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Supplementary Information for

Silver(I) and thallium(I) cations as unsupported bridges between two metal bases

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General Considerations. All manipulations were performed under an inert atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were distilled over alkali metals (in the case of dichloromethane P_2O_5 was used), degassed and stored over molecular sieves (4 Å) under argon. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored under argon over molecular sieves. NMR experiments were performed on Bruker Avance 500 (^{1}H: 500.1 MHz; ^{11}B{^{1}H}: 160.5 MHz; ^{13}C{^{1}H}: 125.8 MHz; ^{31}P{^{1}H}: 202.5 MHz, ^{195}Pt{^{1}H}: 107.5 MHz) or Bruker Avance 400 (^{1}H: 400.1 MHz; ^{13}C{^{1}H}: 100.6 MHz; ^{31}P{^{1}H}: 162.0 MHz) spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated to TMS. External standards were used for ^{31}P{^{1}H} (85% H_3PO_4), and ^{195}Pt{^{1}H} NMR spectra ($Na_2[PtCl_6]$ in D_2O). Infrared spectra were measured on a JASCO FT/IR-6200 spectrometer. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer and Leco Instruments CHNS 932 elemental analyzer. $[(Cy_3P)_2Pt]$ (**1**),[S1] $[(OC)_3(Me_3P)_2Fe]$ (**2**)[S2] and $Tl[BAr^{Cl}_4]$ were prepared according to published methods.[S3]

Synthesis of $Ag[BAr^{Cl}_4]$: $NaBAr^{Cl}_4$ (2.70 g, 4.37 mmol) was dissolved in 150 mL hot water and filtered into a dark Schlenk flask. A solution of $AgNO_3$ (2.20 g, 12.9 mmol, 3 equiv) in 10 mL water was added, at which point a colourless, light sensitive material precipitated. The very light sensitive solid was filtered in the dark and washed with hot water. The solid was taken up in acetone, the solvent removed under vacuum and the solid dried for two days at 120 °C under vacuum.

Synthesis of $[\{(Cy_3P)_2Pt\}_2(\mu\text{-}Ag)][BAr^{Cl}_4]$ (3): $Ag[BAr^{Cl}_4]$ (11 mg, 13 µmol) was added to a solution of $[(Cy_3P)_2Pt]$ (**1**) (20 mg, 26 µmol) in THF in a dark Young NMR tube, whereupon the colour of the solution changed to red and a dark solid precipitated. The solution was filtered and the solvent was removed under vacuum. The deep red residue was rinsed with pentane. Single crystals for X-ray diffraction were prepared by dissolving the precipitate in THF and crystallizing at −30 °C over 24 h. (28 mg, 23 µmol, 90%). ^{1}H NMR (400.1 MHz, d_8-THF): δ = 7.05−7.02 (m, 8H, C2+C6, Ar), 6.96−6.94 (m, 4H, C4, Ar), 2.23 (br d, $^3J_{HH}$ = 11 Hz, 24H, Cy), 2.19−2.11 (br m, 12H, *Cy*), 1.87 (br d, $^3J_{HH}$ = 12 Hz, 24H, Cy), 1.79–1.72 (m, 12H, Cy), 1.72–1.62 (m, 24H, Cy), 1.41–1.25 (br m, 36H, Cy) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, d_8-THF): δ = −7.8 ppm. ^{13}C{^{1}H} NMR (100.6 MHz, d_8-THF): δ = 165.4 (q, $^1J_{CB}$ = 50 Hz, C1, Ar), 133.9 (q, $^2J_{CB}$ = 2 Hz, C2+C6, Ar), 133.5 (q, $^3J_{CB}$ = 4 Hz, C3+C5, Ar), 123.5 (s, C4, Ar), 36.8 (vt, N = $|^1J_{PC}+^3J_{PC}|$ = 26 Hz, C1, Cy), 32.4 (s, C3 and C5, Cy), 28.2 (vt, N = $|^2J_{PC}+^4J_{PC}|$ = 12 Hz, C2 and C6, Cy), 26.9 (s, C4, Cy) ppm. ^{31}P{^{1}H} NMR (202.5 MHz, d_8-THF): δ = 57.4 ($^1J_{PPt}$ = 3174 Hz, $^2J_{PAg}$ = 3 Hz) ppm. ^{195}Pt{^{1}H} NMR (86.02 MHz, d_8-THF): δ = –4853 ($^1J_{PPt}$ = 3174 Hz) ppm. Elemental analysis (%) calculated for $C_{96}H_{144}AgBCl_8P_4Pt_2$: C 52.07; H 6.55; found: C 51.95; H 6.34.

