Electronic Supporting information:

$[(CF_3)_4Au_2(C_5H_4N)_2]$ – the first alkyl gold(II) derivative with an extremely short Au-Au bond

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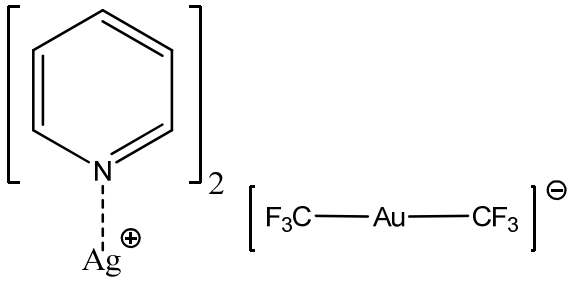
Routine NMR spectra were recorded on the Bruker spectrometer AVANCE II 300 at 298 K; frequencies (external standards): ^{13}C 75.5 MHz (TMS), ^{19}F 282.4 MHz (CCl_3F), ^{1}H 300.1 MHz (TMS); positive shifts denote downfield resonances. ^{109}Ag NMR experiment was run on a Bruker Avance 400 spectrometer (resonance frequency for ^{1}H 400.13 MHz, ^{13}C 100.6 MHz and ^{109}Ag 18.61 MHz) at ambient temperature. C, H and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus. Light irradiation experiments were enforced by an UV reactor of Helios Italquartz (λ = 352 nm).

Reaction procedure $[Ag(Py)_2][Au(CF_3)_2]$:

$[NMe_4][Au(CF_3)_2]$ was synthesized as reported recently.[1] 0.463 g (1 eq, 1.13 mmol) of $[NMe_4][Au(CF_3)_2]$ was solved in a mixture of 15 ml dried methylene chloride and 2 ml of pyridine in an N_2 atmosphere. 0.219 g (1 eq, 1.13 mmol) $Ag[BF_4]$ was added to the colourless, light protected and well stirred solution; Instantly $[NMe_4][BF_4]$ precipitated as white flocculation. After 3 h of stirring the reaction was finished and the solution was cooled down to -19 °C to achieve complete precipitation of $[NMe_4][BF_4]$. To obtain the solid yellowish white product in nearly quantitative yield, all volatile products were removed carefully at 0 °C under reduced pressure ($1 \cdot 10^{-2}$ mbar).

Formula:



^{1}H NMR (400.13 MHz, CD_3CN, ppm) δ: 8.62 (H-2,6), 7.95 (H4), 7.54(H-3,5); ^{13}C APT NMR (100.6 MHz, CD_3CN, ppm) δ: 163.0 ($[Au(\mathbf{C}F_3)_2]^-$ qq, ($^{1}J(F,C)$ = 347 Hz, $^{3}J(F,C)$ = 19 Hz), 151.9 (C-2,6), 139.2 (C-3,5), 126.0 (C4); ^{19}F NMR (282.4 MHz, CD_3CN, ppm) δ:

- 28.0 s, (^{1}J(F,C) = 347 Hz, ^{3}J(F,C) = 19 Hz, ^{4}J(F,F) = 2 Hz); ^{109}Ag NMR (18.61 MHz, pyridine-d_5, ppm) δ: +404 s; CHNS analytic data for $[Ag(Py)_2][Au(CF_3)_2]$ in %: C: 23.7 (calculated 24.0); H: 2.4 (1.7); N: 5.0 (4.7).

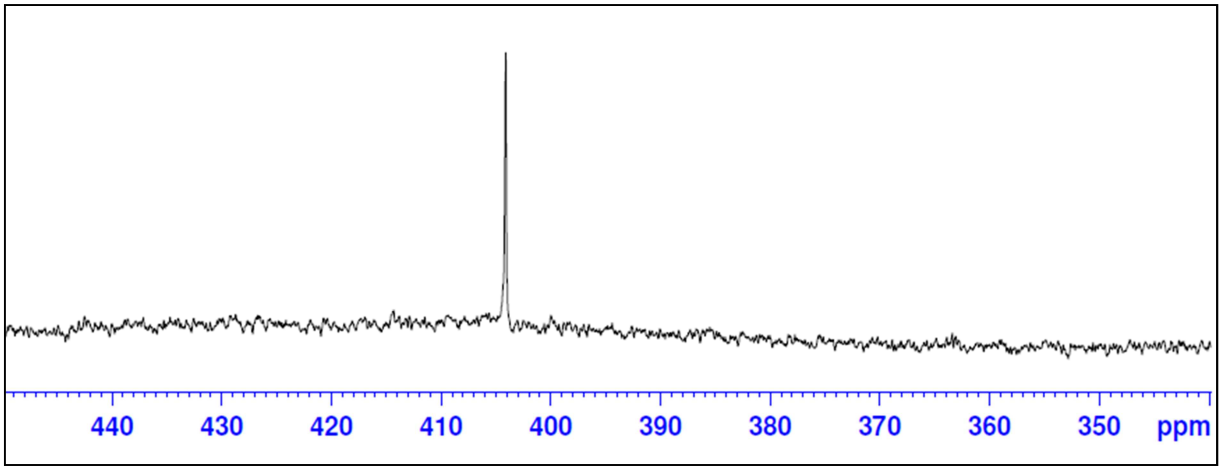


Figure 1: ^{109}Ag NMR of $[Ag(Py)_2][Au(CF_3)_2]$ in pyridine-d_5.

