Supporting Information

for

Synthesis, structure and reactivity of an NHC silyl gold(I) complex

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1. General comments

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox under an inert atmosphere, unless otherwise stated. Dry, oxygen-free solvents were employed. Melting points were determined with a Stuart SMP40 apparatus and are uncorrected. Solution $^1H$, $^{13}C$, and $^{29}Si$ NMR spectra were recorded on a Bruker Avance 300 spectrometer at 298 K. Chemical shifts ($\delta$) are expressed with a positive sign, in parts per million. $^1H$ and $^{13}C$ chemical shifts reported are referenced internally to residual protio ($^1H$) or deuterio ($^{13}C$) solvent, while $^{29}Si$ chemical shifts are relative to SiMe$_4$ external references, respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. The $^1H$ and $^{13}C$ resonance signals were attributed by means of 2D HSQC and HMBC experiments. Mass spectra were recorded on a Waters UPLC Xevo G2 Q TOF apparatus. [AuCl(IPr)] was obtained as a generous gift from Umicore (Brussels, Belgium). All other starting materials were purchased from Aldrich (Saint-Quentin Fallavier, France), ABCR (Karlsruhe, Germany) or AlfaAesar (Schiltigheim, France). Chlorodimethylphenylsilane was distilled prior to use.
2. Synthesis and analytical data of the new complexes

Complex 1, (IPr)Au(SiMePh). A solution of PhMeSiCl (137 mg, 135 µL, 0.81 mmol, 1 equiv) in tetrahydrofuran (2 mL) was added to finely cut, shiny lithium (167 mg, 24.15 mmol, 30 equiv) in tetrahydrofuran (2 mL) placed in a Schlenk flask. The reaction mixture was stirred overnight at room temperature. The resulting dark brown solution was cooled down to 0 °C and then quickly added by cannula transfer to a dispersion of (IPr)AuCl (500 mg, 0.81 mmol, 1 equiv) in tetrahydrofuran (15 mL) at 0 °C. The solution was stirred for 2 minutes at 0 °C and then warmed up to room temperature.

Volatiles were removed under vacuum. The yellowish residue was re-dissolved in dichloromethane (2 mL), filtered over oven-dried alumina using dichloromethane (10 mL) as the eluent. The solvent of the clear-yellow filtrate was removed in vacuo. The off-white residue was washed twice with pentane (2 mL) and dried under vacuum to give silyl gold complex 1 as a white powder. Yield: 440 mg (75%). Crystals suitable for X-ray diffraction were grown at ~30 °C by slow diffusion of pentane into a concentrated solution of 1 in a dichloromethane/toluene (1:2) mixture. Mp: decomposition without melting at around 170 °C; \( ^1H \) NMR (300 MHz, CDCl₃): δ 7.62–7.46 (m, 2H, H₆), 7.36–6.97 (m, 9H, H₇), 6.29 (s, 2H, NCH₃CH₂N), 2.62 (sept, 3J\(^{HH} = 6.9\) Hz, 4H, CH₃CH₂N), 1.44 (d, 3J\(^{HH} = 6.9\) Hz, 12H, HCH₃CH₂N), 1.09 (d, 3J\(^{HH} = 6.9\) Hz, 12H, HCH₃CH₂N), 0.47 (s, 6H, HSiCH₂Ph); \( ^{13}Si\)\(^{[H]} \) NMR (60 MHz, CDCl₃): δ 12.87 (s); \( ^{13}C\)\(^{[H]} \) NMR (75 MHz, CDCl₃): δ 217.4 (s, C=O), 171.5 (s, C=O), 145.8 (s, C=O), 134.7 (s, C=O or C=O), 130.3 (s, C=O), 126.5 (s, C=O or C=O), 124.0 (s, C=O or C=O), 122.4 (s, C=O), 7.97 (m, 13H, H₆). HRMS (ESI+): calcd for [M+Na]⁺: C₃₈H₇₄N₆NaSiAu⁺: 743.3072. Found: 743.3083.

