

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 N₂-filled Vacuum Atmospheres Co. glove box or on a Schlenk line using N₂. 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]PF₆ and [Bu₄N]PF₆ were purchased from Sigma Aldrich. All other commercially available reagents were used as received. Bu₄N[Au(C₆F₅)₂] and Bu₄N[Au(C₆Cl₅)₂] were synthesized following literature procedure.¹

S2. Instrumentation:

S2A. X-Ray Diffraction: Data for complexes [Au(C₆F₅)₃(CH₃CN)] and [Au(C₆Cl₅)₂(CH₃CN)₂]PF₆ 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.^{2,3} Absorption corrections were applied using SADABS supplied by George Sheldrick.⁴ The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F², SHELXL-97, incorporated in SHELXTL-PC V 5.03.^{5,6} The structures of [Au(C₆F₅)₃(CH₃CN)] and [Au(C₆Cl₅)₂(CH₃CN)₂]PF₆ 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 [Bu₄N]PF₆ 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 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. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX 300 and JEOL 400 in CDCl_3 . Chemical shifts are reported relative to SiMe_4 (^1H external) and CFCl_3 (^{19}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 CH_3CN was added 40 mg (0.222 mmol) $[\text{NO}]\text{PF}_6$ dissolved in 2 mL CH_3CN . The solution turned beige immediately and stirring continued for 2 hrs. The evolution of nitric oxide gas ceased after few minutes of stirring. The CH_3CN was evaporated under vacuum and the residues were dissolved in CH_2Cl_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}F NMR (CDCl_3): δ -121.57 (m, 2F, F_0), -122.58 (m, 4F, F_0), -156.47 (t, 3F, F_p , $^3J_{F_p-F_m}$ 19 Hz), -161.09 (m, 4F, F_m), -161.59 (m, 2F, F_m). ^{13}C NMR (CDCl_3): δ = 2.25 and 118.7 ppm. ^1H NMR (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 CH_3CN was added 34 mg $[\text{NO}]\text{PF}_6$ (0.19 mmol) dissolved in 2 mL CH_3CN . 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 CH_3CN was evaporated to 1 mL under vacuum and 4 mL CH_2Cl_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}C NMR (CDCl_3) δ = 2.25, 137.8, 136.6, 132.1, 131.4, and 118.7 ppm. ^1H NMR (CDCl_3): 1.95 ppm.

S4. References:

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