# Supporting Information

# Stepwise Alkyne Insertion in Au(I) Acetylides: Influence of the Nuclearity

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2
3
19
40
41
49
54
64
79
81
83

## 1. General considerations

Unless stated otherwise, all reactions were performed in a glovebox or on a Schlenk line under an atmosphere of pure Ar or high purity N<sub>2</sub> using standard Schlenk techniques. All solvents were dried and degassed prior to use.  $C_6D_6$  and  $Tol-d_8$  were distilled under Ar and stored over 3 Å molecular sieves for at least 24 h prior to use. THF- $d_8$  was dried over sodium/benzophenone before being distilled and degassed by three freeze-pump-thaw cycles. Dimethyl acetylenedicarboxylate was distilled and stored under N<sub>2</sub>. [IPrAuCI] (1),<sup>[1]</sup> [SIPrAuCI] (2),<sup>[1]</sup> [IPrAuOH] (5),<sup>[2]</sup> [IPrAuOTf],<sup>[3]</sup> LiC=CSiMe<sub>3</sub>,<sup>[4]</sup> LiC=CPh<sup>[4]</sup> and bis(4-(methoxycarbonyl)phenyl)acetylene<sup>[5]</sup> were prepared according to literature procedures. The reported complexes SIPrAuOH (6)<sup>[6]</sup> IPrAuC=CH (9),<sup>[7]</sup> and IPrAuCCPh (12)<sup>[8]</sup> were synthesized following a modified procedure. CD<sub>3</sub>CN and all other reagents were purchased from commercial suppliers and used as received.

#### NMR spectroscopy

NMR spectra were recorded on Bruker Avance NEO 500, Avance NEO 400, Avance NEO 300 spectrometers, and they were referenced to external SiMe<sub>4</sub> ( $\delta$  0 ppm) using the residual protio solvent peaks as internal standard (<sup>1</sup>H NMR experiments) or the characteristic resonances of the solvent nuclei (<sup>13</sup>C NMR experiments). Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate.

#### Mass Spectrometry

Electrospray Ionization Mass Spectrometry (ESI-MS) or Atmospheric-Pressure Chemical Ionization (APCI) measurements were performed on a Bruker Orbitrap Elite apparatus at the Mass Spectrometry service of the University of Seville Research, Technology and Innovation Centre.

#### Elemental analysis

Elemental analyses were performed by José Manuel Pérez Falcón at the Microanalytical Facility at IIQ (Instituto de Investigaciones Químicas de Sevilla), using a LECO TruSpec CHN analyzer for determination of %C, %H, %N and %S.

#### Vibrational spectroscopy

FT-IR spectra were acquired using a Bruker Tensor 27 spectrometer with a Platinum ATR accessory (Thermo Scientific Nicolet iS5 iD7)

Raman spectra of solid samples were acquired at ICMS (Instituto de Ciencia de Materiales de Sevilla) by Dr. Miguel Ángel Avilés Escaño using a LabRAM Horiba Jobin Yvon confocal microscope equipped with 3 excitation lasers (785 nm red, 532 nm green, and 325 nm UV).

- 2. Synthesis and characterization
- [IPrAuC≡CSiMe<sub>3</sub>] (3)



In a N<sub>2</sub>-filled glovebox, a 13 mL scintillation vial was charged with a stir bar, complex **1** (217 mg, 0.349 mmol) and lithium (trimethylsilyl)acetylide (40 mg, 0.384 mmol). Dry toluene (6 mL) was added to the mixture of solids, and the reaction mixture was left stirring at 25 °C for 1.5 h, after which it was filtered through a 0.2  $\mu$ m PTFE filter. The reaction vial and filter were rinsed with toluene (5 mL) and the combined filtrates were transferred to a 25 mL round-bottom flask, which was taken out of the glovebox. The resulting pale yellow solution was evaporated under vacuum, and the resulting solid was washed with *n*-pentane (2 x 5 mL). The supernatant was carefully removed, and the solid was dried under vacuum, giving complex **3** as a colorless solid (218 mg, 0.319 mmol, 91% yield). Colorless crystals suitable for X-ray diffraction analysis were grown from a cold *n*-pentane solution of **3** at -30 °C.

<sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.18 - 7.13 (m, 2H, C<u>H</u> Ph<sub>para</sub>)\*, 6.99 (d, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 6.21 (s, 2H, C<u>H</u><sub>imid</sub>), 2.51 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.37 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.03 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.10 (s, 9H, Si(C<u>H</u><sub>3</sub>)<sub>3</sub>) ppm. <sup>1</sup>H NMR (400 MHz, Tol-*d*<sub>8</sub>, 298 K): δ 7.14 (t, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 2H, C<u>H</u> Ph<sub>para</sub>), 6.98 (d, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 6.31 (s, 2H, C<u>H</u><sub>imid</sub>), 2.51 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.04 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.05 (s, 9H, Si(C<u>H</u><sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 192.84 (Au<u>C</u><sub>carbene</sub>), 150.09 (Au<u>C</u><sub>alkyne</sub>), 145.64 (<u>C</u>q Phorto), 134.54 (N<u>C</u>q Phipso), 130.78 (<u>C</u>H Ph<sub>para</sub>), 124.26 (<u>C</u>H Ph<sub>meta</sub>), 122.73 (=<u>C</u>H<sub>imid</sub>), 107.21 (Si<u>C</u><sub>alkyne</sub>), 29.01 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.88 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.90 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 1.46 (Si(<u>C</u>H<sub>3</sub>)<sub>3</sub>) ppm. <sup>29</sup>Si NMR (HMBC <sup>1</sup>H-<sup>29</sup>Si, 300-60 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -25.78 (<u>Si</u>(CH<sub>3</sub>)<sub>3</sub>) ppm.

\*Overlaps with the residual signal of the deuterated solvent C<sub>6</sub>D<sub>6</sub>.

**Elem. Anal.** Calcd for: C<sub>32</sub>H<sub>45</sub>AuN<sub>2</sub>Si: C, 56.29; H, 6.64; N, 4.1. Found: C, 56.49; H, 6.25; N, 3.91.

**IR** (ATR) 2054 (v<sub>C≡C</sub>) cm<sup>-1</sup>

• [SIPrAuC≡CSiMe<sub>3</sub>] (4)



In a N<sub>2</sub>-filled glovebox, a 13 mL scintillation vial was charged with a stir bar, chloride complex **2** (98 mg, 0.157 mmol) and lithium (trimethylsilyl)acetylide (21.3 mg, 0.204 mmol). Dry toluene (2.6 mL) was added to the mixture of solids, and the reaction mixture was left stirring at 25 °C for 4 h, after which it was filtered through a 0.2  $\mu$ m PTFE filter. The reaction vial and filter were rinsed with toluene (3 mL) and the combined filtrates were transferred to a 25 mL round-bottom flask, which was taken out of the glovebox. The resulting colorless solution was evaporated under vacuum, and the resulting solid was washed with *n*-pentane (2 x 1.5 mL). The supernatant was carefully removed, and the solid was dried under vacuum, giving complex **4** as a white solid (95 mg, 0.138 mmol, 88% yield).

<sup>1</sup>H NMR (500 MHz, ToI-*d*<sub>8</sub>, 298 K): δ 7.09 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 2H, C<u>*H*</u> Ph<sub>para</sub>), 6.96 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 3.27 (s, 4H, C<u>*H*</u><sub>2-imid</sub>), 2.94 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.44 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.15 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 0.00 (s, 9H, Si(C<u>*H*</u><sub>3</sub>)<sub>3</sub>) ppm. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.12 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 2H, C<u>*H*</u> Ph<sub>para</sub>), 6.98 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 3.10 (s, 4H, C<u>*H*<sub>2-imid</sub>), 2.92 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 4H, C<u>*H*(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>), 1.14 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>), 0.06 (s, 9H, Si(C<u>*H*<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, ToI-*d*<sub>8</sub>, 298 K): δ 212.63 (Au<u>C</u><sub>carbene</sub>), 150.75 (Au<u>C</u><sub>alkyne</sub>), 146.53 (<u>C</u><sub>q</sub> Phorto</sub>), 134.54 (N<u>C</u><sub>q</sub> Phipso</sub>), 130.04 (<u>C</u>H Ph<sub>para</sub>), 124.53 (<u>C</u>H Ph<sub>meta</sub>), 107.35 (Si<u>C</u><sub>alkyne</sub>), 53.53 (<u>C</u>H<sub>2-imid</sub>), 29.11 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 25.31 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.05 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 1.31 (Si(<u>C</u>H<sub>3</sub>)<sub>3</sub>) ppm. <sup>29</sup>Si NMR (HMBC <sup>1</sup>H-<sup>29</sup>Si, 400-79 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -26.57 (<u>Si</u>(CH<sub>3</sub>)<sub>3</sub>) ppm.</u></u></u></u></u>

**Elem. Anal.** Calcd for: C<sub>32</sub>H<sub>47</sub>AuN<sub>2</sub>Si: C, 56.13; H, 6.92; N, 4.09. Found: C, 56.07; H, 6.74; N, 4.2.

IR (ATR) 2056 (vc≡c) cm<sup>-1</sup>

## • [SIPrAuOH] (6)



This procedure is based on that reported by Nolan, Cazin *et al.*<sup>[2]</sup> In a N<sub>2</sub>-filled glovebox, a solution of potassium *tert*-amylate in toluene (191  $\mu$ L, 0.325 mmol, 1.7 M) was added to a J. Young flask containing a stir bar and a cloudy suspension of SIPrAuCl complex **2** (135 mg, 0.217 mmol) in dry toluene (4.5 mL) under vigorous stirring. The suspension became a colorless clear solution after 5 min. Then, the solution was taken out of the glovebox and exposed to air for 1 min, after which the J. Young flask was closed, and the resulting clear suspension was left stirring at 25 °C for 2 h. The reaction mixture was filtered through Celite (2 cm height in a Pasteur pipette) with additional toluene (20 mL).\* The combined filtrates were collected in a 50 mL round bottom flask, after which 0.5 mL of water was added to ensure complete hydrolysis. Then, the solution was concentrated under vacuum to approximately 0.5-1 mL. At this point, *n*-pentane (20 mL) was added with vigorous stirring. The supernatant was carefully removed, and the product was dried under vacuum, giving complex **6** as a colorless solid (118 mg, 0.195 mmol, 90% yield).

