Supporting Information
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Elementary Steps in Gold Catalysis: The Significance of \textit{gem-Diauration}**

\textit{Günter Seidel, Christian W. Lehmann, and Alois Fürstner*}

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**General:** All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, (Mg/anthracene), CH₂Cl₂ (CaH₂), pentane, hexane, toluene (Na/K), iPrOH (Mg). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, and AV 400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: δC≡53.8 ppm; residual CHDCl₂: δH≡5.32 ppm). MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker). All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

**Starting Materials.**

Pinacol boronate 9 was used as received from the commercial supplier. The other starting materials were prepared according to literature procedures and showed the following spectral data:

**Borionate 6:**

$^1$H NMR (400 MHz, CD₂Cl₂): δ = 7.20 - 7.18 (m, 2 H), 7.10 (q, J = 1.5 Hz, 1 H), 7.05 – 7.03 (m, 2 H), 4.05 (q, J = 7.2 Hz, 2 H), 1.80 (d, J = 1.5 Hz, 3 H), 1.32 ppm (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (75 MHz, CD₂Cl₂, −60 °C): δ = 159.4 (BC=C), 148.0, 122.1, 111.7, 96.5 (BC=C), 69.1, 15.3, 9.4 ppm.

**Boronic acid 13:**

$^1$H NMR (400 MHz, CD₂Cl₂): δ = 6.80 (br s, OH), 2.33 (s, 3 H), 1.68 ppm (s, 6 H); $^{13}$C NMR (75 MHz, CD₂Cl₂, −60 °C): δ = 180.8, 167.8, 105.5, 92.5 (BC), 24.5, 20.5 ppm.

**Borionate 15:**

$^1$H NMR (400 MHz, CDCl₃): δ = 7.33 (s, 1 H), 7.20 – 7.18 (m, 2 H), 7.05 – 7.03 (m, 2 H), 2.43 (s, 3 H), 2.39 (t, 2 H), 1.52 (m, 2 H), 1.39 (m, 2 H), 0.94 ppm (t, 3 H); $^{13}$C

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**NMR (75 MHz, −60 °C, CD$_2$Cl$_2$):** δ = 148.4 (BC=CH), 147.9, 125.5 (BC=C), 122.3, 112.0, 30.7, 30.3, 22.8, 16.9, 14.0 ppm.

**Aurations.**

**Compound 14:** A mixture containing boronic acid 13 (100 mg, 0.54 mmol), (Ph$_3$P)AuBr (291 mg, 0.54 mmol) and Cs$_2$CO$_3$ (176 mg, 0.54 mmol) in isopropanol (5 mL) was stirred at 50 °C for 2 h. For work up, the solvent was distilled off under reduced pressure (10⁻³ mbar), the residue was suspended in CH$_2$Cl$_2$ (5 mL), the remaining insoluble materials were filtered off through a short pad of Celite, and the filtrate was evaporated to give complex 14 as a colorless solid (278 mg, 86 %). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.63 – 7.45 (m, 15 H), 2.13 (d, $^3$J$_{PC} = 0.8$ Hz, 3 H), 1.62 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ = 169.9 (d, $^3$J$_{PC} = 5$ Hz), 167.5 (d, $^3$J$_{PC} = 2.4$ Hz), 134.6 (d, $^2$J$_{PC} = 14$ Hz), 131.7 (d, $^4$J$_{PC} = 1.9$ Hz), 131.1 (d, $^1$J$_{PC} = 52$ Hz), 130.1 (d, $^2$J$_{PC} = 117$ Hz), 104.1, 25.4, 24.0 ppm; $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ = 44.4 ppm.