Behaviour of $[Ag(Py)_2][Au(CF_3)_2]$ in solution upon irradiation:

Time dependent ^{19}F NMR measurements (282.4 MHz, CD_3CN) shows the advancing oxidation of the $[Au^{(+I)}(CF_3)_2]^-$ unit by silver$^{(+I)}$ leading to $[Au_2^{(+II)}(CF_3)_4(Py)_2]$, which spontaneously disproportionated in solution into the couple $[Au^{(+I)}(CF_3)\cdot Py]$ and $[Au^{(+III)}(CF_3)_3)\cdot Py]$ (equation 3). At the moment we can not exclude $[Au^{(+III)}(CF_3)_4]^-$ is part of this equilibrium reaction such as equation 4 or had been brought in as impurity of the previous syntheses.

$[Au^{(+I)}(CF_3)\cdot Py]$:

^{19}F NMR (282.4 MHz, CD_3CN, ppm) δ: $[Au^{(+I)}(C\mathbf{F_3})\cdot Py]$: -23.7 s, (^{1}J(C,F) = 338 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ: $[Au^{(+I)}(\mathbf{C}F_3)\cdot Py]$ 139.9.

$[Au^{(+III)}(CF_3)_3)\cdot Py]$:

^{19}F NMR (282.4 MHz, CD_3CN, ppm) δ: $[Au^{(+III)}(C\mathbf{F_3})_3)\cdot Py]$ -29.9 sept, (^{1}J(C,F) = 347 Hz, ^{4}J(F,F) = 6 Hz); -38.1 qu, (^{1}J(C,F) = 361 Hz, ^{4}J(F,F) = 6 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ: $[Au^{(+III)}(\mathbf{C}F_3)_3)\cdot Py]$ 110.4, 136.3.

$[Au^{(+III)}(CF_3)_4]^-$:[2]

^{19}F NMR (282.4 MHz, CD_3CN, ppm) δ: $[Au^{(+III)}(C\mathbf{F_3})_4]$ – 34.7 s, (^{1}J(C,F) = 354 Hz), ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ: 135.9.

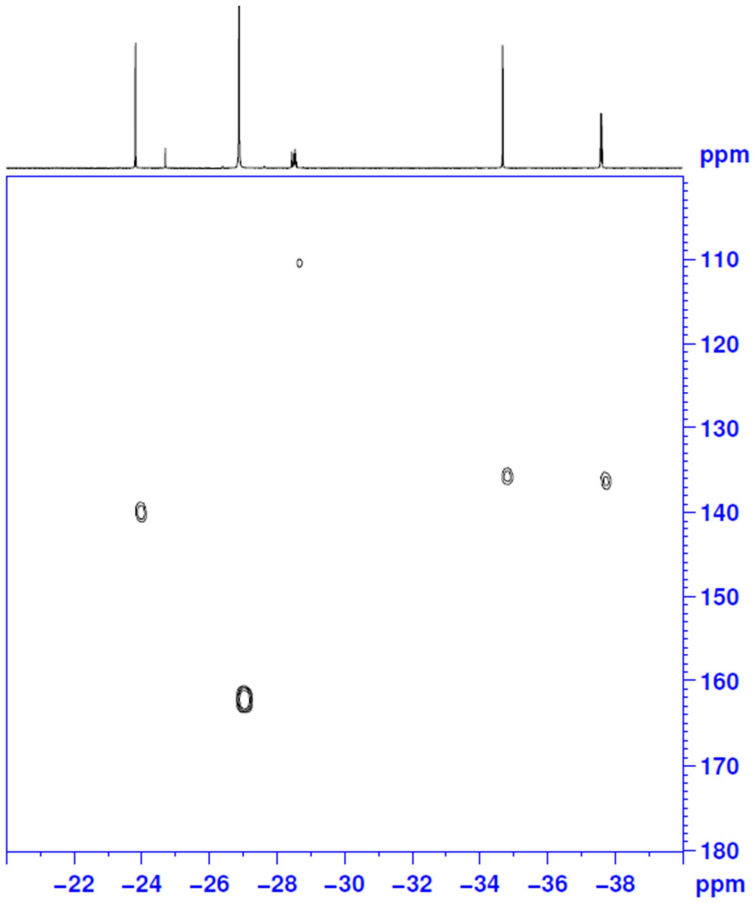


Figure 2: F,C-HSQC experiment of $[Ag(Py)_2][Au(CF_3)_2]$ in CD_3CN upon 20 h UV irradiation.

Literature

[1] D. Zopes, S. Kremer, H. Scherer, L. Belkhoura, I. Pantenburg, W. Tyrra, S. Mathur, *Eur. J. Inorg. Chem.* **2011**, 273–280.

[2] E. Bernhardt, M. Finze, H. Willner, *J. Fluorine Chem.* **2004**, *125*, 967-973.