\*Filtration had to be performed using external pressure to minimize exposure to air, according to the reported method.<sup>[2]</sup>

The NMR chemical shifts for this sample in CDCl<sub>3</sub> match those described in the literature.<sup>[6]</sup>

<sup>1</sup>**H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):**  $\delta$  7.19 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 2H, C<u>*H*</u> Ph<sub>para</sub>), 7.04 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 3.17 (s, 4H, C<u>*H*</u><sub>2-imid</sub>), 2.98 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.51 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.17 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.17 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 0.35 (s, 1H, Au-O<u>*H*</u>) ppm.

• [IPrAuC≡CAuIPr] (7)



Under air, a J. Young flask was charged with a stir bar, complex **3** (100 mg, 0.147 mmol) and hydroxide species **5** (88.3 mg, 0.147 mmol). Technical-grade toluene (3 mL) was added to the mixture of solids, and the resulting suspension was left stirring at 100 °C in an oil bath for 15 h. Then, the resulting pale yellow solution was concentrated under vacuum to approximately 1 mL. Addition of *n*-pentane (5 mL) under vigorous stirring resulted in the immediate precipitation of bimetallic acetylide **7**. The supernatant was carefully removed, and the precipitate was washed with *n*-pentane (2 x 3 mL). Then, the product was dried under vacuum, giving complex **7** as a colorless solid (159 mg, 0.133 mmol, 91% yield). Colorless crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-pentane into a benzene solution of **7**.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.15 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> Ph<sub>para</sub>), 6.96 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 8H, C<u>H</u> Ph<sub>meta</sub>), 6.16 (s, 4H, C<u>H</u><sub>imid</sub>), 2.49 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 8H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.99 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>1</sup>H NMR (400 MHz, Tol-d<sub>8</sub>, 298 K):  $\delta$  7.10 (t, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 4H, C<u>H</u> Ph<sub>para</sub>), 6.92 (d, <sup>3</sup>J<sub>H-H</sub> = 7.7 Hz, 8H, C<u>H</u> Ph<sub>meta</sub>), 6.26 (s, 4H, C<u>H</u><sub>imid</sub>), 2.48 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 8H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.99 (d, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  7.49 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> Ph<sub>para</sub>), 7.33 (s, 4H, C<u>H</u>imid), 7.31 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 8H, C<u>H</u> Ph<sub>para</sub>), 7.33 (s, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.17 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  195.00 (Au<u>C</u><sub>carbene</sub>), 145.73 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 142.92 (Au<u>C</u><sub>alkyne</sub>), 134.91 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 130.37 (<u>C</u>H Ph<sub>para</sub>), 124.11 (<u>C</u>H Ph<sub>meta</sub>), 122.20 (=<u>C</u>H<sub>imid</sub>), 28.94 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.78 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.95 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.

**Elem. Anal.** Calcd for: C<sub>56</sub>H<sub>72</sub>Au<sub>2</sub>N<sub>4</sub>: C, 56.28; H, 6.07; N, 4.69. Found: C, 56.17; H, 6.27; N, 4.45.

**HRMS** (APCI) *m*/*z* calculated for  $[C_{56}H_{72}Au_2N_4]^+$ : 1195.5161, found: 1195.5157. The sample undergoes fragmentation under the experimental conditions, giving terminal alkyne complex **9** as the main species in the mass spectrum (Figure S43).

Raman 2012 (v<sub>C≡C</sub>) cm<sup>-1</sup>

• [SIPrAuC≡CAuSIPr] (8)



Under air, a J. Young flask was charged with a stir bar, complex **4** (72 mg, 0.105 mmol) and complex **6** (64 mg, 0.105 mmol). Technical-grade toluene (2.5 mL) was added to the mixture of solids, and the resulting suspension was left stirring at 110 °C in an oil bath for 15 h. Then, the resulting pale yellow solution was evaporated under vacuum to give a yellow residue that was dissolved in THF (3 mL) and transferred to a vial. The yellow solution was layered with *n*-pentane (6 mL) and the resulting bilayer was left to stand at room temperature for 1 day, after which X-ray quality colorless crystals were observed. The supernatant was carefully removed, and the crystals were washed with *n*-pentane (3 mL). Then, the product was dried under vacuum, giving complex **8** as a white solid (105.8 mg, 0.0882 mmol, 84% yield).

<sup>1</sup>H NMR (500 MHz, ToI-*d*<sub>8</sub>, 298 K): δ 7.03 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 4H, C<u>*H*</u> Ph<sub>para</sub>), 6.87 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.7 Hz, 8H, C<u>*H*</u> Ph<sub>meta</sub>), 3.17 (s, 4H, C<u>*H*</u><sub>2-imid</sub>), 2.86 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 8H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.28 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 24H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.08 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 24H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 21.08 (C<u>*H*(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 21.08 (C<u>*H*(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 22.24 (C<u>*H*(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 22.24 (C<u>*H*(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 24.08 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.</u></u></u></u>

**Elem. Anal.** Calcd for: C<sub>56</sub>H<sub>76</sub>Au<sub>2</sub>N<sub>4</sub>: C, 56.09; H, 6.39; N, 4.67. Found: C, 56.15; H, 6.46; N, 4.67.

Raman 2003 (v<sub>C=C</sub>) cm<sup>-1</sup>

#### • [IPrAuC≡CH] (9)



This procedure is based on that reported by Roesky et al.<sup>[9]</sup> In a N<sub>2</sub>-filled glovebox, a solution of ethynylmagnesium bromide in THF (387 µL, 0.194 mmol, 0.5 M) was added to a 13 mL scintillation vial containing a stir bar and a solution of complex 1 (80 mg, 0.129 mmol) in dry THF (2.8 mL). The reaction mixture was left stirring at 25 °C for 8 h, after which it was transferred to a J. Young flask and connected to a Schlenk line. The solution was evaporated under vacuum and the resulting orange oil was treated with n-pentane, after which a colorless solid was obtained. The remaining solid was extracted with toluene (3 mL) and filtered via cannula to a 25 mL round bottom flask subsequently exposed to air. The resulting pale yellow solution was evaporated under vacuum, giving complex 9 as a colorless solid. The yield obtained following this procedure is 110% (86.8 mg, 0.142 mmol). <sup>1</sup>H NMR analysis exhibits a clean spectrum (Figure S16), which implies the presence of an impurity not visible by NMR. NMR analysis of this sample with a known quantity of the internal standard 1,3,5-trimethoxybenzene exhibits a 74% purity (see Figure S17). The spectroscopic yield obtained for complex **5** is then 81% (63.4 mg, 0.105 mmol).

The NMR chemical shifts for this sample in CDCI<sub>3</sub> match those described in the literature.<sup>[7]</sup>

<sup>1</sup>**H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):**  $\delta$  7.18 - 7.15 (m, 2H, C<u>*H*</u> Ph<sub>para</sub>)\*, 7.02 (d, <sup>3</sup>*J*<sub>H</sub> = 7.7 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 6.23 (s, 2H, C<u>*H*</u><sub>imid</sub>), 2.54 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.54 (s, 1H, AuC≡C<u>*H*</u>) 1.40 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.04 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>) ppm.

\*Overlaps with the residual signal of the deuterated solvent C<sub>6</sub>D<sub>6</sub>.

• [IPrAuC(COOMe)=C(COOMe)C=CAuIPr] (10)



In a N<sub>2</sub>-filled glovebox, dimethyl acetylenedicarboxylate (5.38  $\mu$ L, 0.0439 mmol) was added to a J. Young flask containing a stir bar and a solution of **7** (50 mg, 0.0418 mmol) in dry toluene (3.2 mL). The flask was taken out of the glovebox, and the reaction mixture was left stirring at 70 °C in an oil bath for 16 h. The resulting pale yellow solution was concentrated under vacuum to approximately 1 mL. Addition of *n*-pentane (6 mL) under vigorous stirring led to the immediate precipitation of insertion product **10**. Excess dimethyl acetylenedicarboxylate had to be removed by washing the resulting solid with toluene (3 x 3 mL) and *n*-pentane (3 x 3 mL). Then, the product was dried under vacuum, giving complex **10** as a colorless solid (49 mg, 0.0366 mmol, 87% yield). Colorless crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-pentane into a benzene solution of **10**.

<sup>1</sup>H NMR (500 MHz, Tol-*d*<sub>8</sub>, 298 K): δ 7.29 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 2H, C<u>*H*</u> Ph<sub>para</sub>), 7.14 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 7.08 (m, 2H, C<u>*H*</u> Ph<sub>para</sub>)\*, 7.00 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 4H, C<u>*H*</u> Ph<sub>meta</sub>), 6.40 (s, 4H, C<u>*H*</u>imid)\*\*, 3.46 (s, 3H, C(O)OC<u>*H*</u><sub>3</sub>), 3.12 (s, 3H, C(O)OC<u>*H*</u><sub>3</sub>), 2.67 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 2.55 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.49 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.38 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.14 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.4 Hz, 24H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>)\*\*\*ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Tol-*d*<sub>8</sub>, 298 K): δ 194.30 (Au<u>C</u><sub>carbene</sub>), 194.00 (Au<u>C</u><sub>carbene</sub>), 177.99 (Au<u>C</u><sub>alkene</sub>), 175.70 (<u>C</u>(O)OCH<sub>3</sub>), 166.92 (<u>C</u>(O)OCH<sub>3</sub>), 145.82 (<u>C</u><sub>q</sub> Phorto</sub>), 145.77 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 135.07 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 134.58 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 130.67 (<u>C</u>H Ph<sub>para</sub>), 130.55 (<u>C</u>H Ph<sub>para</sub>), 124.33 (Au<u>C</u><sub>alkyne</sub>), 124.29 (<u>C</u>H Ph<sub>meta</sub>), 124.03 (<u>C</u>H Ph<sub>meta</sub>), 122.76 (=<u>C</u>H<sub>imid</sub>), 122.34 (=<u>C</u>H<sub>imid</sub>), 104.77 (AuC=<u>C</u>), 50.38 (O<u>C</u>H<sub>3</sub>), 49.82 (O<u>C</u>H<sub>3</sub>), 29.17 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.09 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm.