**Complex 8:** [(Ph$_3$P)AuNTf$_2$] (828 mg, 1.12 mmol) was added to a solution of compound 6 (114 mg, 0.56 mmol) and Cs$_2$CO$_3$ (182 mg, 0.56 mmol) in THF (5 mL) and the resulting mixture was stirred at ambient temperature for 1 h. At this point, inspection of the reaction mixture by $^{31}$P NMR showed the formation of a major product (δ$_P$ = 37.1 ppm, ca. 90 %), together with small amounts of unreacted [(Ph$_3$P)AuNTf$_2$] (δ$_P$ = 31.0 ppm, ca. 7 %) and [(Ph$_3$P)$_2$Au][NTf$_2$] (δ$_P$ = 45.3 ppm, ca. 3 %). For work up, all volatile materials were distilled off under vacuum (15 mbar) and the residue was passed through a short silica gel column (ca. 10 cm, $\varnothing$ 2 cm), eluting with CH$_2$Cl$_2$ (200 mL). The combined product-containing fractions were evaporated and the residue dried in vacuo to give complex 8 as a colorless oil (383 mg), which contained trace impurities of [(Ph$_3$P)$_2$Au][NTf$_2$] and (Ph$_3$P)AuCl (likely formed by activation of CH$_2$Cl$_2$ during the work up, δ$_P$ = 33.8 ppm). Crystals of 8 suitable for X-ray structure analysis were grown by slowly cooling a solution of the complex in CH$_2$Cl$_2$, layered
with cold pentane, to –78 °C. 1H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.70 – 7.33 (m, 30-35H), 7.30 (s, 1 H), 4.34 (q, J = 7.1 Hz, 2 H), 2.09 (q, J = 1.5 Hz, 3 H), 1.43 ppm (t, J = 7.1 Hz, 3 H); 13C NMR (100 MHz, CD$_2$Cl$_2$): δ = 174.8 (t, $^3$JC$P$ = 2.4 Hz), 134.4 (d, $^2$JC$P$ = 13.8 Hz), 132.5 (d, $^4$JC$P$ = 2.6 Hz), 129.8 (d, $^3$JC$P$ = 11.5 Hz), 129.3 (d, JC$F$ = 56.7 Hz), 120.4 (q, JC$F$ = 322 Hz), 116.6 (t, JC$F$ = 60.6 Hz), 71.8, 20.3, 15.4 ppm; 31P NMR (162 MHz, CD$_2$Cl$_2$): δ = 37.5 ppm; MS (ESI): m/z 1003 (M$^+$ – NTf$_2$); 721 [(PPh$_3$)$_2$Au$^+$]; 280 (NTf$_2$); HRMS (ESI): m/z: calcd for C$_{41}$H$_{39}$Au$_2$OP$_2$ [M$^+$]: 1003.1801, found: 1003.1792.

**Compound 10**: [(PPh$_3$)AuNTf$_2$] (665 mg, 0.90 mmol) was added at –78 °C to a mixture containing pinacol boronate 9 (88 mg, 0.45 mmol) and Cs$_2$CO$_3$ (147 mg, 0.45 mmol) in THF (4 mL). The resulting mixture was allowed to reach ambient temperature. After stirring for 1 h, the solvent was distilled off under vacuum from the resulting red suspension, and the residue was rapidly passed through a silica gel column (6 cm, Ø = 2.5 cm), eluting with CH$_2$Cl$_2$ (80 mL). Evaporation of the product containing fractions afforded complex 10 as a colorless solid, which contained trace impurities of [(PPh$_3$)$_2$Au][NTf$_2$] (δ$_P$ = 45.1 ppm) and (PPh$_3$)AuCl (likely formed by activation of CH$_2$Cl$_2$ during the work up, δ$_P$ = 33.2 ppm) (414 mg, ca. 72 %). Crystals suitable for X-ray diffraction were grown by slowly cooling a solution of the complex in THF/pentane to –20 °C. 1H NMR (400 MHz, CD$_2$Cl$_2$): δ = 7.7 – 7.2 (m, 30H), 6.92 (dd, J = 18.3, 8.7 Hz, 1 H), 6.24 (d, J = 18.3 Hz, 1 H), 2.06 – 1.93 (m, 1 H), 1.33 – 1.20 (m, 2 H), 1.04 – 0.92 ppm (m, 2 H); 13C NMR (100 MHz, CD$_2$Cl$_2$, characteristic signals): δ = 192.2, 132.2 (d), 131.4, 128.7 (d), ca. 128.5 (C$_1$ according to HSQC; the signal is hidden by the signals of the Ph rings), 128.0 (d, J = 58.5 Hz), 119.2 (q, JC$F$ = 320 Hz), 21.7, 13.1 ppm; 31P NMR (162 MHz, CD$_2$Cl$_2$): δ = 37.0 ppm; MS (ESI): m/z 985 (M$^+$ – NTf$_2$), 721 [(PPh$_3$)$_2$Au]; HRMS (ESI): m/z: calcd for C$_{41}$H$_{37}$Au$_2$P$_2$ [M$^+$ – NTf$_2$]: 985.1696, found: 985.1701.

