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Supporting Information

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SUPPORTING INFORMATION

Elementary Steps of Gold Catalysis. NMR Spectroscopy Reveals the Highly Cationic Character of a "Gold Carbenoid"

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Complex 4a. Prepared according to the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.6 – 7.5 (m, 3H), 7.51 – 7.46 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.1 (d, $^{2}J_{PC}$ = 13.9 Hz), 132.6 (d, $^{4}J_{PC}$ = 2.8 Hz), 129.6 (d, $^{3}J_{PC}$ = 12.2 Hz), 126.2 (d, J_{PC} = 66.2 Hz), 119.4 ppm (q, J_{CF} = 323 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): δ = –75.5 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.3 ppm; MS (70 eV): *m/z* (%): 739 (23) [M^+], 670 (4), 459 (100), 262 (87), 183 (79), 152 (9), 108 (25), 69 (10).

Complex 4b. [(Me_3P)AuCl] (1.427 g, 4.6 mmol) was added to a solution of $AgNTf_2$ (1.796 g, 4.6 mmol) in CH_2Cl_2 (30 mL), causing the spontaneous precipitation of AgCl. After stirring for 30 min at ambient temperature, the mixture was filtered through a pad of Celite, the filtrate was evaporated and the residue dried in vacuo (10^{-3} mbar) to give complex **4b** as a colorless solid (2.334 g, 91 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.70 ppm (d, J_{PH} = 11.9 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 120.1 (q, J_{CF} = 324 Hz), 16.2 ppm (d, J_{PC} = 42.9 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = –12.4 ppm; MS (70 eV): *m/z* (%): 553 < 1 [M^+], 484 (24), 273(100), 258 (4), 76 (11), 61 (14).

Complex 4c. Prepared analogously from [(Cy_3P)AuCl]; colorless solid (3.42 g, 91%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.2 – 1.65 (m, 18H), 1.65 – 1.15 ppm (m, 15H); ^{13}C NMR (100 MHz,

[1] N. Mézailles, L. Ricard, F. Gagosz, Org. Lett., **2005,** *7*, 4133–4136.

CD_2Cl_2): δ = 120.0 (q, J_{CF} = 327 Hz), 33.4 (d, $^1J_{PC}$ = 32 Hz), 31.3, 27.2 (d, $^3J_{PC}$ = 12.5 Hz), 26.2 ppm; ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +56.1 ppm; MS (70 eV): *m/z* (%): 757 (9) [M^+], 675 (26), 477 (100), 394 (90), 312 (12), 280 (17), 198 (50), 117 (61), 83 (23), 81 (27), 69 (13), 55 (28).

Organogold Derivatives *Z*/*E*-5. Complex **4a** (155 mg, 0.21 mmol) was added at –78°C to a solution of cyclopropene **3a** (33 mg, 0.29 mmol) in CD_2Cl_2 (1 mL). Upon raising the temperature to –20°C, the resulting yellow solution turns dark orange-red. ***E*-5**: ^{1}H NMR (400 MHz, 253 K, CD_2Cl_2): δ = 9.71 (dd, $^3J_{HH}$ = 19.1 Hz, $^3J_{PH}$ = 2.2 Hz, 1H), 7.6 – 7.4 (m, 15H), 6.51 (dd, $^3J_{HH}$ = 19.1 Hz, $^4J_{PH}$ = 6.6 Hz, 1H), 4.93 (t, $^3J_{HH}$ = 5.6 Hz, 4H), 2.5 ppm (m, 2H); ^{13}C NMR (100 MHz, 253 K, CD_2Cl_2): δ = 212.9 (d, $^2J_{PC}$ = 114 Hz, J_{CH} = 142 Hz), 172.9 (d, $^4J_{PC}$ = 11.2 Hz), 134.2 (d, $^2J_{PC}$ = 13.7 Hz), 131.8 (d, $^4J_{PC}$ = 2.2 Hz), 129.36 (d, $^3J_{PC}$ = 11 Hz), 129.35 (d, $^1J_{PC}$ = 53.7 Hz), 127.1 (J_{CH} = 175 Hz), 119.8 (q, J_{CF} = 320 Hz), 71.4, 20.4 ppm; ^{31}P NMR (162 MHz, 253 K, CD_2Cl_2): δ = 42.5 ppm; ***Z*-5**: ^{1}H NMR (400 MHz, 253 K, CD_2Cl_2): δ = 9.19 (d, $^3J_{HH}$ = 13.9 Hz, 1H), 7.6 – 7.4 (m, 15H), 6.85 (t, $^3J_{HH}$ = 13.9 Hz, $^4J_{PH}$ = 13.9 Hz, 1H), 4.86 (t, $^3J_{HH}$ = 5.5 Hz, 4H), 2.5 ppm (m, 2H); ^{13}C NMR (100 MHz, 253 K, CD_2Cl_2): δ = 214.6 (d, $^2J_{PC}$ = 111 Hz, J_{CH} = 138 Hz), 178.0 (d, $^4J_{PC}$ = 4.6 Hz), 134.2 (d, $^2J_{PC}$ = 13.5 Hz), 131.9 (d, $^4J_{PC}$ = 2.7 Hz), 129.42 (d, $^3J_{PC}$ = 11.0 Hz), 129.41 (d, $^1J_{PC}$ = 54.3 Hz), 127.8 (J_{CH} = 169 Hz), 119.8 (q, J_{CF} = 320 Hz), 71.36, 20.29 ppm; ^{31}P NMR (162 MHz, 253 K, CD_2Cl_2): δ = 42.3 ppm.

