1959515	7.7854755
H	-1.0448344	-6.8384075	7.5981235
H	0.1208074	-7.1842533	8.8797583
C	0.9889577	-6.2379688	7.1412906
H	0.7926805	-6.1732902	6.0570771

H	0.8677746	-5.2167735	7.5413062
C	0.8296923	-3.6325739	4.0298914
H	0.4173363	-2.7620252	4.5408375
C	0.1832104	-4.1934870	2.9305865
H	-0.7525149	-3.7651232	2.5736229
C	0.7615664	-5.2991863	2.3101300
H	0.2898460	-5.7653096	1.4448737
C	1.9519690	-5.8131647	2.8294519
H	2.4221634	-6.6883449	2.3814559
C	2.5390951	-5.2141816	3.9491516
C	7.1537419	-5.0279973	4.5996415
H	7.0638518	-5.2297520	5.6841135
C	8.2516940	-3.9569055	4.4455266
H	8.4145986	-3.7501199	3.3754634
H	7.9311714	-3.0045313	4.9033336
C	9.5599076	-4.4597083	5.0739048
H	9.4102714	-4.5825924	6.1625430
H	10.3510303	-3.7061687	4.9471129
C	9.9903242	-5.8014646	4.4649077
H	10.2531344	-5.6462221	3.4046387
H	10.9013531	-6.1667347	4.9599580
C	8.8766536	-6.8527437	4.5590491
H	9.1879188	-7.7861246	4.0683560
H	8.6920528	-7.1019791	5.6189456
C	7.5684584	-6.3465335	3.9293702
H	6.7753486	-7.1039063	4.0222380
H	7.7240994	-6.1803296	2.8525610
C	5.1889697	-3.9805437	2.4341360
H	4.1080150	-3.7393761	2.4362604
C	5.9226690	-2.7114447	1.9595314
H	7.0097842	-2.8891092	1.9571686
H	5.7349451	-1.8854941	2.6647224
C	5.4643401	-2.3303829	0.5437174

H	6.0207291	-1.4455423	0.2004326
H	4.4001564	-2.0408322	0.5781005
C	5.6409825	-3.4936015	-0.4404632
H	6.7166196	-3.7078153	-0.5624132
H	5.2659852	-3.2100329	-1.4342673
C	4.9302227	-4.7594206	0.0560965
H	3.8396606	-4.5851043	0.0834041
H	5.0993877	-5.5941593	-0.6393435
C	5.4111206	-5.1486179	1.4620453
H	4.9004743	-6.0590383	1.8121636
H	6.4841365	-5.3896007	1.4214227

Complex *syn*-**[9a*Cu]$_2$**$^{2+}$

Cu	4.9389335	-4.1070225	7.9006871
P	6.7884720	-4.6598088	9.0475672
P	7.8352993	-2.6698896	8.9686513
P	7.8726235	-2.5029604	6.7257811
N	5.0795424	-2.1476091	8.6349903
C	8.0054785	-5.9311880	8.4648702
H	8.0781489	-5.7252983	7.3809743
C	7.3817459	-7.3351509	8.6057567
H	7.2062478	-7.5637118	9.6698272
H	6.3997174	-7.3598702	8.1087992
C	8.3138500	-8.4020335	8.0150260
H	7.8658915	-9.3977532	8.1487916
H	8.3968771	-8.2343712	6.9297164
C	9.7134460	-8.3427388	8.6349917
H	10.3655399	-9.0969165	8.1717594
H	9.6540872	-8.5955097	9.7071076
C	10.3200039	-6.9439815	8.4768940
H	10.4605675	-6.7253273	7.4027203
H	11.3157398	-6.8952540	8.9407636
C	9.4081883	-5.8721513	9.0904556
H	9.3274530	-6.0437673	10.1760040

H	9.8529053	-4.8714174	8.9661359
C	6.4987663	-4.9303868	10.8765274
H	6.5951462	-6.0258030	10.9867770
C	7.4938105	-4.2575661	11.8382294
H	8.5289967	-4.5364039	11.5961015
H	7.4286702	-3.1613633	11.7162858
C	7.1650824	-4.6155206	13.2962844
H	7.3139479	-5.6989884	13.4440960
H	7.8734499	-4.1083830	13.9671350
C	5.7214638	-4.2427334	13.6548156
H	5.4977464	-4.5383322	14.6896568
H	5.6079091	-3.1454387	13.6105490
C	4.7232895	-4.8935720	12.6897153
H	3.6949790	-4.5826133	12.9266537
H	4.7564791	-5.9898238	12.8112506
C	5.0475938	-4.5435350	11.2311590
H	4.9144103	-3.4588061	11.0750080
H	4.3468110	-5.0475105	10.5451659
C	3.9775493	-1.3837827	8.7629625
H	3.0642788	-1.7985072	8.3366204
C	3.9811638	-0.1421173	9.3943011
H	3.0570307	0.4286074	9.4771716
C	5.1827283	0.3370748	9.9150475
H	5.2272944	1.3016915	10.4213525
C	6.3317606	-0.4459145	9.7834793
H	7.2873636	-0.1045645	10.1822084
C	6.2561973	-1.6854188	9.1387892
C	9.4329934	-3.3939169	6.2415594
H	9.2921138	-4.3677257	6.7429594
C	9.4617259	-3.6907763	4.7299039
H	9.6124867	-2.7541843	4.1686820
H	8.4898187	-4.0979686	4.4090191
C	10.5966875	-4.6755036	4.4140360

H	10.3716470	-5.6426971	4.8996044
H	10.6326612	-4.8686601	3.3316976
C	11.9505515	-4.1536482	4.9135296
H	12.2229842	-3.2513565	4.3390814
H	12.7387280	-4.8948575	4.7187839
C	11.9070880	-3.8051829	6.4071449
H	12.8680612	-3.3801143	6.7305344
H	11.7560209	-4.7245865	6.9980802
C	10.7728481	-2.8158077	6.7201054
H	10.7444101	-2.5840986	7.7954875
H	10.9674981	-1.8685441	6.1922812
C	7.9914791	-0.6562813	6.4917317
H	7.0160182	-0.3387928	6.9103678
C	7.9797690	-0.3018511	4.9918563
H	8.9390955	-0.6006335	4.5390075
H	7.1929937	-0.8729437	4.4694037
C	7.7701093	1.2081703	4.8034066
H	7.8005773	1.4569135	3.7326389
H	6.7595089	1.4773732	5.1599839
C	8.8149582	2.0221731	5.5778733
H	9.8112507	1.8421561	5.1390924
H	8.6165163	3.0977534	5.4656292
C	8.8429404	1.6368569	7.0628796
H	7.8826719	1.9128460	7.5347416
H	9.6256528	2.2000671	7.5910354
C	9.0771247	0.1288016	7.2432580
H	9.0884166	-0.1379007	8.3111088
H	10.0678087	-0.1347159	6.8466383
Cu	6.0674780	-3.2121785	5.6646373
P	5.2803805	-4.6076399	4.0947655
P	3.0911592	-4.5317857	4.6143473
P	3.2383680	-5.0008872	6.8149922
N	4.2773355	-2.0915544	5.3954748
C	5.2654494	-3.7021784	2.4591166