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3 Because of the mentioned trace impurities, the integral for the aromatic protons is variable and slightly higher than expected.

4 In the $^{13}$C NMR spectrum recorded at –80 °C, the corresponding signal was detected at 128.4 ppm (t, JC$P$ = 57.8 Hz).
**Compound 11:** An NMR sample of complex 10 in CD$_2$Cl$_2$ was kept overnight at ambient temperature, causing the formation of a black precipitate. NMR inspection showed the presence of compound 11 as the only detectable organic product, which had formed in ca. 90 % yield. The $^{31}$P NMR showed the formation of [(Ph$_3$P)$_2$Au][NTf$_2$] ($\delta_P = 45.1$ ppm, ca. 90 %) and residual 10 ($\delta_P = 37.0$ ppm, ca. 10 %). Characteristic data of compound 11: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 6.05$ (m, 2 H), 5.09 (m, 2 H), 1.37 (m, 2 H), 0.72 (m, 4 H), 0.37 ppm (m, 4 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 134.3$, 127.0, 14.1, 7.3 ppm; GC/MS: m/z: 134 ($M^+$, 30), 119 (21), 117 (9), 115 (5), 105 (29), 91 (100), 79 (38), 77 (48), 65 (19), 51 (14).

**Compound 12:** A mixture containing pinacol boronate 9 (85 mg, 0.44 mmol), (Ph$_3$P)AuBr (237 mg, 0.44 mmol) and Cs$_2$CO$_3$ (143 mg, 0.44 mmol) in isopropanol (3 mL) was stirred at 50 °C for 2 h. For work up, the solvent was distilled off under reduced pressure (10$^{-3}$ mbar), the residue was suspended in CH$_2$Cl$_2$ (3 mL), the remaining insoluble materials were filtered off through a short pad of Celite, and the filtrate was evaporated to give complex 12 as an amorphous solid (177 mg, 76 %). When kept in CD$_2$Cl$_2$ solution, the material undergoes isomerization, leading to a Z:E = 29:71 mixture. Characteristic data of E-12: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.60 – 7.40$ (m, 15 H), 6.70 (d, $J = 18.6$ Hz, 1 H), 5.35 (dd, $J = 18.5$, 8.2 Hz, 1 H), 1.42 (m, 1 H), 0.67 – 0.60 (m, 2 H), 0.37 – 0.30 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 155.6$, 150.8, 134.6, (d, $J_{PC} = 13.8$ Hz), 131.54 (d, $J_{PC} = 2$ Hz), 131.50 (d, $J_{PC} = 49$ Hz), 129.4 (d, $J_{PC} = 10.7$ Hz), 18.5, 7.0 ppm; $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 44.4$ ppm; Characteristic data of Z-12: $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.6 – 7.4$ (m, 15 H), 6.55 (d, $J = 11.9$ Hz, 1 H), 6.02 (dd, $J = 11.9$, 3 Hz, 1 H), 1.82 – 1.71 (m, 1 H), 0.75 – 0.68 (m, 2 H), 0.46 – 0.40 ppm (m, 2 H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 155.3$, 149.1, 134.6, ($J_{PC} = 13.8$ Hz), 131.54 ($J_{PC} = 2$ Hz), 131.50 ($J_{PC} = 49$ Hz), 129.4 ($J_{PC} = 10.7$ Hz), 19.1, 7.5 ppm; $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 44.4$ ppm.