The resonance for one of the alkene carbons was not observed.

\*Overlaps with the residual signal of the deuterated solvent Tol-*d*<sub>8</sub>. \*\*Two singlets are observed upon dilution of the sample. \*\*\*Two doublets are observed upon dilution of the sample.

**Elem. Anal.** Calcd for: C<sub>62</sub>H<sub>78</sub>Au<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C, 55.69; H, 5.88; N, 4.19. Found: C, 55.87; H, 5.98; N, 3.82.

**IR** (ATR) 1693 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations.

• [SIPrAuC(COOMe)=C(COOMe)C=CAuSIPr] (11)



In a N<sub>2</sub>-filled glovebox, dimethyl acetylenedicarboxylate (9  $\mu$ L, 0.0734 mmol) was added to a J. Young flask containing a stir bar and a solution of **8** (44 mg, 0.0367 mmol) in dry toluene (1.8 mL). The flask was taken out of the glovebox, and the pale yellow reaction mixture was left stirring at 70 °C in an oil bath for 16 h, after which it was concentrated under vacuum to approximately 0.5 mL. Addition of *n*-pentane (3 mL) under vigorous stirring led to the immediate precipitation of insertion product **11**. Excess dimethyl acetylenedicarboxylate had to be removed by washing the resulting solid with toluene (2 x 0.5 mL) and *n*-pentane (2 x 3 mL). Then, the product was dried under vacuum, giving complex **11** as a colorless solid (41 mg, 0.0306 mmol, 83% yield).

<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K): δ 7.50 (t,  ${}^{3}J_{H-H} = 7.8$  Hz, 2H, C<u>H</u> Ph<sub>para</sub>), 7.38 (t,  ${}^{3}J_{H-H} = 7.8$  Hz, 2H, C<u>H</u> Ph<sub>para</sub>), 7.36 (d,  ${}^{3}J_{H-H} = 7.8$  Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 7.20 (d,  ${}^{3}J_{H-H} = 7.8$  Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 4.00 (s, 4H, C<u>H</u><sub>2-imid</sub>), 3.94 (s, 4H, C<u>H</u><sub>2-imid</sub>), 3.32 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 3.19 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 3.01 (sept,  ${}^{3}J_{H-H} = 6.8$  Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.34 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.26 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.13 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.34 (d,  ${}^{2}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.33 (d,  ${}^{3}J_{H-H} = 6.8$  Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, CH<sub>3</sub>)<sub>2</sub>), 1.35.61 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 133.11 (AuC=<u>C</u>), 130.76 (<u>C</u>H Ph<sub>para</sub>), 130.47 (<u>C</u>H Ph<sub>para</sub>), 123.73 (Au<u>C</u><sub>alkyne</sub>), 125.55 (<u>C</u>H Ph<sub>meta</sub>), 125.19 (<u>C</u>H Ph<sub>meta</sub>), 104.14 (AuC=<u>C</u>), 54.84 (=<u>C</u>H<sub>2-imid</sub>), 54.61 (=<u>C</u>H<sub>2-imid</sub>), 51.77 (O<u>C</u>H<sub>3</sub>), 50.64 (O<u>C</u>H<sub>3</sub>), 29.54 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 25.91 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 25.74 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.38 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.

**Elem. Anal.** Calcd for: C<sub>62</sub>H<sub>82</sub>Au<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C, 55.52; H, 6.16; N, 4.18. Found: C, 55.62; H, 6.3; N, 3.92.

**IR** (ATR) 1703 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations for related complexes.

#### • [IPrAuC≡CPh] (12)



In a N<sub>2</sub>-filled glovebox, a 13 mL scintillation vial was charged with a stir bar, chloride complex **1** (125 mg, 0.202 mmol) and lithium phenylacetylide (28.4 mg, 0.263 mmol). Dry toluene (6 mL) was added to the mixture of solids, and the reaction mixture was left stirring at 25 °C for 6 h, after which it was filtered through Celite (1.5 cm height in a Pasteur pipette). The reaction vial and filter were rinsed with toluene (8 mL) and the combined filtrates were transferred to a 25 mL round-bottom flask, which was taken out of the glovebox. The resulting solution was evaporated under vacuum, and the resulting solid was washed with *n*-pentane (5 mL). The supernatant was carefully removed, and the solid was transferred to a vial as a suspension in *n*-pentane (3 mL). Then, the solid was dried under vacuum, giving complex **12** as a colorless solid (127 mg, 0.185 mmol, 92% yield).

The NMR chemical shifts for this sample in  $C_6D_6$  match those described in the literature.<sup>[8]</sup>

<sup>1</sup>H NMR (500 MHz, ToI-*d*<sub>8</sub>, 298 K): δ 7.26 (d,  ${}^{3}J_{H-H} = 7.9$  Hz, 2H, C<u>*H*</u> C≡C-Ph<sub>orto</sub>), 7.17 (t,  ${}^{3}J_{H-H} = 7.8$  Hz, 2H, C<u>*H*</u>  ${}^{IPr}Ph_{para}$ ), 7.01 (d,  ${}^{3}J_{H-H} = 7.8$  Hz, 4H, C<u>*H*</u>  ${}^{IPr}Ph_{meta}$ ), 6.82 (t,  ${}^{3}J_{H-H} = 7.4$  Hz, 2H, C<u>*H*</u> C≡C-Ph<sub>meta</sub>), 6.77 (t,  ${}^{3}J_{H-H} = 7.4$  Hz, 1H, C<u>*H*</u> C≡C-Ph<sub>para</sub>), 6.34 (s, 2H, C<u>*H*</u><sub>imid</sub>), 2.57 (sept,  ${}^{3}J_{H-H} = 6.9$  Hz, 4H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.41 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>), 1.07 (d,  ${}^{3}J_{H-H} = 6.9$  Hz, 12H, CH(C<u>*H*</u><sub>3</sub>)<sub>2</sub>) ppm. • [IPrAuC(COOMe)=C(COOMe)C=CSiMe<sub>3</sub>] (13)



In a N<sub>2</sub>-filled glovebox, dimethyl acetylenedicarboxylate (44 µL, 0.359 mmol) was added to a J. Young flask containing a stir bar and a solution of 3 (108 mg, 0.158) mmol) in dry toluene (3 mL). The flask was taken out of the box, and the colorless reaction mixture was left stirring at 110 °C in an oil bath for 15 h, after which the reaction mixture became a dark orange solution. Then, the solvent was evaporated under vacuum, giving a dark orange oil. Diethyl ether (4 mL) was added to the oil, after which the resulting brown mixture was transferred to a dram vial and stored at -30 °C for 2 days. After this time, crystals of 13 were observed in the vial. The yield obtained following this procedure is 49% (64 mg, 0.078 mmol). However, <sup>1</sup>H NMR analysis exhibits a very small amount of DMAD left in the sample (9% relative to the insertion product 13, see Figure S24). Further purification involves washing the crystals with toluene (1 mL) and *n*-pentane (6 mL) to ensure complete removal of DMAD (Figure S23). This treatment gives complex **13** as a white powder (21 mg, 0.0255 mmol, 16% yield). Macroscopically orange crystals suitable for X-ray diffraction analysis were grown from a cold diethyl ether solution of **13** at -30 °C.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 7.18 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 2H, C<u>H</u> Ph<sub>para</sub>), 7.06 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 6.28 (s, 2H, C<u>H</u><sub>imid</sub>), 3.58 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 3.17 (s, 3H, C(O)OC<u>H</u><sub>3</sub>) 2.56 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.49 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.49 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.25 (s, 9H, Si(C<u>H</u><sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 192.10 (Au<u>C</u><sub>carbene</sub>), 188.95 (Au<u>C</u><sub>alkene</sub>), 174.74 (<u>C</u>=O), 164.64 (<u>C</u>=O), 145.50 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 134.24 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 130.71 (<u>C</u>H Ph<sub>para</sub>), 124.10 (<u>C</u>H Ph<sub>meta</sub>), 122.77 (=<u>C</u>H<sub>imid</sub>), 120.09 (AuC=<u>C</u>), 108.48 (<u>C</u>=CSiMe<sub>3</sub>), 90.00 (Si<u>C</u><sub>alkyne</sub>), 51.08 (O<u>C</u>H<sub>3</sub>), 50.26 (O<u>C</u>H<sub>3</sub>), 28.91 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.76 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.81 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 0.44 (Si(<u>C</u>H<sub>3</sub>)<sub>3</sub>) ppm. <sup>29</sup>Si NMR (HMBC <sup>1</sup>H-<sup>29</sup>Si, 400-79 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -18.76 (<u>Si</u>(CH<sub>3</sub>)<sub>3</sub>) ppm.

**Elem. Anal.** Calcd for: C<sub>38</sub>H<sub>51</sub>AuN<sub>2</sub>O<sub>4</sub>Si: C, 55.33; H, 6.23; N, 3.4. Found: C, 55.59; H, 5.89; N, 3.1.

**IR** (ATR) 1713 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations.

• [SIPrAuC(COOMe)=C(COOMe)C=CSiMe<sub>3</sub>] (14)



In a N<sub>2</sub>-filled glovebox, dimethyl acetylenedicarboxylate (31.3  $\mu$ L, 0.256 mmol) was added to a J. Young flask containing a stir bar and a solution of **4** (35 mg, 0.0511 mmol) in dry toluene (1.2 mL). The flask was taken out of the box, and the colorless reaction mixture was left stirring at 120 °C in an oil bath for 15 h. The reaction mixture was then transferred to a dram vial. Then, the reaction flask was rinsed with toluene (0.5 mL) and the rinses were also added to the dram vial. The vial was stored at -30 °C for 1 week, after which red crystals were observed. The supernatant was discarded, and the crystals were triturated and washed with *n*-pentane (6 mL). Then, the supernatant was carefully removed, and the resulting solid was dried under vacuum, giving complex **14** as a brown powder (32 mg, 0.0388 mmol, 76% yield).