H	4.7062522	-2.7735978	2.6754198
C	6.7127810	-3.2955231	2.1129529
H	7.3310535	-4.2003182	1.9769959
H	7.1539211	-2.7395016	2.9560673
C	6.7533261	-2.4551146	0.8283498
H	7.7969891	-2.2127931	0.5790663
H	6.2412675	-1.4944607	1.0133933
C	6.0712577	-3.1785204	-0.3384898
H	6.0850537	-2.5460662	-1.2374004
H	6.6438188	-4.0888298	-0.5889008
C	4.6314683	-3.5668471	0.0166308
H	4.0313370	-2.6536254	0.1715745
H	4.1617916	-4.1130686	-0.8140820
C	4.5810769	-4.4265268	1.2900961
H	5.0981216	-5.3812641	1.0938771
H	3.5389420	-4.6741234	1.5441139
C	5.7880710	-6.3512387	3.7017861
H	6.3806032	-6.2139705	2.7772061
C	4.6371536	-7.3243810	3.3870784
H	3.9913385	-6.9192892	2.5954059
H	4.0052287	-7.4335834	4.2818354
C	5.1707289	-8.7073877	2.9884312
H	5.6964078	-8.6286172	2.0217378
H	4.3262799	-9.3938606	2.8288504
C	6.1306537	-9.2647840	4.0449326
H	6.5294211	-10.2370627	3.7230956
H	5.5782150	-9.4482810	4.9845992
C	7.2749573	-8.2840352	4.3213759
H	7.9574322	-8.6939040	5.0786508
H	7.8738752	-8.1496447	3.4042851
C	6.7406157	-6.9173245	4.7709980
H	6.2051162	-7.0194116	5.7320038
H	7.5646615	-6.2097886	4.9552757

C	4.2652607	-0.7589654	5.5898330
H	5.1887361	-0.3308695	5.9786312
C	3.1559556	0.0409135	5.3249657
H	3.2066251	1.1152612	5.4977711
C	1.9996357	-0.5645389	4.8339379
H	1.1104748	0.0258802	4.6114671
C	2.0038943	-1.9447501	4.6198644
H	1.1220617	-2.4515809	4.2272203
C	3.1542021	-2.6876105	4.9080533
C	1.6533145	-4.2495206	7.4483236
H	1.8105254	-3.1876977	7.1718841
C	1.5908823	-4.3026828	8.9874083
H	1.4207674	-5.3415062	9.3124118
H	2.5553687	-3.9911438	9.4238461
C	0.4502778	-3.4118560	9.5012688
H	0.6813063	-2.3585311	9.2596105
H	0.3920482	-3.4766950	10.5976001
C	-0.8924210	-3.7961454	8.8653513
H	-1.1763629	-4.8059814	9.2064221
H	-1.6844586	-3.1170054	9.2119435
C	-0.8153813	-3.7861058	7.3330287
H	-1.7715255	-4.1105317	6.8978476
H	-0.6419842	-2.7539352	6.9791768
C	0.3196981	-4.6880408	6.8233212
H	0.3716795	-4.6658729	5.7237661
H	0.1085582	-5.7304150	7.1057530
C	3.2494302	-6.8552542	6.8987021
H	4.1878695	-7.0770538	6.3538368
C	3.4620125	-7.3475632	8.3440267
H	2.5489417	-7.1666057	8.9335511
H	4.2714604	-6.7736464	8.8233569
C	3.7787135	-8.8499880	8.3397887
H	3.9177303	-9.2047646	9.3716654
H	4.7391478	-9.0111977	7.8181732

C	2.6762625	-9.6524748	7.6364120
H	1.7459289	-9.5809795	8.2247299
H	2.9438738	-10.7183866	7.6056096
C	2.4170214	-9.1297356	6.2175254
H	3.3064972	-9.3131673	5.5900391
H	1.5870103	-9.6788198	5.7501409
C	2.1054398	-7.6249343	6.2203844
H	1.9300193	-7.2623455	5.1957954
H	1.1725838	-7.4514894	6.7775974

Intermediate **[9a*Cu]$_2$**$^{2+}$

P	-0.3035053	8.1851934	9.3082395
P	0.0384021	7.6287449	7.1422765
P	0.8692807	5.5477313	7.4222704
N	2.4944496	8.4169837	8.2829667
C	-1.9632978	7.6087537	9.9209768
H	-2.3312531	8.5075144	10.4519323
C	-1.8000187	6.4939950	10.9702425
H	-1.3790861	5.5944118	10.4915142
H	-1.0712426	6.8036467	11.7351166
C	-3.1496845	6.1353500	11.6032498
H	-3.0145774	5.3177123	12.3271778
H	-3.5243365	7.0018042	12.1748635
C	-4.1752406	5.7447970	10.5327277
H	-3.8387305	4.8190340	10.0332276
H	-5.1436590	5.5127232	10.9979947
C	-4.3419070	6.8552657	9.4880909
H	-4.7799680	7.7465328	9.9684401
H	-5.0481835	6.5458789	8.7038847
C	-3.0001179	7.2385520	8.8455121
H	-3.1349128	8.0664534	8.1355925
H	-2.6266450	6.3830653	8.2602742
C	-0.4306644	10.0441422	9.1454852

H	0.4249588	10.3212964	8.5048747
C	-0.1808847	10.6644178	10.5364906
H	-0.9605546	10.3265285	11.2423519
H	0.7814797	10.3009584	10.9339835
C	-0.1905074	12.1983437	10.4654893
H	-0.0576864	12.6133392	11.4758796
H	0.6762259	12.5329521	9.8696024
C	-1.4804729	12.7248609	9.8265034
H	-1.4492951	13.8215001	9.7589697
H	-2.3381465	12.4755603	10.4747553
C	-1.6983596	12.1133161	8.4378752
H	-0.8897167	12.4388879	7.7609833
H	-2.6392982	12.4747154	7.9988017
C	-1.7185198	10.5772457	8.4995270
H	-2.5908491	10.2600519	9.0951341
H	-1.8481632	10.1536331	7.4914640
C	1.7230657	8.4459616	7.1592905
C	2.1522620	9.1092342	6.0075368
H	1.5141005	9.1239216	5.1241077
C	3.3915289	9.7567233	6.0039976
H	3.7386682	10.2752201	5.1099994
C	4.1652190	9.7374335	7.1630230
H	5.1330012	10.2349550	7.2100794
C	3.6800983	9.0574135	8.2782762
H	4.2523822	8.9918010	9.2042185
C	1.4680526	5.0326882	5.7231906
H	1.2373204	3.9504814	5.7154818
C	2.9963973	5.1955430	5.6111943
H	3.2517100	6.2667452	5.6902696
H	3.4936279	4.6903315	6.4565234
C	3.5179877	4.6383570	4.2802039
H	4.6046036	4.7989372	4.2143284
H	3.3600514	3.5461589	4.2621107
C	2.8029580	5.2769705	3.0844667

H	3.1622220	4.8338105	2.1449447
H	3.0544665	6.3513150	3.0401370
C	1.2833436	5.1178852	3.2025854
H	1.0180533	4.0483961	3.1433976
H	0.7745257	5.6126841	2.3627111
C	0.7604455	5.6941095	4.5272765
H	0.9613187	6.7791465	4.5468823
H	-0.3294654	5.5788268	4.5934392
C	-0.5933447	4.4821103	7.8300586
H	-1.0578349	5.0000752	8.6867227
C	-0.1148437	3.1070575	8.3362904
H	0.4060176	2.5706714	7.5244542
H	0.6180025	3.2404616	9.1483536
C	-1.3116110	2.2729424	8.8167878
H	-0.9629923	1.2889815	9.1632813
H	-1.7658401	2.7746761	9.6896841
C	-2.3688639	2.1198656	7.7171254
H	-3.2279350	1.5471574	8.0946164
H	-1.9452527	1.5352668	6.8826985
C	-2.8287505	3.4867468	7.1983287
H	-3.3528193	4.0289144	8.0040387
H	-3.5529849	3.3670975	6.3798378
C	-1.6417190	4.3330957	6.7144482
H	-1.9894454	5.3184551	6.3674931
H	-1.1794373	3.8362183	5.8459842
P	4.5128783	5.0039616	9.8818272
P	4.8319037	6.6383438	11.3464213
P	2.7019054	6.8848549	11.9115524
N	7.2411376	5.9606892	12.0955251
C	5.8264222	5.1323148	8.5655132
H	5.5345451	4.2994291	7.8959995
C	5.6241186	6.4554702	7.8029327
H	5.8822141	7.2866614	8.4797971