**Compound 16:** (Ph$_3$P)AuCl (371 mg, 0.75 mmol) was added to a suspension of catechol boronate 15 (186 mg, 0.75 mmol) and Cs$_2$CO$_3$ (244 mg, 0.75 mmol) in isopropanol (6 mL)
and the resulting mixture was stirred at 50 °C for 1 h. The solvent was evaporated in vacuum (10⁻³ mbar) and the residue suspended in CH₂Cl₂ (5 mL). Insoluble materials were filtered off through a short pad of Celite and the filtrate was evaporated to give product 16 as a yellow syrup (345 mg, ca. 60 % of 16). Residual (Ph₃P)AuCl (δ = 34.3 ppm) was removed by layering a solution of the crude product in the minimum amount of CH₂Cl₂ with pentane. ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.60 – 7.40 (15-21 H), 5.77 (t, J = 1.6 Hz, 1 H), 2.48 (dt, J = 7.4, 1.6 Hz, 2 H), 2.26 (s, 3 H), 1.67 (quint, J = 7.7 Hz, 2 H), 1.46 (sext., J = 7.6 Hz, 2 H), 0.93 ppm (t, J = 7.3 Hz, 3 H); ¹³C NMR (100 MHz, CD₂Cl₂): δ = 177.6, 134.5 (d, Jₚc = 13.7 Hz), 131.8 (d, Jₚc = 1.7 Hz), 131.5 (d, Jₚc = 48 Hz), 129.4 (d, Jₚc = 11 Hz), 129.4, 38.7, 34.9, 23.2, 17.3, 14.5 ppm; ³¹P NMR (162 MHz, CD₂Cl₂): δ = 42.6 ppm.
Figure S-1. Structure of [(Ph₃P)₂Au][NTf₂] in the solid state. The anisotropic displacement parameters are drawn at the 50 % probability level; hydrogen atoms are omitted for clarity.

**X-ray crystal structure analysis of the gem-digold complex 8**: C₄₇H₄₆Au₂F₆NO₅.75 P₂ S₂, \( M_r = 1350.84 \ \text{g·mol}^{-1} \), orange plate, crystal size 0.032 x 0.023 x 0.014 mm, orthorhombic, space group \( P2_12_12_1 \), \( a = 13.3293(19) \ \text{Å} \), \( b = 17.012(3) \ \text{Å} \), \( c = 21.382(3) \ \text{Å} \), \( V = 4848.7(12) \ \text{Å}^3 \), \( T = 100 \ \text{K} \), \( Z = 4 \), \( D_{\text{calc}} = 1.850 \ \text{g·cm}^{-3} \), \( \lambda = 0.71073 \ \text{Å} \), \( \mu(\text{Mo-K}α) = 6.267 \ \text{mm}^{-1} \), Gaussian absorption correction (\( T_{\text{min}} = 0.82, T_{\text{max}} = 0.92 \)), Nonius KappaCCD diffractometer, \( 1.53 < \theta < 27.50^\circ \), 109700 measured reflections, 11130 independent reflections, 10476 reflections with \( I > 2\sigma(I) \), Structure solved by direct methods and refined to \( R_I = 0.068 \ [I > 2\sigma(I)] \), \( wR_2 = 0.169 \), absolute structure parameter = 0.059(16), 362 parameters, H atoms riding, \( S = 1.337 \), residual electron density 1.9/-4.7 \ \text{Å}^{-3} \). Data quality and severe disorder of the [NTf₂]⁻ anion permitted only isotropic refinement of all light atoms.