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  7.44 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 2H, C<u>H</u> Ph<sub>para</sub>), 7.30 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 4.03 (s, 4H, C<u>H</u><sub>2-imid</sub>), 3.48 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 3.34 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 3.15 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.37 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.37 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.08 (s, 9H, Si(C<u>H</u><sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  209.44 (Au<u>C</u><sub>carbene</sub>), 189.25 (Au<u>C</u><sub>alkene</sub>), 175.60 (<u>C</u>=O), 165.56 (<u>C</u>=O), 148.18 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 135.52 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 130.69 (<u>C</u>H Ph<sub>para</sub>), 125.38 (<u>C</u>H Ph<sub>meta</sub>), 107.03 (AuC=<u>C</u>), 92.77 (Si<u>C</u><sub>alkyne</sub>), 75.95 (<u>C</u>=CSiMe<sub>3</sub>), 54.77 (=<u>C</u>H<sub>2-imid</sub>), 52.32 (O<u>C</u>H<sub>3</sub>), 50.97 (O<u>C</u>H<sub>3</sub>), 29.50 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 25.72 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.33 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 0.25 (Si(<u>C</u>H<sub>3</sub>)<sub>3</sub>) ppm. <sup>29</sup>Si NMR (HMBC <sup>1</sup>H-<sup>29</sup>Si, 400-79 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$  -18.76 (<u>Si</u>(CH<sub>3</sub>)<sub>3</sub>) ppm.

**Elem. Anal.** Calcd for: C<sub>38</sub>H<sub>53</sub>AuN<sub>2</sub>O<sub>4</sub>Si: C, 55.2; H, 6.46; N, 3.39. Found: C, 55.37; H, 6.24; N, 3.22.

**IR** (ATR) 1707 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations.

• [IPrAuC(COOMe)=C(COOMe)C=CPh] (15)



In a N<sub>2</sub>-filled glovebox, dimethyl acetylenedicarboxylate (71 µL, 0.579 mmol) was added to a J. Young flask containing a stir bar and a solution of **12** (40 mg, 0.0579 mmol) in dry toluene (2 mL). The flask was taken out of the box, and the pale yellow reaction mixture was left stirring at 110 °C in an oil bath for 22 h, after which it became an orange solution, which was transferred to a dram vial. Then, the orange solution was layered with *n*-pentane (2 mL). The resulting bilayer was left to stand at -30 °C for 1 day, after which orange crystals were observed. The supernatant was discarded, and the crystals were vigorously stirred in *n*-pentane (2 x 2 mL) for 1 min. The supernatant was carefully removed, and the resulting solid was dried under vacuum, giving complex **15** as a yellow powder (37 mg, 0.0446 mmol, 77% yield). Colorless crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-pentane into a toluene solution of **15**.

<sup>1</sup>H NMR (500 MHz, Tol-*d*<sub>8</sub>, 298 K):\* δ 7.30 (m, 2H, C<u>H</u> C≡CPhorto), 7.11 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 2H, C<u>H</u> <sup>IPr</sup>Ph<sub>para</sub>), 6.99 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> <sup>IPr</sup>Ph<sub>meta</sub>), 6.35 (s, 2H, C<u>H</u><sub>imid</sub>), 3.56 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 3.22 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 2.52 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.39 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.06 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.06 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.06 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, Tol-*d*<sub>8</sub>, 298 K):\* δ 192.66 (Au<u>C</u><sub>carbene</sub>), 189.47 (Au<u>C</u><sub>alkene</sub>), 174.44 (<u>C</u>=O), 164.43 (<u>C</u>=O), 145.67 (<u>C</u><sub>q</sub> <sup>IPr</sup>Phorto), 134.41 (N<u>C</u><sub>q</sub> <sup>IPr</sup>Ph<sub>ipso</sub>), 132.28 (<u>C</u>H C≡CPhorto), 130.71 (<u>C</u>H <sup>IPr</sup>Ph<sub>para</sub>), 124.16 (<u>C</u>H <sup>IPr</sup>Ph<sub>meta</sub>), 122.91 (=<u>C</u>H<sub>imid</sub>), 119.88 (AuC=<u>C</u>), 92.48 (<u>C</u>≡CPh), 85.46 (C≡<u>C</u>Ph), 51.05 (O<u>C</u>H<sub>3</sub>), 50.19 (O<u>C</u>H<sub>3</sub>), 29.08 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.65 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.91 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.

\*Aromatic protons and carbons (meta and para, <u>**CH**</u> C=CPh) are not assigned due to overlap with the residual signal of the deuterated solvent Tol- $d_8$ .

**Elem. Anal.** Calcd for: C<sub>41</sub>H<sub>47</sub>AuN<sub>2</sub>O<sub>4</sub>: C, 59.42; H, 5.72; N, 3.38. Found: C, 59.65; H, 5.77; N, 3.4.

**IR** (ATR) 1709 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations.

[IPrAuC(COOMe)=C(Ph)C=CAuIPr] (16)



In a N<sub>2</sub>-filled glovebox, methyl phenylpropiolate (37  $\mu$ L, 0.251 mmol) was added to a dram vial containing a solution of **7** (30 mg, 0.0251 mmol) in dry toluene (0.8 mL). The resulting yellow solution was transferred to a J. Young NMR tube, which was left to stand at 120°C in an oil bath for 16 h. Then, the reaction mixture was transferred to a dram vial and layered with *n*-pentane (7 mL). The resulting bilayer was left to stand at room temperature for 1 day, after which colorless crystals were observed. The supernatant was carefully removed, and the crystals were washed with *n*-pentane (3 mL). Then, the product was dried under vacuum, giving complex **16** as a white solid (28 mg, 0.0206 mmol, 82% yield). Colorless crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-pentane into a C<sub>6</sub>D<sub>6</sub> solution of **16**.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.55 (m, 2H, C<u>H</u> Ph<sub>ortho</sub>), 7.29 (t, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 2H, C<u>H</u> <sup>IPr</sup>Ph<sub>para</sub>), 7.14 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> <sup>IPr</sup>Ph<sub>meta</sub>), 7.11 - 7.08 (m, 2H, C<u>H</u> <sup>IPr</sup>Ph<sub>para</sub>), 7.02 (d, <sup>3</sup>J<sub>H-H</sub> = 7.8 Hz, 4H, C<u>H</u> <sup>IPr</sup>Ph<sub>meta</sub>), 6.92 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 2H, C<u>H</u> Ph<sub>meta</sub>), 6.83 (tt, <sup>3</sup>J<sub>H-H</sub> = 7.4 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.3 Hz, 1H, C<u>H</u> Ph<sub>para</sub>), 6.35 (s, 2H, C<u>H</u><sub>imid</sub>), 6.31 (s, 2H, C<u>H</u><sub>imid</sub>), 3.27 (s, 3H, C(O)OC<u>H</u><sub>3</sub>), 2.64 (m, 8H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.50 (t, <sup>3</sup>J<sub>H-H</sub> = 7.6 Hz, 24H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.17 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.12 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  194.91 (Au<u>C</u><sub>carben</sub>), 194.00 (Au<u>C</u><sub>carben</sub>), 176.76 (<u>C</u>(O)OCH<sub>3</sub>), 165.43 (<u>C</u><sub>alken</sub>), 145.87 (<u>C</u><sub>q</sub> <sup>IPr</sup>Ph<sub>orto</sub>), 133.42 (Au<u>C</u>=C), 130.68 (<u>C</u>H <sup>IPr</sup>Ph<sub>para</sub>), 130.55 (<u>C</u>H <sup>IPr</sup>Ph<sub>para</sub>), 128.93 (<u>C</u>H <sup>IPr</sup>Ph<sub>ipso</sub>), 133.42 (Au<u>C</u>=C), 130.68 (<u>C</u>H <sup>IPr</sup>Ph<sub>para</sub>), 124.30 (<u>C</u>H <sup>IPr</sup>Ph<sub>meta</sub>), 124.10 (<u>C</u>H <sup>IPr</sup>Ph<sub>meta</sub>), 122.64 (=<u>C</u>H<sub>imid</sub>), 125.19 (CH Ph<sub>para</sub>), 124.30 (CH (<u>C</u>H<sub>3</sub>)<sub>2</sub>), 29.10 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.13 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. The resonance of one of the alkene carbons was not observed.

**Elem. Anal.** Calcd for:  $C_{66}H_{80}Au_2N_4O_2$ : C, 58.49; H, 5.95; N, 4.13. Found: C, 58.67; H, 6.15; N, 3.85.

**IR** (ATR) 1680 ( $v_{C=O}$ ) cm<sup>-1</sup>. The  $v_{C=C}$  stretch was not observed, in agreement with its expected low intensity as corroborated by DFT calculations.