H	4.5653074	6.5860344	7.5301658
C	6.5117124	6.5217435	6.5555405
H	6.3564550	7.4840385	6.0426573
H	6.1972128	5.7341557	5.8495253
C	7.9884969	6.3296773	6.9201411
H	8.3234331	7.1836486	7.5337979
H	8.6095787	6.3310678	6.0131861
C	8.1953221	5.0307289	7.7079664
H	7.9721090	4.1677473	7.0571091
H	9.2483659	4.9295515	8.0085067
C	7.3027314	4.9690466	8.9592270
H	7.4690285	4.0241333	9.4898170
H	7.5733909	5.7697276	9.6636854
C	4.5156176	3.3282495	10.6994991
H	3.8546727	3.5050495	11.5674352
C	3.8169804	2.3117931	9.7715522
H	4.4591829	2.1202379	8.8949449
H	2.8727516	2.7298964	9.3813676
C	3.5491418	0.9973687	10.5183459
H	3.0828364	0.2709225	9.8365033
H	2.8165027	1.1924672	11.3208643
C	4.8331824	0.4207669	11.1270336
H	4.6036408	-0.4861305	11.7047329
H	5.5117828	0.1104720	10.3143601
C	5.5465255	1.4516237	12.0094976
H	4.9201671	1.6869379	12.8887145
H	6.4883476	1.0385629	12.3984039
C	5.8342689	2.7488428	11.2371483
H	6.5034366	2.5207555	10.3938080
H	6.3563821	3.4696526	11.8781318
C	5.9992964	5.9449713	12.6085332
C	5.7169140	5.5105939	13.9072064
H	4.7067975	5.5372280	14.3029721
C	6.7749313	5.0425388	14.6901425

H	6.5921320	4.6939433	15.7072973
C	8.0620944	5.0230383	14.1531236
H	8.9108687	4.6601732	14.7319674
C	8.2465461	5.4985507	12.8509064
H	9.2390555	5.5178161	12.3947877
C	1.6978054	5.5055553	12.6830480
H	0.8394328	6.0923537	13.0603806
C	1.1394078	4.5471862	11.6192094
H	1.9594616	3.9636408	11.1733516
H	0.6839074	5.1299137	10.8021173
C	0.1197132	3.5767585	12.2242289
H	-0.2396959	2.8864468	11.4474881
H	-0.7589627	4.1460448	12.5729299
C	0.7275701	2.7988493	13.3967177
H	-0.0209319	2.1256937	13.8384811
H	1.5436621	2.1567798	13.0214126
C	1.2825296	3.7512851	14.4596454
H	0.4527569	4.3229461	14.9090394
H	1.7519221	3.1871316	15.2785336
C	2.3030558	4.7323761	13.8620040
H	3.1855495	4.1708261	13.5127500
H	2.6463104	5.4282597	14.6409057
C	2.6908764	8.3476349	13.0760634
H	3.0579552	9.1509876	12.4092620
C	1.2409302	8.6943004	13.4697188
H	0.8542503	7.9214460	14.1558701
H	0.5915395	8.6884164	12.5793545
C	1.1924271	10.0534950	14.1806769
H	0.1562118	10.2848415	14.4687856
H	1.5083192	10.8410883	13.4749775
C	2.1090128	10.0606454	15.4113780
H	2.0992198	11.0512253	15.8879591
H	1.7138980	9.3508997	16.1584759

C	3.5450188	9.6654863	15.0451924
H	3.9847435	10.4399366	14.3931462
H	4.1741108	9.6228184	15.9459209
C	3.6017431	8.3134371	14.3132573
H	4.6401484	8.0862977	14.0308755
H	3.2685283	7.5128479	14.9945766
Cu	1.7426585	7.6226771	10.0520249
Cu	2.5402165	5.4269161	8.8878809

Compound **19**$^{2+}$

P	-0.8739240	1.5515963	-0.4216423
P	0.2273768	-0.2268302	0.3488246
C	-0.0820091	-0.1915820	2.1697884
C	-0.5505715	0.8871777	2.9268397
N	0.2498855	-1.3887180	2.6844791
C	-0.6986207	0.6921675	4.3029911
H	-0.7723712	1.8509075	2.4662773
C	0.1122334	-1.5548820	4.0091551
C	-0.3651677	-0.5462927	4.8535467
H	-1.0637803	1.5013804	4.9361958
H	0.3912002	-2.5339372	4.4033589
H	-0.4719638	-0.7337094	5.9217360
C	0.2270073	3.0153909	-0.6457644
C	0.6614567	3.6139044	-1.8341289
N	0.4725438	3.5369639	0.5706973
C	1.3796955	4.8101331	-1.7469870
H	0.4536213	3.1704278	-2.8054198
C	1.1619804	4.6848660	0.6395971
C	1.6342824	5.3596410	-0.4907096
H	1.7304405	5.3063020	-2.6524817
H	1.3305709	5.0831740	1.6419196
H	2.1791810	6.2969073	-0.3834837
P	-1.3812680	0.6512097	-2.4073492
P	2.4092190	0.2421332	0.4786695

C	-2.7396089	-0.4509736	-1.9158595
H	-3.1528244	-0.9421401	-2.8048214
H	-2.3680944	-1.2162893	-1.2219998
H	-3.5234347	0.1364321	-1.4223325
C	2.9570662	0.8349391	-1.1455333
H	2.4649324	1.7811219	-1.3946746
H	4.0428621	0.9893314	-1.1217541
H	2.7199527	0.0798171	-1.9036338
C	-2.0608699	1.9631136	-3.5088412
C	-2.8093895	1.3591755	-4.7203413
C	-2.9450485	2.9679728	-2.7383758
H	-1.1737916	2.4976438	-3.8892421
C	-3.3049521	2.4829036	-5.6462755
H	-3.6748821	0.7767545	-4.3652155
H	-2.1601423	0.6705213	-5.2799534
C	-3.4457840	4.0708646	-3.6843888
H	-3.8093031	2.4409706	-2.3019510
H	-2.3880736	3.4196632	-1.9025249
C	-4.1842870	3.4860805	-4.8932485
H	-3.8554460	2.0350210	-6.4857193
H	-2.4346095	3.0023351	-6.0817155
H	-4.0968122	4.7561681	-3.1236115
H	-2.5831992	4.6669448	-4.0289773
H	-4.5005958	4.2928830	-5.5687473
H	-5.1056326	2.9840887	-4.5527180
C	-0.0658817	-0.3575857	-3.2395282
C	-0.6242385	-1.5766530	-4.0098836
C	0.8555017	0.5045789	-4.1252934
H	0.5217083	-0.7526001	-2.3894752
C	0.5313180	-2.4019897	-4.5988004
H	-1.2832889	-1.2375496	-4.8245120
H	-1.2277429	-2.2111953	-3.3469451
C	1.9890175	-0.3466888	-4.7194826

H	0.2690654	0.9399893	-4.9502792
H	1.2763092	1.3444387	-3.5519745
C	1.4411800	-1.5518127	-5.4899906
H	0.1146575	-3.2487908	-5.1620680
H	1.1205116	-2.8347015	-3.7716288
H	2.6149442	0.2833690	-5.3670880
H	2.6439212	-0.7068586	-3.9057134
H	2.2691810	-2.1598866	-5.8800714
H	0.8734602	-1.1982044	-6.3670056
C	2.7882561	1.4914131	1.7925992
C	3.0424424	0.8423778	3.1707999
C	3.9334105	2.4458863	1.3866672
H	1.8566914	2.0815156	1.8545195
C	3.2406517	1.9340974	4.2321591
H	3.9478919	0.2173578	3.1294212
H	2.2111689	0.1871698	3.4579397
C	4.1571090	3.5025528	2.4819353
H	4.8647910	1.8765057	1.2334769
H	3.6998604	2.9502194	0.4367130
C	4.3926904	2.8711414	3.8571050
H	3.4256404	1.4589653	5.2060816
H	2.3053632	2.5115229	4.3347017
H	5.0031612	4.1429350	2.1939623
H	3.2694357	4.1548040	2.5326537
H	4.5117015	3.6561480	4.6168380
H	5.3381211	2.3027349	3.8450304
C	3.2398923	-1.3676145	0.8001391
C	2.7796577	-2.4846982	-0.1591736
C	4.7789365	-1.2106665	0.7725717
H	2.9137140	-1.6313554	1.8211497
C	3.4684610	-3.8099662	0.2069460
H	3.0414137	-2.2138940	-1.1973593
H	1.6874961	-2.6063763	-0.1128399
C	5.4457103	-2.5448252	1.1480209