**X-ray crystal structure analysis of the gem-digold complex 10**: C₄₃H₃₇Au₂F₆NO₄P₂S₂, \( M_r = 1265.73 \ \text{g·mol}^{-1} \), colorless plate, crystal size 0.24 x 0.05 x 0.05 mm, monoclinic, space group \( P2_1n \), \( a = 18.930(2) \ \text{Å} \), \( b = 9.5511(7) \ \text{Å} \), \( c = 24.231(3) \ \text{Å} \), \( β = 100.889(9)^\circ \), \( V = \)
4302.2(8) Å³, T = 100 K, Z = 4, D_{calc} = 1.954 g·cm⁻³, \lambda = 0.71073 Å, \mu(Mo-K_{\alpha}) = 7.053 mm⁻¹, Gaussian absorption correction (T_{min} = 0.36, T_{max} = 0.74), Nonius KappaCCD diffractometer, 2.61 < \theta < 33.22°, 82522 measured reflections, 16479 independent reflections, 12033 reflections with I > 2\sigma(I), Structure solved by direct methods and refined by full-matrix least-squares against F² to R_f = 0.050 [I > 2\sigma(I)], wR_f = 0.121, absolute structure parameter = 0.059(16), 536 parameters, H atoms riding, S = 1.036, residual electron density 1.9/–4.7 Å⁻³.

X-ray crystal structure analysis of complex 14: C_{25}H_{24}AuO_3P, M_r = 600.38 g·mol⁻¹, colorless plate, crystal size 0.20 x 0.19 x 0.05 mm, triclinic, space group P\bar{1}, a = 8.7693(6) Å, b = 8.8472(7) Å, c = 15.0475(11) Å, \alpha = 76.534(2)°, \beta = 75.610(4)°, \gamma = 84.256(4)°, V = 1098.62(14) Å³, T = 100 K, Z = 2, D_{calc} = 1.815 g·cm⁻³, \lambda = 0.71073 Å, \mu(Mo-K_{\alpha}) = 6.792 mm⁻¹, Gaussian absorption correction (T_{min} = 0.31, T_{max} = 0.72), Nonius KappaCCD diffractometer, 3.02 < \theta < 33.26°, 24223 measured reflections, 8374 independent reflections, 7677 reflections with I > 2\sigma(I), Structure solved by direct methods and refined by full-matrix least-squares against F² to R_f = 0.038 [I > 2\sigma(I)], wR_f = 0.098, 274 parameters, H atoms riding, S = 1.041, residual electron density 3.7/–4.9 e Å⁻³.

X-ray crystal structure analysis of [(Ph₃P)₂Au][NTf₂]: C_{38}H_{30}AuF_6NO_4P_2S_2, M_r = 1001.66 g·mol⁻¹, colorless plate, crystal size 0.26 x 0.18 x 0.09 mm, orthorhombic, space group Pna2₁, a = 16.7142(2) Å, b = 24.1511(3) Å, c = 9.22800(10) Å, V = 3725.03(8) Å³, T = 100 K, Z = 4, D_{calc} = 1.786 g·cm⁻³, \lambda = 0.71073 Å, \mu(Mo-K_{\alpha}) = 4.220 mm⁻¹, Empirical absorption correction (T_{min} = 0.74, T_{max} = 0.99), Nonius KappaCCD diffractometer, 2.96 < \theta < 33.21°, 66232 measured reflections, 14191 independent reflections, 12127 reflections with I > 2\sigma(I), Structure solved by direct methods and refined by full-matrix least-squares against F² to R_f = 0.030 [I > 2\sigma(I)], wR_f = 0.066, absolute structure parameter = 0.000(5), 488 parameters, H atoms riding, S = 1.047, residual electron density 2.4/–1.9 Å⁻³.

CCDC 777626 (8), 779085 (10), 777624 (14) and 777625 ([((Ph₃P)₂Au][NTf₂]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif.