Electronic Supporting information:

\[ [(\text{CF}_3)_4\text{Au}_2(\text{C}_5\text{H}_4\text{N})_2] \] – 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}\text{C} 75.5 \text{ MHz (TMS)}, \(^{19}\text{F} 282.4 \text{ MHz (CCl}_3\text{F)}, \(^1\text{H} 300.1 \text{ MHz (TMS)}); positive shifts denote downfield resonances. \(^{109}\text{Ag} \text{ NMR experiment was run on a Bruker Avance 400 spectrometer (resonance frequency for} \(^1\text{H} 400.13 \text{ MHz,} \(^{13}\text{C} 100.6 \text{ MHz and} \(^{109}\text{Ag} 18.61 \text{ MHz}) \text{ at ambient temperature.} \text{ 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 \([\text{Ag(Py)}_2][\text{Au(CF}_3)_2]\):

\([\text{NMe}_4][\text{Au(CF}_3)_2]\] was synthesized as reported recently. \(^1\) 0.463 g (1 eq, 1.13 mmol) of \([\text{NMe}_4][\text{Au(CF}_3)_2]\] was solved in a mixture of 15 ml dried methylene chloride and 2 ml of pyridine in an \(\text{N}_2\) atmosphere. 0.219 g (1 eq, 1.13 mmol) Ag[BF\(_4\)] was added to the colourless, light protected and well stirred solution; Instantly \([\text{NMe}_4][\text{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 \([\text{NMe}_4][\text{BF}_4]\). To obtain the solid yellowish white product in nearly quantitative yield, all volatile products were removed carefully at 0 °C under reduced pressure (1 \(\times\) 10\(^{-2}\) mbar).

Formula:

\[
\begin{align*}
\text{N} & \quad 2 \\
\text{Ag} & \quad \begin{array}{c}
\text{F}_2\text{C} \quad \text{Au} \quad \text{CF}_3
\end{array}
\end{align*}
\]

\(^1\text{H} \text{ NMR (} 400.13 \text{ MHz, CD}_3\text{CN, ppm}) \delta: 8.62 \text{ (H-2,6)}, 7.95 \text{ (H4), 7.54(H-3,5);} \text{ } \(^{13}\text{C} \text{ APT NMR (} 100.6 \text{ MHz, CD}_3\text{CN, ppm}) \delta: 163.0 \text{ ([Au(CF}_3)_2]^{-qq, (}J(\text{F,C}) = 347 \text{ Hz,} 3J(\text{F,C}) = 19 \text{ Hz), 151.9 \text{ (C-2,6), 139.2 \text{ (C-3,5), 126.0 \text{ (C4);} \text{ } \(^{19}\text{F} \text{ NMR (} 282.4 \text{ MHz, CD}_3\text{CN, ppm}) \delta:}
\end{align*}
\]

28.0 s, $^1J(F,C) = 347$ Hz, $^3J(F,C) = 19$ Hz, $^4J(F,F) = 2$ 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$_3$CN) 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$_3$)Py] and [Au$^{(+III)}$(CF$_3$)$_3$]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$_3$)Py]:

$^{19}$F NMR (282.4 MHz, CD$_3$CN, ppm) δ: [Au$^{(+I)}$(CF$_3$)Py]: -23.7 s, ($^1J(C,F) = 338$ Hz); $^{13}$C NMR (75.5 MHz, CDCl$_3$, ppm) δ: [Au$^{(+I)}$(CF$_3$)Py] 139.9.

[Au$^{(+III)}$(CF$_3$)$_3$]Py:

$^{19}$F NMR (282.4 MHz, CD$_3$CN, ppm) δ: [Au$^{(+III)}$(CF$_3$)$_3$]Py: -29.9 sept, ($^1J(C,F) = 347$ Hz), -38.1 qu, ($^1J(C,F) = 361$ Hz, $^4J(F,F) = 6$ Hz). $^{13}$C NMR (75.5 MHz, CDCl$_3$, ppm) δ: [Au$^{(+III)}$(CF$_3$)$_3$]Py 110.4, 136.3.

[Au$^{(+III)}$(CF$_3$)$_4$]$^-[2]$

$^{19}$F NMR (282.4 MHz, CD$_3$CN, ppm) δ: [Au$^{(+III)}$(CF$_3$)$_4$]$^-$: -34.7 s, ($^1J(C,F) = 354$ 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$_3$CN upon 20 h UV irradiation.

Literature