H	5.1003500	-0.9243073	-0.2423229
H	5.1128402	-0.4156917	1.4542952
C	4.9949580	-3.6750777	0.2173530
H	3.1521593	-4.5894071	-0.5009784
H	3.1155956	-4.1269407	1.2020390
H	6.5375480	-2.4217685	1.1116333
H	5.1898862	-2.7942880	2.1912078
H	5.4560975	-4.6240646	0.5244071
H	5.3535544	-3.4703648	-0.8062538

Compound **20**$^+$

P	-0.2480472	-0.0139661	-0.2938070
P	-0.2550787	-1.0776499	1.5694355
P	-0.8086844	1.9841434	0.2772816
C	0.2342865	-2.7858322	1.0286045
C	1.7416060	-2.9061251	0.7257576
C	-0.2350717	-3.9218379	1.9612235
H	-0.3146874	-2.8885768	0.0732018
C	2.0559459	-4.2723292	0.1006423
H	2.3030186	-2.8120010	1.6691639
H	2.0734126	-2.0911270	0.0659103
C	0.1031363	-5.2883187	1.3413181
H	0.2607390	-3.8301419	2.9405638
H	-1.3178784	-3.8647019	2.1400523
C	1.5937161	-5.4159661	1.0102536
H	3.1357533	-4.3443288	-0.0955875
H	1.5514404	-4.3482436	-0.8774577
H	-0.2118336	-6.0853985	2.0306913
H	-0.4887700	-5.4176694	0.4190512
H	1.7946940	-6.3874945	0.5359168
H	2.1790838	-5.3962872	1.9456235
C	-1.2397736	2.7452755	-1.3572851
C	-2.5066889	2.0917709	-1.9553477

C	-1.3824409	4.2800204	-1.3234353
H	-0.3774554	2.4896406	-1.9998666
C	-2.7914320	2.6452815	-3.3590950
H	-3.3680298	2.3143140	-1.3030763
H	-2.3989118	0.9983026	-1.9866926
C	-1.6882471	4.8258536	-2.7287083
H	-2.1991749	4.5627634	-0.6373863
H	-0.4661634	4.7501966	-0.9433226
C	-2.9305492	4.1709266	-3.3398970
H	-3.7037621	2.1766529	-3.7558714
H	-1.9690004	2.3560771	-4.0356106
H	-1.8109056	5.9174528	-2.6724378
H	-0.8172083	4.6397615	-3.3797141
H	-3.1003849	4.5536607	-4.3568206
H	-3.8194183	4.4485378	-2.7472252
C	0.5436032	2.9301963	1.1231343
C	1.7539763	3.1206679	0.1890033
C	0.1410279	4.2431164	1.8257114
H	0.8473678	2.2253421	1.9172758
C	2.9419399	3.7146003	0.9583032
H	1.4780927	3.8020660	-0.6324085
H	2.0312252	2.1604745	-0.2734374
C	1.3485877	4.8175105	2.5856856
H	-0.2079777	4.9809701	1.0892310
H	-0.6895866	4.0739069	2.5260812
C	2.5559342	5.0204510	1.6631121
H	3.7811621	3.8801048	0.2673188
H	3.2884442	2.9826631	1.7070151
H	1.0612989	5.7655745	3.0637731
H	1.6240908	4.1249716	3.4003465
H	3.4095525	5.4112070	2.2358739
H	2.3102811	5.7845603	0.9060790
C	0.8149443	-0.4040043	2.9288861
C	0.8941754	-1.2919236	4.1878713

C	2.2270042	0.0218449	2.4849441
H	0.2568689	0.5141322	3.2072524
C	1.6004400	-0.5312728	5.3228582
H	1.4658489	-2.2034521	3.9472922
H	-0.1024841	-1.6155344	4.5200608
C	2.9182119	0.7977674	3.6139408
H	2.8217662	-0.8730814	2.2496049
H	2.1859154	0.6107493	1.5582989
C	2.9884311	-0.0365288	4.8990558
H	1.6755610	-1.1802122	6.2075034
H	0.9755942	0.3299250	5.6179590
H	3.9267136	1.0980339	3.2936548
H	2.3609070	1.7319735	3.8092686
H	3.4464140	0.5473489	5.7105658
H	3.6467566	-0.9052273	4.7276772
C	-1.9073381	-1.2352596	2.3380588
H	-2.6146857	-1.5917768	1.5797532
H	-1.8850288	-1.9376000	3.1803234
H	-2.2387586	-0.2570817	2.7026422
C	-2.2802367	2.1701820	1.3456885
H	-3.0636347	1.4798166	1.0152593
H	-2.0128367	1.9551663	2.3879226
H	-2.6503462	3.2024577	1.2880052

Compound **21**$^{+}$

C	-2.0099862	-2.6694794	-0.0002198
C	-0.6002997	-2.7568588	-0.0000622
C	0.1573870	-1.6140897	-0.0000868
C	-1.8172307	-0.2843641	-0.0001664
C	-2.6218075	-1.4289848	-0.0003070
H	-2.6157236	-3.5743046	-0.0002949
H	-0.0983035	-3.7226910	0.0000552
H	1.2460479	-1.6138909	-0.0000343

H	-3.7059228	-1.3403756	-0.0005069
C	-1.1353434	1.9403403	-0.0000751
C	-1.4250429	3.3274888	-0.0000647
C	-2.7267316	3.7639381	0.0001074
C	-3.7928563	2.8200140	0.0002074
C	-3.5281891	1.4836533	0.0000230
H	-0.5938867	4.0320950	-0.0001486
H	-2.9486757	4.8302757	0.0001951
H	-4.8300065	3.1490044	0.0004393
H	-4.3008945	0.7206250	-0.0000081
N	-2.2142521	1.0407930	-0.0001053
N	-0.4422383	-0.3742863	-0.0000969
P	0.4290810	1.1585869	0.0001106

Compound **23**$^{+}$

C	-1.9582353	-2.7225911	-0.0004410
C	-0.5433378	-2.7567666	0.0006098
C	0.1789512	-1.5922667	0.0005197
C	-1.8561901	-0.3161089	-0.0008412
C	-2.6061457	-1.5043280	-0.0012192
H	-2.5275487	-3.6506011	-0.0005272
H	-0.0071500	-3.7043089	0.0016150
H	1.2675228	-1.5636462	0.0008094
H	-3.6931110	-1.4423787	-0.0021005
C	-1.4266177	3.2712116	-0.0007351
C	-2.7003078	3.7766804	0.0004112
C	-3.8166905	2.9066524	0.0010327
C	-3.6119989	1.5420610	0.0000806
H	-0.5349991	3.8962508	-0.0010621
H	-2.8340642	4.8571641	0.0009751
H	-4.8266386	3.3132737	0.0021531
H	-4.4485136	0.8453169	0.0001904
N	-0.4647727	-0.3725135	-0.0002160
P	0.3545457	1.1624824	-0.0005701