Organogold Derivatives *Z*/*E*-8: Prepared analogously from **3a** (36 mg, 0.32 mmol) and **4b** (144 mg, 0.26 mmol) in CD_2Cl_2 (1 mL). ***E*-8**: ^{1}H NMR (400 MHz, 223 K, CD_2Cl_2): δ = 9.62 (dd, $^3J_{HH}$ = 19.2 Hz, $^3J_{PH}$ = 2.6 Hz, 1H), 6.47 (dd, $^3J_{HH}$ = 19.2 Hz, $^4J_{PH}$ = 6.9 Hz, 1H), 4.88 (t, $^3J_{HH}$ = 5.6 Hz, 4H), 2.45 (m, 2H), 1.45 ppm (d, J_{PH} = 10.1 Hz, 9H); ^{13}C NMR (100 MHz, 223 K, CD_2Cl_2): δ = 213.9 (d, $^2J_{PC}$ = 116 Hz), 172.3 (d, $^4J_{PC}$ = 11.4 Hz), 126.9 (d, $^3J_{PC}$ = 2.9 Hz), 119.4 (q, J_{CF} = 321 Hz), 70.92, 20.01, 15.1 ppm (d, J_{PC} = 34.6 Hz); ^{31}P NMR (162 MHz, 213 K, CD_2Cl_2): δ = 3.2 ppm; ***Z*-8**: ^{1}H NMR (400 MHz, 223 K, CD_2Cl_2): δ = 9.14 (dd, $^3J_{HH}$ = 13.9 Hz, $^3J_{PH}$ = 0.6 Hz, 1H), 6.78 (dd, $^3J_{HH}$ = 14.3 Hz, $^4J_{PH}$ = 14.3 Hz, 1H), 4.91 (t, $^3J_{HH}$ = 5.6 Hz, 4H), 2.45 (m, 2H), 1.47 ppm (d, J_{PH} = 10.1 Hz, 9H); ^{13}C NMR (100 MHz, 223 K, CD_2Cl_2): δ = 216.1 (d, $^2J_{PC}$ = 114 Hz), 177.6 (d, $^4J_{PC}$ = 5.3 Hz), 127.6, 119.4 (q, J_{CF} = 321 Hz), 71.04, 20.0, 14.8 ppm (d, J_{PC} = 35 Hz); ^{31}P NMR (162 MHz, 213 K, CD_2Cl_2): δ = 3.3 ppm.