Synthesis of $[\{(Cy_3P)_2Pt\}_2(\mu\text{-}Tl)][BAr^{Cl}_4]$ (4): $Tl[BAr^{Cl}_4]$ (11 mg, 13 µmol) was added to a solution of $[(Cy_3P)_2Pt]$ (**1**) (20 mg, 26 µmol) in THF in a dark Young NMR tube, whereupon the colour of the solution changed to red and a dark solid precipitated. The solution was filtered and the solvent was removed under vacuum. The deep red residue was rinsed with pentane. Single crystals for X-ray diffraction were prepared by dissolving the precipitate in THF and crystallization at −30 °C over 24 h. (28 mg, 23 µmol, 90%). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 7.05−7.02 (m, 8H, C2+C6, Ar), 7.01−6.99 (m, 4H, C4, Ar), 2.05 (br d, $^3J_{HH}$ = 11 Hz, 24H, Cy), 1.99−1.93 (br m, 12H, *Cy*), 1.85 (br d, $^3J_{HH}$ = 12 Hz, 24H, Cy), 1.74 (br d, $^3J_{HH}$ = 12 Hz, 12H, Cy), 1.57–1.44 (br m, 24H, Cy), 1.35–1.22 (br m, 36H, Cy) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, CD_2Cl_2): δ = −7.0 ppm. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ = 165.1 (q, $^1J_{CB}$ = 49 Hz, C1, Ar), 133.5 (m, $^2J_{CB}$ = 2 Hz, C2+C6, Ar), 133.3 (q, $^3J_{CB}$ = 4 Hz, C3+C5, Ar), 123.4 (s, C4, Ar), 37.5 (vt, N = $|^1J_{PC}+^3J_{PC}|$ = 26 Hz, C1, Cy), 31.5 (s, C3 and C5, Cy), 27.9 (vt, N = $|^2J_{PC}+^4J_{PC}|$ = 12 Hz, C2 and C6, Cy), 26.8 ppm (s, C4, Cy) ppm. ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 57.9 ($^1J_{PPt}$ = 4040 Hz) ppm. ^{195}Pt{^{1}H} NMR (86.02 MHz, CD_2Cl_2): δ = –4697 ($^1J_{PPt}$ = 4040 Hz) ppm. Elemental analysis (%) calculated for $C_{96}H_{144}BCl_8P_4Pt_2Tl$: C 49.89; H 6.28; found: C 49.79; H 5.91.

Synthesis of $[\{(OC)_3(Me_3P)_2Fe\}_2(\mu\text{-}Ag)]$ (5): $Ag[BAr^{Cl}_4]$ (48 mg, 69 µmol) was dissolved in benzene and added to a solution of $[Fe(CO)_3(PMe_3)_2]$ (**2**) (40 mg, 137 µmol) in benzene in a dark Young NMR tube. Immediately a white solid precipitated, which was filtered and washed with benzene and pentane. The white solid was dried under vacuum and recrystallized in CH_2Cl_2 to yield a white crystalline solid (67 mg, 52 µmol, 76%). IR (CH_2Cl_2): 1988, 1926, 1902 (ν_{CO}) cm^{-1}. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 7.03−7.01 (m, 8H, C2+C6, Ar), 7.00−6.98 (m, 4H, C4, Ar), 1.69 (d, $^2J_{PH}$ = 8.8 Hz, 32H, PMe$_3$) ppm. ^{11}B{^{1}H} NMR (160.5 MHz, CD_2Cl_2): δ

= −7.8 ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ = 23.3 (d, $^2J_{PAg}$ = 17.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ = 214.1 (br, CO), 165.1 (q, $^1J_{CB}$ = 49 Hz, C1, Ar), 133.5 (m, $^2J_{CB}$ = 2 Hz, C2+C6, Ar), 133.3 (q, $^3J_{CB}$ = 4 Hz, C3+C5, Ar), 123.4 (s, C4, Ar), 22.7-23.1 (m, 12C, CH_3) ppm. Elemental analysis (%) calculated for $C_{42}H_{48}AgBCl_8P_4Fe_2O_6$: C 39.20; H 3.76; found: C 39.86; H 3.63.

General crystallographic details: The crystal data of **4**, **5** and **6** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques.[S4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1027225 (**3**), 1027226 (**4**) and 1027227 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal data for 3: $C_{103}H_{158}AgBCl_8OP_4Pt_2$, M_r = 2328.63, red block, 0.160×0.100×0.060 mm³, monoclinic space group $P2_1/c$, a = 23.5269(9) Å, b = 16.7472(7) Å, c = 27.9343(11) Å, β = 111.5480(10)°, V = 10237.1(7) Å³, Z = 4, ρ_{calcd} = 1.511 g·cm⁻³, μ = 3.233 mm⁻¹, $F(000)$ = 4752, T = 100(2) K, R_1 = 0.0317, wR^2 = 0.0526, 20925 independent reflections [2θ≤52.74°] and 1127 parameters.

Crystal data for 4: $C_{96}H_{144}BCl_8P_4Pt_2Tl$, M_r = 2310.94, red block, 0.15×0.10×0.08 mm³, monoclinic space group $P2_1/c$, a = 20.429(7) Å, b = 17.201(6) Å, c = 27.925(10) Å, β = 99.446(9)°, V = 9680(6) Å³, Z = 4, ρ_{calcd} = 1.586 g·cm⁻³, μ = 4.875 mm⁻¹, $F(000)$ = 4632, T = 100(2) K, R_1 = 0.0383, wR^2 = 0.0637, 19803 independent reflections [2θ≤52.744°] and 1165 parameters.

Crystal data for 5: $C_{42}H_{53}AgBCl_8P_4Fe_2O_6$ M_r = 1382.76, colourless plate, 0.195×0.079×0.057 mm³, Orthorhombic space group $Pbca$, a = 18.930(5) Å, b = 23.904(3) Å, c = 26.047(3) Å, V = 11786(4) Å³, Z = 8, ρ_{calcd} = 1.559 g·cm⁻³, μ = 1.333 mm⁻¹, $F(000)$ = 5584, T = 100(2) K, R_1 = 0.0587, wR^2 = 0.0677, 12550 independent reflections [2θ≤53.6°] and 692 parameters.

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