C	-2.3019479	1.0340561	-0.0007882
N	-1.2176252	1.9078496	-0.0009353

Intermediate **22**$^{2+}$

P	-0.5006974	1.2624899	1.2678195
P	0.9903504	-0.2712119	1.5521942
C	0.3572523	2.6722820	2.1280042
C	1.7136624	2.9891819	1.9858654
N	-0.3640749	3.3889228	3.0527263
C	2.3069192	3.9896708	2.7486105
H	2.3082388	2.4168547	1.2748373
C	0.2055826	4.3518684	3.8347468
C	1.5399193	4.6741564	3.7008203
H	3.3613928	4.2312705	2.6134995
H	-0.4639420	4.8504843	4.5331169
H	1.9663695	5.4555176	4.3273799
P	-0.4132125	2.0421405	-0.8870687
P	-0.5188521	-1.7828548	1.9681904
C	-2.1596633	2.1042671	-1.3812798
H	-2.2543542	2.4771704	-2.4091998
H	-2.5907867	1.0961228	-1.3204542
H	-2.6950774	2.7673967	-0.6908425
C	-1.5127931	-1.4362009	3.4569346
H	-2.0988565	-0.5222541	3.2927315
H	-2.1910824	-2.2717693	3.6727783
H	-0.8331763	-1.2825096	4.3033634
C	0.3259257	3.7110719	-1.1451409
C	0.4845363	4.0689392	-2.6419239
C	-0.4592854	4.8169544	-0.4109712
H	1.3341591	3.6315034	-0.7006632
C	1.1974512	5.4249983	-2.7823614
H	-0.5106232	4.1245856	-3.1129023
H	1.0520957	3.2962681	-3.1770813

C	0.2686136	6.1620843	-0.5475701
H	-1.4632030	4.9026840	-0.8585237
H	-0.6226737	4.5673459	0.6451901
C	0.4710605	6.5374927	-2.0198897
H	1.2806730	5.6771651	-3.8491507
H	2.2286767	5.3255167	-2.4025298
H	-0.3039942	6.9416376	-0.0245088
H	1.2481596	6.0949850	-0.0419101
H	1.0308907	7.4795772	-2.1006864
H	-0.5131149	6.7181243	-2.4849753
C	0.4474465	0.7348629	-1.8422596
C	-0.0346174	0.5465578	-3.2950663
C	1.9794279	0.8879334	-1.7474059
H	0.1824300	-0.1785526	-1.2734727
C	0.6813124	-0.6604612	-3.9225435
H	0.1800691	1.4492184	-3.8871584
H	-1.1234984	0.3930089	-3.3284477
C	2.6656689	-0.3272628	-2.3873093
H	2.2986066	1.8053893	-2.2668983
H	2.2916774	0.9806172	-0.6946153
C	2.2056484	-0.5261054	-3.8360946
H	0.3587229	-0.7685880	-4.9679179
H	0.3625714	-1.5769710	-3.3982025
H	3.7565349	-0.1996525	-2.3394374
H	2.4249167	-1.2241374	-1.7912552
H	2.6882334	-1.4140719	-4.2678306
H	2.5335172	0.3335180	-4.4456156
C	-1.6935122	-1.9707912	0.5455375
C	-1.0249827	-2.6839195	-0.6445458
C	-3.0735842	-2.5756798	0.8699557
H	-1.8671213	-0.9150329	0.2544471
C	-1.9335222	-2.6168668	-1.8791737
H	-0.8459248	-3.7397252	-0.3851764
H	-0.0376640	-2.2426679	-0.8592626

C	-3.9705149	-2.5200270	-0.3782006
H	-2.9610413	-3.6210499	1.1955005
H	-3.5537816	-2.0325988	1.6963060
C	-3.3177595	-3.2059384	-1.5834649
H	-1.4598575	-3.1442807	-2.7194510
H	-2.0402744	-1.5613250	-2.1906416
H	-4.9428018	-2.9803615	-0.1508631
H	-4.1756768	-1.4623127	-0.6240137
H	-3.9657635	-3.1194004	-2.4669244
H	-3.2141513	-4.2846875	-1.3779988
C	0.4235688	-3.3399251	2.2587069
C	1.4458356	-3.1840360	3.4064980
C	-0.4888259	-4.5632446	2.4912002
H	0.9801777	-3.4889335	1.3153488
C	2.2795577	-4.4657132	3.5577090
H	0.9072596	-2.9909061	4.3498354
H	2.1044957	-2.3206468	3.2286962
C	0.3581462	-5.8364519	2.6523325
H	-1.0879743	-4.4072246	3.4041568
H	-1.1955596	-4.6922983	1.6595994
C	1.3883417	-5.6930952	3.7771507
H	2.9842046	-4.3427291	4.3926133
H	2.8890729	-4.6081570	2.6493422
H	-0.3076659	-6.6905980	2.8410180
H	0.8759366	-6.0446385	1.7004502
H	2.0032660	-6.6015748	3.8452106
H	0.8643053	-5.5973273	4.7436769
C	-1.8044266	3.1658399	3.2068622
C	-2.2926316	2.6929657	4.4212401
C	-3.6785286	2.5338508	4.5234097
H	-1.6235676	2.4510641	5.2467287
C	-3.8641024	3.3201425	2.2579352
C	-4.4775547	2.8550705	3.4260186

H	-4.1213799	2.1679414	5.4497316
H	-4.4581935	3.5884494	1.3821228
H	-5.5614283	2.7548146	3.4716041
N	-2.5355370	3.4762676	2.1420211

Intermediate *iso*-**22**$^{2+}$

P	-0.3889022	0.7938844	1.1657662
P	1.2378044	-0.5022780	1.7842143
C	0.1936946	2.2817935	2.0350552
C	0.9672335	2.3701924	3.2176666
N	-0.2120832	3.4913715	1.4964569
C	1.2896637	3.5860124	3.7905068
H	1.2942571	1.4445852	3.6889751
C	0.0815934	4.7006766	2.0619661
C	0.8341038	4.7847560	3.2072713
H	1.8769708	3.6147132	4.7087590
H	-0.3112202	5.5679122	1.5342233
H	1.0563388	5.7579889	3.6391469
P	2.5797070	-0.6772488	-0.0575596
P	0.1326356	-2.4092171	2.0469842
C	3.1149505	-2.3501414	-0.5292495
H	3.8050554	-2.2656878	-1.3801308
H	3.6375754	-2.8295271	0.3071653
H	2.2568867	-2.9603393	-0.8298176
C	-0.6156608	-2.1195725	3.6771491
H	-1.2529364	-1.2276107	3.6296918
H	-1.2226422	-2.9895192	3.9572263
H	0.1752055	-1.9676624	4.4217189
C	1.7841284	0.1432607	-1.4917811
C	2.7586559	0.4832826	-2.6399477
C	0.5852420	-0.6777004	-2.0053243
H	1.3938063	1.0855888	-1.0613835
C	2.0067893	1.2474330	-3.7429454
H	3.1863399	-0.4429869	-3.0585530
H	3.5962929	1.0931158	-2.2772072

C	-0.1541537	0.0912381	-3.1082494
H	0.9402407	-1.6401761	-2.4103250
H	-0.1092575	-0.8970502	-1.1813548
C	0.7900409	0.4690121	-4.2548891
H	2.7014975	1.4660343	-4.5662936
H	1.6844356	2.2193967	-3.3337284
H	-0.9910364	-0.5183515	-3.4800641
H	-0.5942890	0.9995886	-2.6649051
H	0.2535093	1.0598988	-5.0108076
H	1.1314749	-0.4480662	-4.7642539
C	4.0609341	0.2416362	0.5527361
C	5.3647832	-0.0275821	-0.2286450
C	3.7576643	1.7508019	0.6782337
H	4.1915287	-0.1663247	1.5738137
C	6.5312572	0.7297875	0.4286463
H	5.2574180	0.3031435	-1.2725028
H	5.5909054	-1.1034982	-0.2524455
C	4.9444022	2.4836168	1.3199045
H	3.5640104	2.1737255	-0.3207871
H	2.8454643	1.9185150	1.2714339
C	6.2417285	2.2301266	0.5443710
H	7.4460790	0.5537383	-0.1545723
H	6.7135087	0.3105127	1.4331385
H	4.7226196	3.5596311	1.3663077
H	5.0628997	2.1381577	2.3612663
H	7.0828823	2.7404069	1.0340079
H	6.1559440	2.6675783	-0.4650329
C	-1.2022853	-2.7249988	0.8041326
C	-0.7057886	-3.5847782	-0.3742133
C	-2.5051496	-3.2987579	1.4032164
H	-1.4348015	-1.7108879	0.4288675
C	-1.7856895	-3.6627887	-1.4631187
H	-0.4760666	-4.6017996	-0.0182126