Organogold Derivatives *Z*/*E*-9: Prepared analogously from **3a** (35 mg, 0.31 mmol) and **4c** (182 mg, 0.24 mmol) in CD_2Cl_2 (1 mL). ***E*-9**: ^{1}H NMR (400 MHz, 253 K, CD_2Cl_2): δ = 9.66 (dd, $^3J_{HH}$ = 19.3 Hz, $^3J_{PH}$ = 1.8 Hz, 1H), 6.47 (dd, $^3J_{HH}$ = 19.3 Hz, $^4J_{PH}$ = 5.7 Hz, 1H), 4.89 (t, $^3J_{HH}$ = 5.6 Hz, 4H), 2.47 (m, 2H), 2.2 – 1.6 (m, 18H), 1.54 – 1.1 ppm (m, 15H); ^{13}C NMR (75 MHz, 253 K, CD_2Cl_2): δ = 219.3 (d, $^2J_{PC}$ = 107 Hz), 172.95 (d, $^4J_{PC}$ = 10 Hz), 126.2, 119.8 (q, J_{CF} = 321 Hz), 71.21, 32.8 (d, $^1J_{PC}$ = 27 Hz), 30.6, 27.1 (d, $^3J_{PC}$ = 11.7 Hz), 25.9, 20.41 ppm; ^{31}P NMR (121 MHz, 253 K, CD_2Cl_2): δ = 56.7 ppm; ***Z*-9**: ^{1}H NMR (400 MHz, 253 K, CD_2Cl_2): δ = 9.19 (d, $^3J_{HH}$ = 14.2 Hz, 1H), 6.85 (dd, $^3J_{HH}$ = 14.2 Hz, $^4J_{PH}$ = 13.1 Hz, 1H), 4.89 (t, $^3J_{HH}$ = 5.6 Hz, 4H), 2.47 (m, 2H), 2.2 – 1.6 (m, 18H), 1.54 – 1.1 ppm (m, 15H); ^{13}C NMR (75 MHz, 253 K, CD_2Cl_2): δ = 221.0 (d, $^2J_{PC}$ = 104 Hz), 178.1 127.1, 119.8 (q, J_{CF} = 321 Hz), 71.12, 32.8 (d, J_{PC} = 27 Hz), 30.6, 27.1 (d, J_{PC} = 11.7 Hz), 25.9, 20.41 ppm; ^{31}P NMR (121 MHz, 253 K, CD_2Cl_2): δ = 56.5 ppm.

Organogold Derivative *Z*-10a. Prepared analogously from **3b** (48 mg, 0.48 mmol) and **4a** (280 mg 0.38 mmol) in CD_2Cl_2 (1 mL). ^{1}H NMR (400 MHz, 193 K, CD_2Cl_2): δ = 9.50 (dd, $^3J_{HH}$ = 13.9 Hz, 1H), 7.7 – 7.2 (m, 15H), 7.09 (t, $^3J_{HH}$ = 13.9 Hz, $^4J_{PH}$ = 13.9 Hz, 1H), 4.50 (s, 3H), 4.14 ppm (s, 3H); ^{13}C NMR (100 MHz, 193 K, CD_2Cl_2): δ = 221.0 (d, $^2J_{PC}$ = 111 Hz), 179.8 (d, $^4J_{PC}$ = 4.5 Hz), 133.7 (d, $^3J_{PC}$ = 13.6 Hz), 131.6, 128.85 (d, $^2J_{PC}$ = 9 Hz), 128.7 (d, J_{PC} = 54 Hz), 119.1 (q, J_{CF} = 322 Hz), 121.6, 62.6, 59.9 ppm.

Organogold Derivatives *Z*/*E*-10b. Prepared analogously from **3b** ((38 mg, 0.38 mmol) and **4b** (177 mg, 0.32 mmol) in CD_2Cl_2 (1 mL). ***E*-10b**: ^{1}H NMR (400 MHz, 193 K, CD_2Cl_2): δ = 10.00 (dd, $^3J_{HH}$ = 18.5 Hz, $^3J_{PH}$ = 3.1 Hz, 1H), 6.81 (dd, $^3J_{HH}$ = 18.5 Hz, $^4J_{PH}$ = 6.8 Hz, 1H), 4.44 (s, 3H), 4.18 (s, 3H), 1.45 ppm (d, J_{PH} = 10.1 Hz, 9H); ^{13}C NMR (100 MHz, 193 K, CD_2Cl_2): δ = 222.5 (d, $^2J_{PC}$ = 116 Hz), 173.5 (d, $^4J_{PC}$ = 9.7 Hz), 121.1, 119.0 (q, J_{CF} = 321 Hz), 62.4, 59.8, 14.7 ppm (d, J_{PC} = 34.8 Hz); ^{31}P NMR (121 MHz, 193 K, CD_2Cl_2): δ = 2.8 ppm; ***Z*-10b**: ^{1}H NMR (400 MHz, 193 K, CD_2Cl_2): δ = 9.51 (dd, $^3J_{HH}$ = 13.9 Hz, $^3J_{PH}$ = 1 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 13.9 Hz, $^4J_{PH}$ = 13.9 Hz, 1H), 4.44 (s, 3H), 4.18 (s, 3H), 1.45 ppm (d, J_{PH} = 10.1 Hz, 9H).