• [IPrAu(κ<sup>1</sup>-CS<sub>2</sub>)C≡CAuIPr] (17)



In a N<sub>2</sub>-filled glovebox, carbon disulfide (30  $\mu$ L, 0.502 mmol) was added to a J. Young flask containing a stir bar and a solution of 7 (60 mg, 0.0502 mmol) in dry benzene (4 mL). The flask was taken out of the glovebox, and the reaction mixture was left stirring at 60 °C in an oil bath for 72 h. The resulting dark orange solution was evaporated under vacuum for 2 h to ensure removal of excess CS<sub>2</sub>, giving an orange oil. In the glovebox, the orange residue was dissolved in THF (1 mL) and transferred to a dram vial. Addition of *n*-pentane (8 mL) led to the immediate precipitation of insertion product 17. The supernatant was carefully removed, and the resulting solid was rinsed with *n*-pentane (3 mL). Then, the product was dried under  $N_2$ , giving complex **17** as a red solid (24 mg, 0.0189) mmol, 38% yield). The supernatant and *n*-pentane washings were combined and evaporated under vacuum. The resulting yellow powder was dissolved in THF (1.5 mL) and layered with *n*-pentane (6 mL). Then, the bilayer was left to stand at -30 °C for 1 day, after which crystals of the product **17** were observed (17 mg, 0.0134 mmol, 27% yield). The combined yield achieved taking into account both fractions is 65%. Red crystals suitable for X-ray diffraction analysis were grown from a cold MeCN solution of **17** at -30 °C.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.19 – 7.15 (m, 4H, C<u>H</u> Ph<sub>para</sub>)\*, 6.99 (d, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 6.98 (d, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, 4H, C<u>H</u> Ph<sub>meta</sub>), 6.25 (s, 2H, C<u>H</u><sub>imid</sub>), 6.19 (s, 2H, C<u>H</u><sub>imid</sub>), 2.53 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 2.45 (sept, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 1.23 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.99 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>), 0.99 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 12H, CH(C<u>H</u><sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  223.98 (<u>C</u>(=S)S), 192.52 (Au<u>C</u><sub>carbene</sub>), 187.14 (Au<u>C</u><sub>carbene</sub>), 145.78 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 145.60 (<u>C</u><sub>q</sub> Ph<sub>orto</sub>), 144.89 (Au<u>C</u><sub>alkyne</sub>), 134.68 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 134.42 (N<u>C</u><sub>q</sub> Ph<sub>ipso</sub>), 130.71 (<u>C</u>H Ph<sub>para</sub>), 124.28 (<u>C</u>H Ph<sub>meta</sub>), 122.70 (=<u>C</u>H<sub>imid</sub>), 122.53 (=<u>C</u>H<sub>imid</sub>), 117.23 (AuC≡<u>C</u>), 29.03 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 28.97 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 24.70 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.58 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.08 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.93 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.

\*Overlaps with the residual signal of the deuterated solvent C<sub>6</sub>D<sub>6</sub>.

**Elem. Anal.** Calcd for: C<sub>57</sub>H<sub>72</sub>Au<sub>2</sub>N<sub>4</sub>S<sub>2</sub>: C, 53.85; H, 5.71; N, 4.41; S, 5.04. Found: C, 53.86; H, 5.68; N, 4.55; S, 5.19.

IR (ATR) 2064 ( $v_{C=C}$ ), 968 ( $v_{C=S}$ ) cm<sup>-1</sup>.

• [IPrAu( $\kappa^1$ -SC(N(p-CF<sub>3</sub>-Ph))C=CAuIPr] (18)



Under air, a solution of 4-(trifluoromethyl)phenyl isothiocyanate (4 mg, 0.02 mmol) in toluene (0.5 mL) was added to a vial containing complex **7** (25 mg, 0.02 mmol) as a solid. After stirring for 30-60 seconds, a pale yellow solution was observed. This mixture was transferred to a NMR tube, which was left to stand at 25 °C. NMR analysis after 3 h revealed the complete consumption of the starting materials. At this point, the mixture was filtered through Celite (1 cm height in a Pasteur pipette) to a 13 mL scintillation vial. The NMR tube and filter were rinsed with toluene (0.5 mL), and pentane (12 mL) was added to the combined filtrates. The mixture was vigorously shaken and stored at -24 °C for 16 h, after which a pale yellow solid deposited at the bottom of the vial. The supernatant was carefully removed, and the solid was slowly warmed up to 25 °C, which caused its transformation to a yellow oil. This residue was dried under vacuum until constant mass, giving analytically pure complex **18** (19.6 mg, 0.014 mmol, 70% yield) as a pale yellow solid after scratching the oily residue with a spatula.

The structural assignment depicted above is based on the lack of data pointing to a C=S bond, as evidenced by NMR (no resonance by  ${}^{13}C{}^{1}H$  NMR around 200 ppm or C=S stretch by IR) – See complex **17** (Figures S35 and S60) for comparison.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub> 298 K): δ 7.45 (d, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 8.2 Hz, C*H* Ph<sub>meta</sub>), 7.21 (t, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, C*H* <sup>IPr</sup>Ph<sub>para</sub>), 7.05 (t, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, C*H* <sup>IPr</sup>Ph<sub>para</sub>), 7.02 (d, 4H, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, C*H* <sup>IPr</sup>Ph<sub>meta</sub>), 6.93 (d, 4H, <sup>3</sup>*J*<sub>H-H</sub> = 7.9 Hz, C*H* <sup>IPr</sup>Ph<sub>meta</sub>), 6.68 (d, 2H, <sup>3</sup>*J*<sub>H-H</sub> = 8.2 Hz, C*H* Ph<sub>ortho</sub>), 6.22 (s, 2H, C*H*<sub>imid</sub>), 6.17 (s, 2H, C*H*<sub>imid</sub>), 2.52 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 2.42 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 4H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 1.33 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C*H*<sub>3</sub>)<sub>2</sub>), 1.22 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, CH(C*H*<sub>3</sub>)<sub>2</sub>), 1.01 (t, <sup>3</sup>*J*<sub>H-H</sub> = 6.7 Hz, 24H, CH(C*H*<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 192.2 (AuC<sub>carbene</sub>), 188.2 (AuC<sub>carbene</sub>), 160.9 (C(N)S), 157.3 (C<sub>q</sub> Ph<sub>ipso</sub>), 145.7 (C<sub>q</sub> <sup>IPr</sup>Ph<sub>ortho</sub>), 145.6 (C<sub>q</sub> <sup>IPr</sup>Ph<sub>ortho</sub>), 139.7 (AuC=C), 134.5 (C<sub>q</sub> <sup>IPr</sup>Ph<sub>ipso</sub>), 130.7 (CH <sup>IPr</sup>Ph<sub>para</sub>), 130.6 (CH <sup>IPr</sup>Ph<sub>para</sub>), 124.7 (q, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz, CH Ph<sub>meta</sub>), 122.4 (CH <sup>IPr</sup>Ph<sub>meta</sub>), 122.3 (q, <sup>2</sup>*J*<sub>C-F</sub> = 31.4 Hz, CH Ph<sub>para</sub>), 100.9 (AuC=C), 29.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ -60.1 (s, CF<sub>3</sub>) ppm. The resonance for the CF<sub>3</sub> carbon atom was not observed.

Anal. Calcd for:  $C_{64}H_{76}Au_2F_3N_5S$ : C, 54.97; H, 5.48; N, 5.01; S, 2.29. Found: C, 54.95; H, 5.56; N, 4.95; S, 2.08.

IR (ATR) 2089 (v C≡C) cm<sup>-1</sup>

• [IPrAuC≡C(η<sup>2</sup>-AuIPr)AuIPr][OTf] (19)



In a N<sub>2</sub>-filled glovebox, a vial was charged with IPrAuOTf (66.4 mg, 0.0904 mmol) and a stir bar. A solution of **7** (108 mg, 0.0904 mmol) in THF (4 mL) was added to the vial, and the reaction mixture was left stirring at 25 °C for 16 h, after which it became a purple solution<sup>\*</sup>, which was filtered through a 0.2 µm PTFE filter. The reaction vial and filter were rinsed with THF (3 mL), and the combined filtrates were transferred to a J. Young flask containing a stir bar. The resulting colorless solution was concentrated under vacuum to approximately 1 mL, giving an orange-brown solution. Addition of *n*-pentane (5 mL) under vigorous stirring led to the immediate precipitation of a colorless solid. The supernatant was carefully removed, and the solid was transferred to a tared vial as a suspension in *n*-pentane (2.5 mL). Then, the solid was dried under vacuum, giving complex **19** as a white solid (147 mg, 0.0764 mmol, 84% yield). Colorless crystals suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-pentane into a THF solution of **19** at -30 °C.

\*The purple color may originate from the formation of gold nanoparticles.

<sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>, 298 K): δ 7.48 (s, 6H, C<u>*H*</u>imid), 7.45 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 6H, C<u>*H*</u> Ph<sub>para</sub>), 7.23 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 12H, C<u>*H*</u> Ph<sub>meta</sub>), 2.50 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 12H, C<u>*H*</u> (CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 36H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>), 1.06 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 36H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>), 1.06 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.8 Hz, 36H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>) ppm. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K): δ 7.51 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 6H, C<u>*H*</u> Ph<sub>para</sub>), 7.35 (s, 6H, C<u>*H*</u>imid), 7.27 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.8 Hz, 12H, C<u>*H*</u> Ph<sub>meta</sub>), 2.38 (sept, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 12H, C<u>*H*</u>(CH<sub>3</sub>)<sub>2</sub>), 1.12 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 36H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>), 1.03 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.9 Hz, 36H, CH(C<u>*H*<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, THF-*d*<sub>8</sub>, 298 K): δ 187.43 (Au<u>C</u><sub>carbene</sub>), 148.83 (Au<u>C</u><sub>alkyne</sub>), 146.48 (<u>C</u><sub>q</sub> Phorto), 135.71 (N<u>C</u><sub>q</sub> Phipso), 131.21 (<u>C</u>H Ph<sub>para</sub>), 125.34 (=<u>C</u>Himid), 124.93 (<u>C</u>H Ph<sub>meta</sub>), 29.67 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 25.38 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 24.31 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>) ppm.</u></u></u></u></u>

**Elem. Anal.** Calcd for: C<sub>84</sub>H<sub>108</sub>Au<sub>3</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>S: C, 52.28; H, 5.64; N, 4.35. Found: C, 52.12; H, 5.37; N, 4.69.

HRMS (ESI) *m*/*z* calculated for [C<sub>83</sub>H<sub>108</sub>Au<sub>3</sub>N<sub>6</sub>]<sup>+</sup>: 1779.7627, found: 1779.7662.

**Raman** analysis of this sample (using either 532 or 785 nm) did not result in the observation of distinguishable signals.

3. NMR spectra





**Figure S2.** <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 400 MHz) of complex **3**.



Figure S3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 101 MHz) of complex 3.



Figure S4.  $^{1}$ H- $^{29}$ Si HMBC spectrum (C<sub>6</sub>D<sub>6</sub>, 300-60 MHz) of complex 3.