H	0.2218208	-3.1737247	-0.7962093
C	-3.5769629	-3.3968017	0.3035773
H	-2.3165928	-4.2985059	1.8273019
H	-2.8750294	-2.6622898	2.2192261
C	-3.0972458	-4.2189615	-0.8971710
H	-1.4233193	-4.2869218	-2.2926599
H	-1.9549356	-2.6525825	-1.8752757
H	-4.4902976	-3.8330246	0.7317664
H	-3.8405452	-2.3775746	-0.0274196
H	-3.8705661	-4.2355016	-1.6779962
H	-2.9445135	-5.2669342	-0.5881370
C	1.2845192	-3.8372951	2.1807020
C	2.5454169	-3.5150042	3.0071423
C	0.5703455	-5.0946179	2.7288247
H	1.5883792	-4.0450179	1.1404057
C	3.5010380	-4.7182684	3.0032607
H	2.2565849	-3.2822060	4.0455740
H	3.0548059	-2.6178858	2.6206290
C	1.5371101	-6.2899077	2.7219916
H	0.2370676	-4.9041910	3.7618408
H	-0.3266375	-5.3303387	2.1376729
C	2.8102747	-5.9865174	3.5176665
H	4.3853900	-4.4834985	3.6127726
H	3.8630901	-4.8893939	1.9737024
H	1.0232487	-7.1700924	3.1333150
H	1.7977937	-6.5373491	1.6786757
H	3.5009244	-6.8395717	3.4672734
H	2.5546165	-5.8548473	4.5827929
C	-0.9440240	3.5207843	0.2278465
C	-2.3351939	3.5781699	0.2413953
C	-2.9775925	3.6639467	-0.9971198
H	-2.8888296	3.5589038	1.1795086
C	-0.8090421	3.6387751	-2.0363129
C	-2.2013974	3.6955717	-2.1556512

H	-4.0649399	3.7166773	-1.0502711
H	-0.1716559	3.6777371	-2.9218782
H	-2.6628052	3.7760851	-3.1394698
N	-0.1739310	3.5503783	-0.8563128

Transition state (scheme 10 in the article)

N_{imag} = -119.21 cm^{-1}

P	-0.3332554	1.2716419	0.7856088
P	0.9685151	-0.3885633	0.1370901
C	0.8280909	2.3544483	1.7079529
C	2.1449855	2.0065593	2.0599557
N	0.3781690	3.5871273	2.1427587
C	2.9396733	2.8426611	2.8290500
H	2.5305306	1.0512279	1.6986686
C	1.1604643	4.4375905	2.8691856
C	2.4433195	4.0929445	3.2336968
H	3.9504243	2.5390098	3.1030383
H	0.7030171	5.3922209	3.1233533
H	3.0450298	4.7940248	3.8085663
P	-0.2197378	0.7110561	-1.6895100
P	0.2066058	-2.0019108	1.4729181
C	-1.4709718	2.0171899	-2.0116739
H	-1.6600854	2.1055346	-3.0892216
H	-2.4069419	1.7721651	-1.4939599
H	-1.0792459	2.9570089	-1.6056096
C	0.3768124	-1.3702597	3.1703664
H	-0.1631465	-0.4189044	3.2647756
H	-0.0508404	-2.0936610	3.8762099
H	1.4380717	-1.2197832	3.4004375
C	1.3343339	1.3074943	-2.5111258
C	1.0731270	1.6944071	-3.9855741
C	2.0153862	2.4623434	-1.7495865
H	2.0055470	0.4326197	-2.4937112

C	2.3944159	2.0910395	-4.6658813
H	0.3789895	2.5487040	-4.0293961
H	0.6048234	0.8656500	-4.5343298
C	3.3144794	2.8840010	-2.4549515
H	1.3259638	3.3209882	-1.6858458
H	2.2422560	2.1594291	-0.7176854
C	3.0778379	3.2433159	-3.9250450
H	2.1884727	2.3659062	-5.7104657
H	3.0651798	1.2156441	-4.6964362
H	3.7605483	3.7317975	-1.9149444
H	4.0395863	2.0541349	-2.3919749
H	4.0307362	3.4963074	-4.4111719
H	2.4444629	4.1442851	-3.9869706
C	-0.9082823	-0.8021637	-2.5618914
C	-1.8720422	-0.5058918	-3.7317628
C	0.2149614	-1.7688475	-2.9819949
H	-1.5069343	-1.2817181	-1.7664464
C	-2.4180067	-1.8209378	-4.3158336
H	-1.3503362	0.0521592	-4.5248233
H	-2.7116239	0.1168415	-3.3953889
C	-0.3460381	-3.0595469	-3.6035738
H	0.8602360	-1.2747566	-3.7265387
H	0.8597012	-2.0122953	-2.1203125
C	-1.2913852	-2.7518168	-4.7679803
H	-3.0913487	-1.5862839	-5.1525533
H	-3.0312356	-2.3276597	-3.5500141
H	0.4906153	-3.6928598	-3.9323922
H	-0.8937865	-3.6348150	-2.8382077
H	-1.7059269	-3.6842814	-5.1764553
H	-0.7258247	-2.2755135	-5.5870437
C	-1.5739498	-2.3719080	1.1375342
C	-1.7121923	-3.3899722	-0.0098771
C	-2.4173609	-2.7900798	2.3575791
H	-1.9592415	-1.3953619	0.7882285

C	-3.1815044	-3.5146010	-0.4322718
H	-1.3516159	-4.3746205	0.3277564
H	-1.0826143	-3.1050220	-0.8652518
C	-3.8892730	-2.9422229	1.9329121
H	-2.0468602	-3.7447969	2.7621399
H	-2.3420104	-2.0449933	3.1630725
C	-4.0573359	-3.9164320	0.7604687
H	-3.2701427	-4.2489044	-1.2465662
H	-3.5269573	-2.5474549	-0.8397643
H	-4.4820627	-3.2742832	2.7971117
H	-4.2804833	-1.9506066	1.6464180
H	-5.1130053	-3.9650573	0.4591763
H	-3.7788138	-4.9331028	1.0854472
C	1.2531139	-3.5045059	1.2945621
C	2.7581747	-3.1780309	1.4037649
C	0.8520771	-4.6193566	2.2863455
H	1.0476014	-3.8534105	0.2661662
C	3.5961697	-4.4451865	1.1685462
H	2.9765535	-2.7847783	2.4116506
H	3.0410166	-2.3957419	0.6826265
C	1.7030336	-5.8765095	2.0428351
H	1.0157735	-4.2646715	3.3176136
H	-0.2154466	-4.8645561	2.1959536
C	3.2013073	-5.5687125	2.1331506
H	4.6625660	-4.1993204	1.2739268
H	3.4525304	-4.7824290	0.1278373
H	1.4201691	-6.6491318	2.7718691
H	1.4664736	-6.2834558	1.0448643
H	3.7870598	-6.4737936	1.9198501
H	3.4522223	-5.2707646	3.1655161
C	-0.9774754	4.0396552	1.8298864
C	-1.8825349	4.2332928	2.8709483
C	-3.1473476	4.7192380	2.5289446

H	-1.6128793	4.0096626	3.9029131
C	-2.4379815	4.7339386	0.2320290
C	-3.4287268	4.9784270	1.1873676
H	-3.8964613	4.8925740	3.3014828
H	-2.6221547	4.9259485	-0.8270512
H	-4.3992403	5.3676017	0.8815169
N	-1.2164812	4.2696309	0.5435514

5. X-ray Diffraction Refinements

Suitable single crystals were coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using either a glass fiber or a nylon loop and frozen in the cold nitrogen stream. Crystals were measured at low temperature on several diffractometers. Crystal and data collection details are given in Tables 1-6 including information about the used diffractometer. Data reduction and absorption correction was performed either with CrysaAlisPro[8] software or Bruker SMART[9] or Bruker SADABS[10]. Using Olex2,[11] the structures were solved with SHELXS/T[12] by direct methods and refined with SHELXL[13] by least-square minimization against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were added to the structure models on calculated positions using the riding model. All other hydrogen atoms were localized in the difference Fourier map. Images of the structures were produced with Olex2[11] software.

