

## Supporting Information

### Oxidative Rearrangement in Gold Organometallics

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**S1. Materials and methods:** Unless stated otherwise, all manipulations were carried out in either a N<sub>2</sub>-filled Vacuum Atmospheres Co. glove box or on a Schlenk line using N<sub>2</sub>. HPLC grade dichloromethane, hexanes, ether, and acetonitrile were dried and deoxygenated by passing through commercial columns of CuO, followed by alumina under argon atmosphere. [NO]PF<sub>6</sub> and [Bu<sub>4</sub>N]PF<sub>6</sub> were purchased from Sigma Aldrich. All other commercially available reagents were used as received. Bu<sub>4</sub>N[Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] and Bu<sub>4</sub>N[Au(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>] were synthesized following literature procedure.<sup>1</sup>

## **S2. Instrumentation:**

**S2A. X-Ray Diffraction:** Data for complexes [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>CN)] and [Au(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> were collected using a Bruker D8 tricycles diffractometer with APEX II detector CCD based equipped with an LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Cell parameters were determined and refined using APEX II software on all observed reflections which corrects for Lp and decay.<sup>2,3</sup> Absorption corrections were applied using SADABS supplied by George Sheldrick.<sup>4</sup> The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F<sup>2</sup>, SHELXL-97, incorporated in SHELXTL-PC V 5.03.<sup>5,6</sup> The structures of [Au(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>CN)] and [Au(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]PF<sub>6</sub> were solved by analysis of systematic absences. Hydrogen atoms were calculated by geometrical methods and refined as a riding model.

**S2B. Electrochemical Studies:** Cyclic voltammetry experiments were conducted using a CH Instruments electrochemical analyzer, Model 660 A, under computer control. CV measurements were performed in acetonitrile with 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> as supporting electrolyte. Fresh solutions containing supporting electrolyte (10 ml) were prepared prior to each CV experiment. Each

solution was deoxygenated by purging with nitrogen for 2-5 minutes. Background CV's were acquired before the addition of the gold complexes. A three-electrode system was used, comprised of a platinum (1.6 mm diameter) working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride (Ag/AgCl) reference electrode. The working electrode was wiped prior to each experiment with fine sand paper and rinsed. Potentials are reported vs. Ag/AgCl at room temperature and are not corrected for junction potentials. Each CV experiment was repeated a number of times at different scan rates.

**S2C. NMR, MS, EA, and IR:** Infrared spectra were recorded in the 4000-200  $\text{cm}^{-1}$  range using a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer in KBr. C, H, and N analyses were carried out with a C.E. Instrument EA-1110 CHNS-O microanalyser. Mass spectra were recorded on a HP-5989B API-Electrospray Mass Spectrometer with interface 59987A.  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker ARX 300 and JEOL 400 in  $\text{CDCl}_3$ . Chemical shifts are reported relative to  $\text{SiMe}_4$  ( $^1\text{H}$  external) and  $\text{CFCl}_3$  ( $^{19}\text{F}$  external).

### S3. Synthesis:

**S3A. Synthesis of  $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{CH}_3\text{CN})]$ :** To a 90 mg (0.116 mmol) of  $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)_2]$  dissolved in 3 mL  $\text{CH}_3\text{CN}$  was added 40 mg (0.222 mmol)  $[\text{NO}]\text{PF}_6$  dissolved in 2 mL  $\text{CH}_3\text{CN}$ . The solution turned beige immediately and stirring continued for 2 hrs. The evolution of nitric oxide gas ceased after few minutes of stirring. The  $\text{CH}_3\text{CN}$  was evaporated under vacuum and the residues were dissolved in  $\text{CH}_2\text{Cl}_2$  and cold ether was added (10 mL) and stirred for 2 hrs. The white precipitate was filtered and dried in air to yield 55 mg (yield 64 %).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -121.57 (m, 2F,  $F_0$ ), -122.58 (m, 4F,  $F_0$ ), -156.47 (t, 3F,  $F_p$ ,  $^3J_{Fp-Fm}$  19 Hz), -161.09 (m, 4F,  $F_m$ ), -161.59 (m, 2F,  $F_m$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.25 and 118.7 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.95 ppm. Mass spectra: MALDI(+)  $m/z$ : 571.5  $[\text{Au}(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})]^+$  and MALDI(-)

$m/z$ : 864.9  $[\text{Au}(\text{C}_6\text{F}_5)_4]^-$ . Elemental analysis calculated for  $(\text{C}_{20}\text{H}_3\text{AuF}_{15}\text{N})$ : %C = 32.50, %H = 0.41, %N = 1.89. Exp: %C = 32.30, %H = 0.40, %N = 2.00.

**S3B. Synthesis of  $[\text{Au}(\text{C}_6\text{Cl}_5)_2(\text{CH}_3\text{CN})_2]\text{PF}_6$ :** To a 90 mg (0.095 mmol) of  $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{Cl}_5)_2]$  dissolved in 3 mL  $\text{CH}_3\text{CN}$  was added 34 mg  $[\text{NO}]\text{PF}_6$  (0.19 mmol) dissolved in 2 mL  $\text{CH}_3\text{CN}$ . The solution turned beige immediately and stirring continued for 2 hrs. The evolution of nitric oxide gas ceased after a few minutes of stirring. The  $\text{CH}_3\text{CN}$  was evaporated to 1 mL under vacuum and 4 mL  $\text{CH}_2\text{Cl}_2$  was added. The reaction mixture was treated with cold ether (10 mL) and stirred for 2 hrs and the white precipitate was filtered and dried in air to yield of 60 mg (yield 68 %). Mass spectra: MALDI(+)  $m/z$ : 694.8  $[\text{Au}(\text{C}_6\text{Cl}_5)_2]^+$ , 922.5  $[\text{Au}(\text{C}_6\text{Cl}_5)_2(\text{CH}_3\text{CN})_2]\text{PF}_6$  and 840.5  $[\text{Au}(\text{C}_6\text{Cl}_5)_2]\text{PF}_6$ . Elemental analysis calculated for  $(\text{C}_{16}\text{H}_6\text{AuBCl}_{10}\text{F}_4\text{N}_4)$ : %C = 24.97%, %H = 0.62, %N = 2.91. Exp: %C = 24.23, %H = 0.70, %N = 3.21.  $[\text{Au}(\text{C}_6\text{Cl}_5)_2(\text{CH}_3\text{CN})_2]\text{BF}_4$ :  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 2.25, 137.8, 136.6, 132.1, 131.4, and 118.7 ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.95 ppm.

#### S4. References:

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