Figure S5. <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 500 MHz) of complex 4.



**Figure S6.** <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 400 MHz) of complex **4**.



Figure S7. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Tol-*d*<sub>8</sub>, 126 MHz) of complex **4**.



Figure S8. <sup>1</sup>H-<sup>29</sup>Si HMBC spectrum (C<sub>6</sub>D<sub>6</sub>, 400-79 MHz) of complex **4**.



Figure S9. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 300 MHz) of complex 6.



**Figure S10.** <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 400 MHz) of complex **7**.



**Figure S11.** <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 400 MHz) of complex **7**.



Figure S12. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 500 MHz) of complex 7.



Figure S13.  ${}^{13}C{}^{1}H$  NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 126 MHz) of complex 7.



Figure S14. <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 500 MHz) of complex 8.



Figure S15. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Tol- $d_8$ , 126 MHz) of complex 8.



Figure S16. <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 500 MHz) of complex 9.



**Figure S17.** <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 500 MHz) of complex **9** with a known quantity of the internal standard 1,3,5-trimethoxybenzene.



Figure S18. <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 500 MHz) of complex 10.



Figure S19.  $^{13}C{^1H}$  NMR spectrum (Tol- $d_8$ , 126 MHz) of complex 10.



Figure S20. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 500 MHz) of complex 11.



Figure S21. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>3</sub>CN, 126 MHz) of complex 11.



Figure S22. <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 500 MHz) of complex **12**.



Figure S23. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 500 MHz) of complex **13**.



**Figure S24.** <sup>1</sup>H NMR spectrum ( $C_6D_6$ , 400 MHz) of crystals of complex **13**. The relative amount of DMAD present is 9%, according to the integration values.



Figure S25. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 126 MHz) of complex 13.



Figure S26. <sup>1</sup>H-<sup>29</sup>Si HMBC spectrum (C<sub>6</sub>D<sub>6</sub>, 400-79 MHz) of complex 13.



Figure S27. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 400 MHz) of complex 14.



Figure S28. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CD<sub>3</sub>CN, 101 MHz) of complex 14.



Figure S29. <sup>1</sup>H-<sup>29</sup>Si HMBC spectrum (CD<sub>3</sub>CN, 400-79 MHz) of complex 14.



Figure S30. <sup>1</sup>H NMR spectrum (Tol-*d*<sub>8</sub>, 500 MHz) of complex 15.



Figure S31. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (Tol-*d*<sub>8</sub>, 126 MHz) of complex 15.





Figure S33.  $^{13}C{^1H}$  NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 126 MHz) of complex 16.



35



Figure S36. <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 500 MHz) of complex **18**.


Figure S38.  ${}^{19}F{}^{1}H{}$  NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 470 MHz) of complex 18.



Figure S39. <sup>1</sup>H NMR spectrum (THF-*d*<sub>8</sub>, 500 MHz) of complex **19**.



Figure S40. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN, 500 MHz) of complex 19.



**Figure S41.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (THF-*d*<sub>8</sub>, 126 MHz) of complex **19**.



**Figure S42.** <sup>1</sup>H NMR spectra (THF- $d_8$ , 500 MHz) of complex **19** at different temperatures.



Figure S43. Mass spectrum of complex 7. Fragmentation of 7 to give species 9 can be observed.



Figure S44. Mass spectrum of complex 19.



**Figure S45.** Mass spectrum of the reaction mixture between **12** and 4-(trifluoromethyl)phenyl isothiocyanate (10 equiv.) after heating to 120 °C for 2 days.

5. Vibrational spectra



Figure S46. IR spectrum of complex 3.



Figure S47. IR spectrum of complex 4.



Figure S48. IR spectrum of complex 7.



Figure S49. Raman spectrum of complex 7.



Figure S50. IR spectrum of complex 8.



Figure S51. Raman spectrum of complex 8.



Figure S52. IR spectrum of complex 10.



Figure S53. IR spectrum of complex 11.



Figure S54. IR spectrum of complex 13.



Figure S55. IR spectrum of complex 14.



Figure S56. IR spectrum of complex 15.



Figure S57. IR spectrum of complex 16.



Figure S58. IR spectrum of complex 17.



Figure S59. IR spectrum of complex 18.



Figure S60. IR spectra of complexes 17 and 18 overlapped.



Figure S61. IR spectrum of complex 19.

6. Reactivity studies





Figure S63. <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>, 300 MHz) of the reaction between complex 7 and acetylene (1.5 bar) at 80  $^{\circ}$ C.



**Figure S64.** <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN, 500 MHz) of complex **19** (bottom) + DMAD under different experimental conditions.

## Extension of the scope

The reactivity of complexes **7** and **12** was explored with a wider array of substrates and/or reaction conditions (see Table S1 below). Exploratory experiments involved the utilization of 10 equivalents of substrate under air, and the behavior of the reaction mixtures was analyzed by NMR spectroscopy from 25 °C to 120 °C for at least 15 h. Those experiments that showed conversion to a mixture of products were repeated under an atmosphere of N<sub>2</sub>, to ensure that their presence was not due to the air present in the sample.

Entry	Substrate	Complex 7	Т (°С)	Complex 12	T (°C)
1	DMAD	Complex 10	25	Complex 15	110
2	3-hexyne	No reaction	120	No reaction	120
3	PhPh	No reaction	120	No reaction	120
4	PhMe	No reaction	120	No reaction	120
5	MeOOCMe	Multiple unidentified products (Figure S66)	120	No reaction	120
6	MeOOCPh	Complex <b>16</b>	120	No reaction	120
7		Multiple unidentified products (Figure S67)	25	No reaction	120
8	CO <sub>2</sub>	No reaction	120	No reaction	120
9	CS <sub>2</sub>	Complex 17	60	No reaction	120
10	F <sub>3</sub> C-V=C=S	Complex 18	25	Unidentified species (see Figure S69)	120
11	N=C=N	No reaction	120	No reaction	120

Table S1. Summar	y of substrates e	xplored with com	plexes 7 and 12.
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Selected examples:



**Figure S65**. 'H NMR spectra ( $d_8$ -toluene, 300 MHz) of complex 7 (bottom) and complex 7 + 10 equivalents of diphenylacetylene after 19 h at 120 °C (top) – Entry 3 of Table S1. Experiment carried out under air.



**Figure S66**.<sup>1</sup>H NMR spectra ( $h_8$ -toluene, 300 MHz) of complex **7** + 10 equivalents of MeC=CCOOMe after 16 h (bottom) and 39 h (top) at 120 °C – Entry 5 of Table S1. Experiment carried out under N<sub>2</sub>. No reaction takes place at 60 °C.



**Figure S67**. <sup>1</sup>H NMR spectra ( $d_8$ -toluene, 300 MHz) of complex **7** + 10 equivalents of bis(4-(methoxycarbonyl)phenyl)acetylene after 30 min (bottom), 3 h (middle) and 45 h (top) at 25 °C – Entry 7 of Table S1. Experiment carried out under N<sub>2</sub>.



**Figure S68**. <sup>1</sup>H NMR spectra ( $d_8$ -toluene, 300 MHz) of complex **7** + 10 equiv. of 4-(trifluoromethyl)phenyl isothiocyanate after 35 min at 25 °C (bottom, product **18** is already formed) and 16 h at 120 °C (top). Inset: <sup>19</sup>F{<sup>1</sup>H} spectra.



**Figure S69**. <sup>1</sup>H NMR spectra (*d*<sub>8</sub>-toluene, 300 MHz) of complex **12** + 10 equivalents of 4-(trifluoromethyl)phenyl isothiocyanate after 45 min at 25 °C (bottom), 21 h at 120 °C (middle) and 46 h at 120 °C (top) – Entry 10 of Table S1. Experiment carried out under air. Inset: <sup>19</sup>F{<sup>1</sup>H} spectra, exhibiting two new singlets in a 1:1 ratio.

## 7. Kinetic studies

### General considerations

All experiments were prepared in a N<sub>2</sub>-filled glovebox using a J. Young NMR tube.  $C_6D_6$  and *p*-Xylene-*d*<sub>10</sub> were distilled under Ar and stored over 3 Å molecular sieves for at least 24 h prior to use. Dimethyl acetylenedicarboxylate (DMAD) was distilled and stored under N<sub>2</sub>. Kinetic experiments were performed with crystalline material.

### Monitoring kinetic data

The progress of the kinetic essays was monitored by <sup>1</sup>H NMR analysis. Hence, a known concentration of internal standard was added to determine the evolution of reactants and products by relative integration of the corresponding signals at fixed time intervals. All NMR spectra and raw integration data sets were processed with MestReNova using the *Data Analysis panel* tool. Reaction profiles were plotted with Microsoft Excel.

### 7.1 Kinetic experiments

7.1.1 Reaction of bimetallic complexes [Au-Au] with DMAD:



In a N<sub>2</sub>-filled glovebox, a 13 mL scintillation vial was charged with a stir bar, complex **7** (or **8**) and mesitylene as an internal standard.  $C_6D_6$  (600 µL) was added to the mixture. Then, it was vigorously stirred until a clear solution was observed. The resulting colorless solution was transferred to a J. Young NMR tube, after which it was introduced into the NMR spectrometer. The sample was measured to acquire a reference spectrum and the adequate temperature was set on the NMR temperature probe. The NMR tube was taken out of the NMR spectrometer and DMAD (>10 equivalents) was added as quickly as possible (brief exposure to air). Immediately, the sample was vigorously shaken and introduced into the NMR spectrometer. <sup>1</sup>H NMR spectra were acquired at fixed time intervals using a d1=10 s value. The reaction was monitored at 4 different temperatures (25 °C, 30 °C, 35 °C and 40 °C) by duplicate.

7.1.2 Reaction of monometallic complex **4** with DMAD:



In a N<sub>2</sub>-filled glovebox, a 13 mL scintillation vial was charged with a stir bar, complex **4**, mesitylene (internal standard) and DMAD ( $\geq$ 10 equivalents). The reaction mixture was dissolved with *p*-Xylene-*d*<sub>10</sub> (600 µL) and transferred to a J. Young NMR tube. The sample was introduced into the NMR spectrometer, a reference spectrum was acquired, and the temperature was increased to 120 °C. <sup>1</sup>H NMR spectra were acquired at this temperature at fixed time intervals using a d1=10 s value. The experiment was run in triplicate.