Table 1: Crystallographic data and details of the structure refinements of **7**, **8** and **9a**.

	7	**8**	**9a**
formula	$C_{15}H_{18}N_5P$	$C_{17}H_{18}N_5PS$	$C_{27}H_{48}NP_3$
M_r in g mol^{-1}	299.31	355.39	503.59
color, habit	Clear colourless, block	colourless, block	Colourless, needle
crystal system	Triclinic	Monoclinic	Monoclinic
space group	P-1	$P2_1/m$	$P2_1/c$
a in Å	8.4080(3)	7.03718(11)	11.06652(11)
b in Å	8.7414(2)	13.3782(2)	23.6010(3)
c in Å	24.3551(7)	8.85308(16)	10.85205(11)
α in °	89.776(2)	90	90
β in °	85.729(3)	98.7503(16)	99.7411(10)
γ in °	61.439(3)	90	90
V in Å^3	1566.81(9)	823.77(2)	2793.48(5)
Z	4	2	4
T in K	100.01(10)	100.00(10)	100.01(10)
crystal size in mm^3	0.623 x 0.575 x 0.278	0.123 x 0.074 x 0.023	0.292 x 0.065 x 0.05
ρ_c in g cm^{-3}	1.269	1.433	1.197
F(000)	632.0	372.0	1096.0
diffractometer	Super Nova	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Cu 1.54184	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	7.284 153.212	10.11 152.746	7.492 152.996
index range	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-30 \leq l \leq 29$	$-8 \leq h \leq 8$ $-14 \leq k \leq 16$ $-9 \leq l \leq 11$	$-13 \leq h \leq 7$ $-29 \leq k \leq 29$ $-13 \leq l \leq 13$
μ in mm^{-1}	1.559	2.733	2.069
abs. correction	Gaussian	Gaussian	Gaussian
reflections collected	14923	3923	14711
reflections unique	6482	1774	5806
R_{int}	0.0200	0.0201	0.0243
reflections obs. [$F>2\sigma(F)$]	6309	1676	5416
residual density in e Å^{-3}	0.31, –0.42	0.47, –0.32	0.33, –0.26
parameters	523	126	490
GOOF	1.054	1.111	1.039
R_1 [$I>2\sigma(I)$]	0.0325	0.0284	0.0277
wR_2 (all data)	0.0859	0.0748	0.0688
CCDC	1950469	1950473	1950471

Table 2: Crystallographic data and details of the structure refinements of **9b**, **9c** and **9d**.

	9b	**9c**	**9d**
formula	$C_{31}H_{48}NP_3S$	$C_{21}H_{40}NP_3$	$C_{19}H_{18}NP_3$
M_r in g mol^{-1}	559.67	399.45	353.25
color, habit	Yellow, plate	Clear, colourless, block	Clear, colourless, block
crystal system	Triclinic	Triclinic	Orthorombic
space group	P-1	P-1	$Pna2_1$
a in Å	16.0052(2)	7.9088(3)	26.5691(4)
b in Å	17.2802(2)	11.2925(4)	10.80809(17)
c in Å	23.3958(3)	14.4882(6)	5.99320(10)
α in °	104.8628(12)	73.202(3)	90
β in °	100.6013(12)	86.167(3)	90
γ in °	90.2605(12)	72.923(3)	90
V in Å^3	6138.29(16)	1183.90(8)	1721.01(5)
Z	8	2	4
T in K	100.00(10)	100.01(10)	100.01(10)
crystal size in mm^3	0.136 x 0.08 x 0.039	0.397 x 0.18 x 0.081	0.408 x 0.301 x 0.115
ρ_c in g cm^{-3}	1.211	1.121	1.363
F(000)	2416.0	436.0	736.0
diffractometer	Super Nova	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Cu 1.54184	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	3.982 153.556	6.374 153.842	6.654 154.09
index range	$-19 \le h \le 20$ $-17 \le k \le 21$ $-29 \le l \le 29$	$-9 \le h \le 9$ $-14 \le k \le 13$ $-17 \le l \le 18$	$-33 \le h \le 32$ $-13 \le k \le 13$ $-7 \le l \le 7$
μ in mm^{-1}	2.555	2.319	3.145
abs. correction	Multi-scan	Gaussian	Gaussian
reflections collected	72032	14550	20567
reflections unique	25591	4930	3535
R_{int}	0.0333	0.0125	0.0280
reflections obs. [F>2σ(F)]	21917	4861	3531
residual density in e Å^{-3}	0.47, –0.55	0.35, –0.26	0.84, –0.39
parameters	1380	238	209
GOOF	1.012	1.057	1.116
R_1 [I>2σ(I)]	0.0336	0.0265	0.0479
wR_2 (all data)	0.0858	0.0692	0.1291
CCDC	1950484	1950474	1950481

Table 3: Crystallographic data and details of the structure refinements of **10**[OTf], **11**$[OTf]_2$, and **13**.

	10[OTf]	**11**$[OTf]_2$	**13**
formula	$C_{31}H_{51}F_3NO_3P_3S$	$C_{33}H_{54}F_6NO_6P_3S_2$	$C_{25}H_{20}N_5P_5$
M_r in g mol^{-1}	667.69	831.80	545.31
color, habit	Yellow, block	Colourless, block	Colourless, block
crystal system	Triclinic	Monoclinic	Monoclinic
space group	P-1	$P2_1/n$	$P2_1/n$
a in Å	10.9026(4)	13.83650(10)	8.88106(6)
b in Å	12.5147(3)	21.99929(12)	19.32439(15)
c in Å	14.0376(4)	13.99782(10)	14.68865(11)
α in °	74.779(3)	90	90
β in °	67.319(3)	109.4646(8)	92.3033(7)
γ in °	84.620(2)	90	90
V in $Å^3$	1705.17(10)	4017.32(5)	2518.84(3)
Z	2	4	4
T in K	100.00(10)	99.97(12)	100.01(10)
crystal size in mm^3	0.192 x 0.118 x 0.054	0.22 x 0.115 x 0.065	0.265 x 0.202 x 0.101
ρ_c in g cm^{-3}	1.300	1.375	1.438
F(000)	712.0	1752.0	1120.0
diffractometer	Super Nova	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Cu 1.54184	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	7.042 153.3	7.782 153.374	7.564 153.066
index range	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-15 \leq l \leq 17$	$-14 \leq h \leq 17$ $-27 \leq k \leq 23$ $-17 \leq l \leq 17$	$-11 \leq h \leq 11$ $-22 \leq k \leq 24$ $-18 \leq l \leq 18$
μ in mm^{-1}	2.581	2.944	3.577
abs. correction	Gaussian	Gaussian	Gaussian
reflections collected	16998	44324	14356
reflections unique	7087	8432	5232
R_{int}	0.0252	0.0272	0.0206
reflections obs. [F>2σ(F)]	6566	8188	5073
residual density in e $Å^{-3}$	0.75, –0.47	0.57, –0.47	0.30, –0.27
parameters	380	462	396
GOOF	1.018	1.027	1.038
R_1 [I>2σ(I)]	0.0365	0.0313	0.0258
wR_2 (all data)	0.1003	0.0838	0.0677
CCDC	1950475	1950482	1950478

Table 4: Crystallographic data and details of the structure refinements of **18** * 0.5 CH_2Cl_2, **19**[OTf]$_2$ and **20**[OTf].