Complex 2, (IPr)AuCH=CCO(CH₃)(SiMePh). Methyl propiolate (125 µL, 0.98 mmol, 10 equiv) was added to silylgold complex 1 (100 mg, 0.14 mmol, 1 equiv) solubilized in a toluene/dichloromethane mixture (1:1, 4 mL) in a Schlenk tube. The Schlenk tube was sealed and heated for 12 hours at 100 °C. After complete conversion, the reaction mixture was cooled down to room temperature, filtered over a Celite pad and eluted with dichloromethane (10 mL). Volatiles were removed in vacuo. The off-white residue was triturated twice with pentane (2 x 3 mL) and then resolubilized in a minimum volume of dichloromethane. Pentane (3 mL) was added. The solution was stored for 3 days at ~80 °C to give complex 2 as a white crystalline solid. Yield: 71 mg (63 %). Crystals suitable for X-ray diffraction were grown from a saturated solution of 2 in a dichloromethane/benzene (1:3) mixture. Mp: 177–178 °C (decomposition); \( ^1H \) NMR (300 MHz, CDCl₃): δ 9.20 (s, 1H, H₆=CH), 7.51–7.97 (m, 13H, H₆=CH & HNCH₃CH₂N), 3.34 (s, 3H, OCH₃), 2.54 (sept, 3J\(^{HH} = 6.9\) Hz, 4H, CH₃CH₂N), 1.23 (d, 3J\(^{HH} = 6.9\) Hz, 12H, HCH₃CH₂N), 1.14 (d, 3J\(^{HH} = 6.9\) Hz, 12H, HCH₃CH₂N), 0.01 (s, 6H, HSiMe₂); \( ^{29}Si\)\(^{[H]} \) NMR (60 MHz, CDCl₃): δ –13.6 (s); \( ^{13}C\)\(^{[H]} \) NMR (75 MHz, CDCl₃): δ 196.8 (s, C=O), 196.7 (s, C=O), 189.5 (s, C=O), 171.5 (s, C=O), 145.6 (s, C=O), 145.0 (s, C=O), 134.6 (s, C=O), 133.8 (s, C=O or C=O), 130.3 (s, C=O), 127.6 (s, C=O), 127.0 (s, C=O or C=O), 124.1 (C=O), 123.0 (s, C=O), 50.5 (s, OCH₃), 28.7 (s, C(CH₃)₃), 24.2 (s, C(CH₃)₃), 24.1 (s, C(CH₃)₃), –0.4 (s, SiMe₂); HRMS (ESI+): calcd for [M+H]⁺: C₃₉H₇₆N₆O₃Si⁺: 805.3474. Found: 805.3464.
3. NMR spectra

Figure S1. $^1$H NMR spectrum of 1.

Figure S2. J-modulated $^{13}$C{$^1$H} NMR spectrum of 1.
Figure S3. $^{29}$Si\{$^1$H\} NMR spectrum of 1.

Figure S4. $^1$H NMR spectrum of 2.
Figure S5. J-modulated $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2.

Figure S6. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of 2. Silicon grease ($\delta = -21.9$ ppm) is present.
4. Crystallographic data

Crystallographic data were collected at 193(2) K on a Bruker-AXS Kappa APEX II Quazar diffractometer, with Mo Kα radiation (λ = 0.71073 Å) using an oil-coated shock-cooled crystal. Phi- and omega-scans were used. Space groups were determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed. The structures were solved using an intrinsic phasing method (SHELXT), and refined using the least-squares method on \( F^2 \). All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp\(^3\) carbon and 1.2 times for all other carbon atoms.

Complex 1: \( \text{Cs}_{36}\text{H}_{67}\text{N}_{2}\text{SiAu.C}_{37}\text{H}_{54} \), \( F_w = 812.93, 0.2 \times 0.1 \times 0.04 \text{ mm}, \) monoclinic, \( P 21/c, a = 10.3925(4), b = 20.4509(6), c = 18.9607(5) \text{ Å}, \) \( \beta = 96.549(2)^\circ, V = 4003.5(2) \text{ Å}^3, Z = 4, D_\alpha = 1.349 \text{ g/cm}^3, \mu = 3.733 \text{ mm}^{-1}. \) A total of 61457 reflections were measured, of which 9910 reflections were unique (\( R_{int} = 0.0842). \) A total of 477 parameters were refined with 255 restraints. \( R_1 [I > 2\sigma(I)]: 0.0376. \) \( wR_2 [\text{all refl.}]: 0.0724. \) Largest diff. peak and hole 2.482 and –1.006 e.Å\(^{-3}\).

Complex 2: \( \text{Cs}_{39}\text{H}_{51}\text{AuN}_{2}\text{O}_{2}\text{Si.}\frac{1}{2}\text{C}_{6}\text{H}_{6} \), \( F_w = 843.93, 0.1 \times 0.08 \times 0.04 \text{ mm}, \) triclinic, \( P \bar{1}, a = 11.3084(3), b = 12.4918(3), c = 16.5026(4) \text{ Å}, \) \( \alpha = 87.2970(10)^\circ, \beta = 80.3440(10)^\circ, \gamma = 64.2190(10)^\circ, V = 2068.54(9) \text{ Å}^3, Z = 2, D_\alpha = 1.355 \text{ g/cm}^3, \mu = 3.619 \text{ mm}^{-1}. \) A total of 30482 reflections were measured, of which 10045 reflections were unique (\( R_{int} = 0.0434). \) A total of 459 parameters were refined with 84 restraints. \( R_1 [I > 2\sigma(I)]: 0.0372. \) \( wR_2 [\text{all refl.}]: 0.0768. \) Largest diff. peak and hole 1.529 and –0.981 e.Å\(^{-3}\).

5. References