# 7.2 Reaction profiles. [Conc.] vs time

## 7.2.1 Complex 7 + DMAD



**Figure S70.** Reaction profiles of kinetic experiment **7.1.1** (Complex **7** + DMAD) at different temperatures.

### 7.2.2 Complex 8 + DMAD



**Figure S71.** Reaction profiles of kinetic experiment **7.1.1** (Complex **8** + DMAD) at different temperatures. A decrease in the concentration of product can be observed in most of the cases due to crystallization of product **11** in the NMR tube.

7.2.3 Complex 4 + DMAD



Figure S72. Reaction profile of kinetic experiments 7.1.2 at different temperatures (see comment on Table S2).

#### 7.3 Determination of reaction order and rate constant

#### Partial order in Au complex

Partial order of complexes **4** (monometallic), **7** and **8** (bimetallic species) with respect to DMAD were evaluated by the isolation method, for which DMAD was used in excess ( $\geq$  10 equiv.), so that its concentration can be considered constant.

Given the following rate equation,

$$v = k[\mathbf{A}\mathbf{u}]^{\alpha}[\mathbf{D}\mathbf{M}\mathbf{A}\mathbf{D}]^{\beta}$$
 Eq. 1

If [DMAD]>>[Au], then,

$$v = k_{obs} [Au]^{\alpha'}$$
 Eq. 2  
 $k_{obs} = k [DMAD]^{\beta}$  Eq. 3

Given the **Eq. 2**, integration and subsequent linearization allow us to determinate the order of the reaction and rate constant. Best fitting of the integrated rate laws reveals a pseudo-first order character of the complexes **4**, **7** and **8**. The observed rate constants ( $k_{obs}$ ) were achieved through the linear regression of the first order plots.



**Figure S73.** Plots of the natural logarithm of [**7**] vs time for a pseudo-first order reaction at 25 °C and 30 °C.



**Figure S74.** Plots of the natural logarithm of [7] vs time for a pseudo-first order reaction at 35 °C and 40 °C.



**Figure S75.** Plots of the natural logarithm of **[8]** vs time for a pseudo-first order reaction at 25 °C and 30 °C.



**Figure S76.** Plots of the natural logarithm of **[8]** vs time for a pseudo-first order reaction at 25 °C and 30 °C.



**Figure S77.** Plots of the natural logarithm of **[4]** vs time for a pseudo-first order reaction at 120 °C.

Experiment	T (°C)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> ) (Du	ıplicate)	k <sub>obs</sub> (Average ± Std. Dev.) (s <sup>-1</sup> )
	25	1.55 x 10 <sup>-4</sup>	1.77 x 1	10-4	1.66 x 10 <sup>-4</sup> ± 1.56 x 10 <sup>-5</sup>
	30	2.61 x 10 <sup>-4</sup>	2.87 x 1	10-4	2.74 x 10 <sup>-4</sup> ± 1.84 x 10 <sup>-5</sup>
[7] + DMAD	35	4.15 x 10 <sup>-4</sup>	4.56 x 10 <sup>-4</sup>		4.36 x 10 <sup>-4</sup> ± 2.90 x 10 <sup>-5</sup>
	40	7.05 x 10 <sup>-4</sup>	8.32 x 1	10-4	7.69 x 10 <sup>-4</sup> ± 8.98 x 10 <sup>-5</sup>
	25	5.64 x 10 <sup>-5</sup>	6.90 x 1	10 <sup>-5</sup>	6.27 x 10 <sup>-5</sup> ± 8.91 x 10 <sup>-6</sup>
	30	1.04 x 10 <sup>-4</sup>	9.28 x 1	10 <sup>-5</sup>	9.84 x 10 <sup>-5</sup> ± 7.92 x 10 <sup>-6</sup>
	35	2.16 x 10 <sup>-4</sup>	1.99 x 1	10-4	2.08 x 10 <sup>-4</sup> ± 1.20 x 10 <sup>-5</sup>
	40	2.85 x 10 <sup>-4</sup>	2.37 x 1	10-4	2.61 x 10 <sup>-4</sup> ± 3.40 x 10 <sup>-5</sup>
[ <b>4</b> ] + DMAD*	120	1.18 x 10 <sup>-4</sup>	5.94 x 10 <sup>-5</sup> (Duplicate)	6.93 x 10 <sup>-5</sup> (Triplicate)	8.22 x 10 <sup>-5</sup> ± 3.14 x 10 <sup>-5</sup>

**Table S2.** Summary of the observed rate constants.

\*Although, as stated in the manuscript (reference 23), complex **4** exhibits the best behavior by <sup>1</sup>H NMR spectroscopy, the error in the determination of  $k_{obs}$  is far from negligible. However, the point of determining an approximate rate constant with the monometallic species is to get an idea of the order of magnitude so that it can be compared to the bimetallic analogues. Regardless of the value, it does not change the message and conclusions of this work, since complexes **3**, **4** and **12** do not exhibit any transformation at temperatures below 100 °C. Moreover, the different observed  $k_{obs}$  values for monometallic complex **4** give an approximate  $\Delta G^{\ddagger}$  value of 30 kcal mol<sup>-1</sup>.

### Partial order in DMAD

Different  $k_{obs}$  values were determined using either complex **4** or **7** and different concentrations of DMAD within the pseudo-first order regime:



• Complex 7

**Figure S78.** Left: plot of the natural logarithm of [**7**] vs time. Right: plot of  $k_{obs}$  vs [DMAD].

A linear correlation is observed, in good agreement with the proposed mechanism. Thus, the second order rate constant can be determined as follows:

 $k_{\rm obs} = k [\mathbf{DMAD}]^{\beta}$  Eq. 3

 $\beta = 1$  (linear correlation), therefore  $k = slope = 3.9 \times 10^{-4} M^{-1} s^{-1}$ 



**Figure S79.** Left: plot of the natural logarithm of [4] vs time. Right: plot of  $k_{obs}$  vs [DMAD].

A random distribution of points is observed. This is likely due to the error obtained during the determination of the kobs value for this complex, which precludes the determination of accurate data that can be reproducibly plotted against [DMAD] (see Table S2 for more information).

## 7.4 Eyring analysis

To obtain an experimental dataset of the activation parameters ( $\Delta S^{\ddagger}$  and  $\Delta H^{\ddagger}$ ), the Eyring-Polanyi equation in the lineal form was plotted (**Eq. 4**).

$$ln \frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + ln \frac{\kappa k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$
 Eq. 4



7.4.1 Eyring plots of kinetic experiments 7.1.1

Figure S80. Eyring plot for reactions of DMAD with complex 7 and 8.

Experiment	∆H <sup>‡</sup> (kcal mol <sup>-1</sup> )	ΔS <sup>‡</sup> (cal mol <sup>-1</sup> K <sup>-1</sup> )	ΔG <sup>‡</sup> (kcal mol⁻¹)
[ <b>7</b> ] + DMAD	18.1 ± 0.3	-15.0 ± 1.0	22.61 (298 K) 22.68 (303 K) 22.76 (308 K) 22.83 (313 K)
[ <b>8</b> ] + DMAD	18.06 ± 3.0	-17.17 ± 9.8	23.17 (298 K) 23.26 (303 K) 23.34 (308 K) 23.43 (313 K)

Table S3.	Thermodynamic	parameters	obtained from	the kinetic	experiments
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# 8. X-ray crystallography

• Complex 3 (IPrAuCCSiMe<sub>3</sub>)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

**Crystal Data** for C<sub>32</sub>H<sub>45</sub>AuN<sub>2</sub>Si (*M* =682.75 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.0241(5) Å, *b* = 12.0583(7) Å, *c* = 15.9337(8) Å, *α* = 80.824(2)°, *β* = 89.441(2)°, *γ* = 78.132(2)°, *V* = 1674.58(16) Å<sup>3</sup>, *Z* = 2, *T* = 193.00 K,  $\mu$ (MoK $\alpha$ ) = 4.448 mm<sup>-1</sup>, *Dcalc* = 1.354 g/cm<sup>3</sup>, 112194 reflections measured (4.002° ≤ 2Θ ≤ 56.594°), 8271 unique (*R*<sub>int</sub> = 0.0589, *R*<sub>sigma</sub> = 0.0231) which were used in all calculations. The final *R*<sub>1</sub> was 0.0208 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.0500 (all data).

Table S4. Crystal data and structure refinement for 3	3.
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Identification code	pr0623a_0m
Empirical formula	C <sub>32</sub> H <sub>45</sub> AuN <sub>2</sub> Si
Formula weight	682.75
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	9.0241(5)
b/Å	12.0583(7)
c/Å	15.9337(8)
α/°	80.824(2)
β/°	89.441(2)
γ/°	78.132(2)
Volume/Å <sup>3</sup>	1674.58(16)
Z	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.354
µ/mm <sup>-1</sup>	4.448
F(000)	688.0
Crystal size/mm <sup>3</sup>	$0.25 \times 0.13 \times 0.07$
Radiation	ΜοΚα (λ = 0.71073)
20 range for data collection/°	4.002 to 56.594

Index ranges $-12 \le h \le 12, -16 \le k \le 16, -21 \le l \le 21$ Reflections collected112194Independent reflections8271 [Rint = 0.0589, Rsigma = 0.0231]Data/restraints/parameters8271/2/357Goodness-of-fit on F<sup>2</sup>1.112Final R indexes [l>=2 $\sigma$  (l)]R1 = 0.0208, wR2 = 0.0457Final R indexes [all data]R1 = 0.0274, wR2 = 0.0500Largest diff. peak/hole / e Å<sup>-3</sup>1.10/-0.82



Figure S81. Solid-state structure of complex 3 at the 50% probability level.