	18 * 0.5 CH_2Cl_2	**19**[OTf]$_2$	**20**[OTf]
formula	$C_{35.5}H_{21}ClN_5P_5S_5$	$C_{38}H_{58}F_6N_2O_6P_4S_2$	$C_{27}H_{50}F_3O_3P_3N$
M_r in g mol^{-1}	868.17	940.86	604.64
color, habit	Colourless, block	Clear colourless, needle	Clear yellow, block
crystal system	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1
a in Å	10.2485(3)	9.5582(7)	12.4338(41)
b in Å	12.3713(3)	9.6936(8)	12.5077(3)
c in Å	15.6969(4)	11.8527(8)	13.0479(4)
α in °	112.462(2)	87.895(6)	114.387(3)
β in °	90.355(2)	80.107(6)	96.369(2)
γ in °	99.439(2)	86.923(6)	116.073(3)
V in Å^3	1809.09(8)	1079.88(14)	1550.40(9)
Z	2	1	2
T in K	100.00(10)	100.01(10)	100.01(10)
crystal size in mm^3	0.135 x 0.081 x 0.052	0.229 x 0.048 x 0.036	0.226 x 0.105 x 0.092
ρ_c in g cm^{-3}	1.594	1.447	1.295
F(000)	882.0	494.0	648.0
diffractometer	Super Nova	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Cu 1.54184	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	6.11 153.416	7.574 136.62	7.966 153.428
index range	$-12 \leq h \leq 10$ $-15 \leq k \leq 15$ $-19 \leq l \leq 19$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-14 \leq l \leq 14$	$-15 \leq h \leq 15$ $-14 \leq k \leq 15$ $-16 \leq l \leq 14$
μ in mm^{-1}	6.032	3.155	2.770
abs. correction	Multi-scan	Analytical	Gaussian
reflections collected	22889	7302	15021
reflections unique	7537	7302	6454
R_{int}	0.0229	0.0953	0.0248
reflections obs. [F>2σ(F)]	7164	5821	5907
residual density in e Å^{-3}	0.89, –0.48	1.39, –0.42	0.43, –0.40
parameters	478	328	336
GOOF	1.025	0.998	1.035
R_1 [I>2σ(I)]	0.0333	0.0700	0.0281
wR_2 (all data)	0.0884	0.1893	0.0729
CCDC	1950477	1950486	1950483

Table 5: Crystallographic data and details of the structure refinements of **21**[OTf], (**9a**)$_2$*CuOTf and (**9a***CuBr)$_2$ * 0.82 THF * 0.93 C_5H_{12}.

	21[OTf]	(**9a**)$_2$*CuOTf	(**9a***CuBr)$_2$ * 0.82 THF * 0.93 C_5H_{12}
formula	$C_{11}H_8F_3N_2O_3PS$	$C_{64}H_{108}CuF_3N_2O_3P_6S$	$C_{65.92}H_{113.69}Br_2Cu_2N_2O_{0.82}P_6$
M_r in g mol^{-1}	336.22	1191.94	1420.29
color, habit	yellow, parallelepiped	Clear colourless, block	Clear colourless, block
crystal system	triclinic	Monoclinic	Triclinic
space group	*P*-1	$P2_1/n$	P-1
a in Å	7.2241(5)	10.16325(10)	10.85215(11)
b in Å	9.0577(7)	25.8990(2)	17.65905(19)
c in Å	10.9162(8)	26.5556(3)	19.63512(16)
α in °	95.055(3)	90	102.4758(8)
β in °	99.126(3)	99.3487(10)	101.6435(8)
γ in °	109.450(3)	90	98.8895(9)
V in Å^3	657.34(8)	6897.07(12)	3520.31(5)
Z	2	4	2
T in K	100.0	100.01(10)	100.01(10)
crystal size in mm^3	0.19 x 0.12 x 0.06	0.36 x 0.208 x 0.144	0.221 x 0.067 x 0.042
ρ_c in g cm^{-3}	1.699	1.244	1.340
F(000)	340.0	2768.0	1496.0
diffractometer	Bruker APEX II	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Mo 0.71073	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	3.822 60.246	6.746 153.264	4.752 153.292
index range	$-10 \leq h \leq 10$ $-10 \leq k \leq 12$ $-15 \leq l \leq 13$	$-12 \leq h \leq 12$ $-32 \leq k \leq 32$ $-33 \leq l \leq 31$	$-13 \leq h \leq 8$ $-22 \leq k \leq 22$ $-24 \leq l \leq 24$
μ in mm^{-1}	0.415	2.453	3.660
abs. correction	multi-scan	Gaussian	Gaussian
reflections collected	8822	41516	38405
reflections unique	3836	14152	14673
R_{int}	0.0175	0.0247	0.0289
reflections obs. [F>2σ(F)]	3277	13572	13137
residual density in e Å^{-3}	0.59, –0.30	0.89, –0.58	0.90, –0.59
parameters	190	843	814
GOOF	1.044	1.12	1.025
R_1 [I>2σ(I)]	0.0340	0.0529	0.0353
wR_2 (all data)	0.0915	0.1311	0.0970
CCDC	1950480	1950479	1950470

Table 6: Crystallographic data and details of the structure refinements of (**9a***CuOTf)$_2$, (**9a***AgOTf)$_2$ and (**9a***AuOTf)$_2$.

	(**9a***CuOTf)$_2$	(**9a***AgOTf)$_2$	(**9a***AuOTf)$_2$
formula	$C_{64}H_{104}Cl_8Cu_2F_6N_2O_6P_6S_2$	$C_{64}H_{102}Ag_2F_6N_4O_6P_6S_2$	$C_{60}H_{96}Au_2F_6N_2O_6P_6S_2$
M_r in g mol^{-1}	1772.11	1603.17	1699.26
color, habit	Clear colourless, plate	Colourless, block	Clear colourless, irregular
crystal system	Triclinic	Monoclinic	Monoclinic
space group	P-1	P2$_1$/c	C2/c
a in Å	12.3686(3)	12.1473(3)	21.8614(6)
b in Å	13.7415(3)	15.0565(4)	16.4069(4)
c in Å	13.9572(3)	20.4248(7)	26.8718(6)
α in °	113.879(2)	90	90
β in °	109.229(2)	102.677(3)	115.147(3)
γ in °	93.1122(18)	90	90
V in Å^3	1999.20(9)	3644.55(18)	8724.8(4)
Z	1	2	4
T in K	100.01(10)	99.97(13)	100.00(11)
crystal size in mm^3	0.307 x 0.194 x 0.047	0.095 x 0.035 x 0.022	0.318 x 0.27 x 0.192
ρ_c in g cm^{-3}	1.472	1.461	1.294
F(000)	920.0	1664.0	3408.0
diffractometer	Super Nova	Super Nova	Super Nova
$\lambda_{XK\alpha}$ in Å	X = Cu 1.54184	X = Cu 1.54184	X = Cu 1.54184
θ_{min} in ° θ_{max} in °	7.208 153.02	7.358 144.254	6.956 153.546
index range	$-13 \leq h \leq 15$ $-17 \leq k \leq 16$ $-14 \leq l \leq 17$	$-14 \leq h \leq 14$ $-10 \leq k \leq 10$ $-25 \leq l \leq 25$	$-26 \leq h \leq 26$ $-16 \leq k \leq 20$ $-29 \leq l \leq 33$
μ in mm^{-1}	5.255	6.637	8.144
abs. correction	Gaussian	Gaussian	Gaussian
reflections collected	19879	23315	23941
reflections unique	8310	7033	9046
R_{int}	0.0231	0.0464	0.0240
reflections obs. [F>2σ(F)]	7795	6108	8619
residual density in e Å^{-3}	0.88, –0.82	1.33, –0.88	1.41, –2.51
parameters	470	407	379
GOOF	1.063	1.026	1.104
R_1 [I>2σ(I)]	0.0323	0.0393	0.0353
wR_2 (all data)	0.0835	0.1065	0.0926
CCDC	1950472	1950476	1950485

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