• Complex 7 (IPrAuCCAuIPr)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX4 v2021.10-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The unit cell contains two benzene molecules which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE.<sup>[12]</sup> The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The hydrogen of hydroxide group was located from difference Fourier maps and included in a refinement with isotropic parameters

**Crystal Data** for C<sub>56</sub>H<sub>72</sub>Au<sub>2</sub>N<sub>4</sub> (*M* =1195.10 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.3309(4) Å, *b* = 12.6622(5) Å, *c* = 14.2997(6) Å, *a* = 72.3960(10)°,  $\beta$  =

72.2550(10)°,  $\gamma$  = 82.124(2)°, *V* = 1531.89(11) Å<sup>3</sup>, *Z* = 1, *T* = 193.00 K, μ(MoKα) = 4.815 mm<sup>-1</sup>, *Dcalc* = 1.295 g/cm<sup>3</sup>, 85738 reflections measured (4.59° ≤ 2Θ ≤ 56.576°), 7612 unique (*R*<sub>int</sub> = 0.0597, *R*<sub>sigma</sub> = 0.0250) which were used in all calculations. The final *R*<sub>1</sub> was 0.0211 (I > 2σ(I)) and *wR*<sub>2</sub> was 0.0477 (all data).

 Table S5
 Crystal data and structure refinement for 7.

Identification code	pr1122a_0m
Empirical formula	C56H72Au2N4
Formula weight	1195.10
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	9.3309(4)
b/Å	12.6622(5)
c/Å	14.2997(6)
α/°	72.3960(10)
β/°	72.2550(10)
γ/°	82.124(2)
Volume/Å <sup>3</sup>	1531.89(11)
Z	1
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.295
µ/mm⁻¹	4.815
F(000)	594.0
Crystal size/mm <sup>3</sup>	0.1 × 0.06 × 0.02
Radiation	ΜοΚα (λ = 0.71073)
2O range for data collection/°	4.59 to 56.576
Index ranges	$-12 \le h \le 12,  -16 \le k \le 16,  -19 \le l \le 19$
Reflections collected	85738
Independent reflections	7612 [ $R_{int} = 0.0597$ , $R_{sigma} = 0.0250$ ]
Data/restraints/parameters	7612/0/288
Goodness-of-fit on F <sup>2</sup>	1.070
Final R indexes [I>=2σ (I)]	$R_1 = 0.0211, wR_2 = 0.0450$
Final R indexes [all data]	R <sub>1</sub> = 0.0271, wR <sub>2</sub> = 0.0477
Largest diff. peak/hole / e Å-3	0.65/-0.76



Figure S82. Solid-state structure of complex 7 at the 50% probability level.

• Complex 8 (SIPrAuCCAuSIPr)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

**Crystal Data** for C<sub>72</sub>H<sub>108</sub>Au<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (*M* =1487.55 g/mol): monoclinic, space group P2<sub>1</sub>/n (no. 14), *a* = 12.7986(5) Å, *b* = 15.2227(5) Å, *c* = 18.1384(7) Å, *β* = 101.8270(10)°, *V* = 3458.9(2) Å<sup>3</sup>, *Z* = 2, *T* = 193.00 K,  $\mu$ (MoK $\alpha$ ) = 4.285 mm<sup>-1</sup>, *Dcalc* = 1.428 g/cm<sup>3</sup>, 124529 reflections measured (4.21° ≤ 2Θ ≤ 61.066°), 10582 unique (*R*<sub>int</sub> = 0.0646, R<sub>sigma</sub> = 0.0283) which were used in all calculations. The final *R*<sub>1</sub> was 0.0232 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.0517 (all data).

 Table S6. Crystal data and structure refinement for 8.

Identification code	pr0424a_0m
Empirical formula	C72H108Au2N4O4
Formula weight	1487.55
Temperature/K	193.00
Crystal system	monoclinic

Space group	P21/n
a/Å	12.7986(5)
b/Å	15.2227(5)
c/Å	18.1384(7)
α/°	90
β/°	101.8270(10)
γ/°	90
Volume/Å <sup>3</sup>	3458.9(2)
Z	2
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.428
µ/mm⁻¹	4.285
F(000)	1516.0
Crystal size/mm <sup>3</sup>	0.15 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
$2\Theta$ range for data collection/°	4.21 to 61.066
Index ranges	$-18 \le h \le 18, -21 \le k \le 21, -25 \le l \le 25$
Reflections collected	124529
Independent reflections	$10582 [R_{int} = 0.0646, R_{sigma} = 0.0283]$
Data/restraints/parameters	10582/5/397
Goodness-of-fit on F <sup>2</sup>	1.063
Final R indexes [I>=2σ (I)]	$R_1 = 0.0232$ , $wR_2 = 0.0477$
Final R indexes [all data]	$R_1 = 0.0318$ , $wR_2 = 0.0517$
Largest diff. peak/hole / e Å $^{\text{-}3}$	0.85/-1.09





• Complex **10** (DMAD insertion on **7**)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a  $I\mu$ S 3.0 microfocus

X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX4 v2021.10-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The unit cell contains two benzene molecules which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE.<sup>[12]</sup>The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

**Crystal Data** for C<sub>62</sub>H<sub>78</sub>Au<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (*M* =1337.21 g/mol): orthorhombic, space group Pcca (no. 54), *a* = 36.539(2) Å, *b* = 12.2149(7) Å, *c* = 29.5810(16) Å, *V* = 13202.6(13) Å<sup>3</sup>, *Z* = 8, *T* = 193.00 K,  $\mu$ (MoK $\alpha$ ) = 4.482 mm<sup>-1</sup>, *Dcalc* = 1.345 g/cm<sup>3</sup>, 313267 reflections measured (4.24° ≤ 2Θ ≤ 52.798°), 13529 unique (*R*<sub>int</sub> = 0.0654, R<sub>sigma</sub> = 0.0213) which were used in all calculations. The final *R*<sub>1</sub> was 0.0542 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.1112 (all data).

 Table S7. Crystal data and structure refinement for 10.

Identification code	pr1323b_0ma_a
Empirical formula	C <sub>62</sub> H <sub>78</sub> Au <sub>2</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	1337.21
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Pcca
a/Å	36.539(2)
b/Å	12.2149(7)
c/Å	29.5810(16)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	13202.6(13)
Z	8
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.345
µ/mm⁻¹	4.482
F(000)	5344.0
Crystal size/mm <sup>3</sup>	0.1 × 0.1 × 0.05
Radiation	ΜοΚα (λ = 0.71073)
2O range for data collection/°	4.24 to 52.798
Index ranges	$-45 \le h \le 45, -15 \le k \le 15, -36 \le l \le 36$
Reflections collected	313267
Independent reflections	13529 [ $R_{int} = 0.0654$ , $R_{sigma} = 0.0213$ ]



Figure S84. Solid-state structure of complex 10 at the 50% probability level.

• Complex **13** (DMAD insertion on **3**)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

**Crystal Data** for C<sub>38</sub>H<sub>51</sub>AuN<sub>2</sub>O<sub>4</sub>Si (*M* =824.86 g/mol): monoclinic, space group P2<sub>1</sub>/n (no. 14), *a* = 12.7366(5) Å, *b* = 15.5654(6) Å, *c* = 19.9574(7) Å, β = 92.718(2)°, *V* = 3952.1(3) Å<sup>3</sup>, *Z* = 4, *T* = 193.00 K, μ(MoKα) = 3.790 mm<sup>-1</sup>, *Dcalc* = 1.386 g/cm<sup>3</sup>, 250490 reflections measured (3.878° ≤ 2Θ ≤ 56.638°), 9826 unique (*R*<sub>int</sub> = 0.0838, R<sub>sigma</sub> = 0.0225) which were used in all calculations. The final *R*<sub>1</sub> was 0.0217 (I > 2σ(I)) and *wR*<sub>2</sub> was 0.0512 (all data).

Table S8. Crystal data and st	ructure refinement for <b>13</b> .
Identification code	pr2723a_0m
Empirical formula	C38H51AuN2O4Si
Formula weight	824.86
Temperature/K	193.00
Crystal system	monoclinic
Space group	P21/n
a/Å	12.7366(5)
b/Å	15.5654(6)
c/Å	19.9574(7)
α/°	90
β/°	92.718(2)
γ/°	90
Volume/Å <sup>3</sup>	3952.1(3)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.386
µ/mm <sup>-1</sup>	3.790
F(000)	1672.0
Crystal size/mm <sup>3</sup>	0.45 × 0.1 × 0.1
Radiation	ΜοΚα (λ = 0.71073)
2O range for data collection/°	3.878 to 56.638
Index ranges	$-16 \leq h \leq 16,  -20 \leq k \leq 20,  -26 \leq l \leq 26$
Reflections collected	250490
Independent reflections	9826 [ $R_{int} = 0.0838$ , $R_{sigma} = 0.0225$ ]
Data/restraints/parameters	9826/0/428
Goodness-of-fit on F <sup>2</sup>	1.070
Final R indexes [I>=2σ (I)]	$R_1 = 0.0217, wR_2 = 0.0462$
Final R indexes [all data]	$R_1 = 0.0339, wR_2 = 0.0512$
Largest diff. peak/hole / e Å-3	1.13/-0.54



Figure S85. Solid-state structure of complex 13 at the 50% probability level.

• Complex **15** (DMAD insertion on **12**)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

**Crystal Data** for C<sub>48</sub>H<sub>55</sub>AuN<sub>2</sub>O<sub>4</sub> (*M* =920.90 g/mol): monoclinic, space group P2<sub>1</sub>/n (no. 14), *a* = 18.4242(9) Å, *b* = 13.8027(7) Å, *c* = 18.9461(10) Å, *β* = 109.094(2)°, *V* = 4553.0(4) Å<sup>3</sup>, *Z* = 4, *T* = 193.00 K,  $\mu$ (MoK $\alpha$ ) = 3.273 mm<sup>-1</sup>, *Dcalc* = 1.343 g/cm<sup>3</sup>, 164776 reflections measured (4.55° ≤ 2Θ ≤ 61.064°), 13925 unique (*R*<sub>int</sub> = 0.0865, R<sub>sigma</sub> = 0.0376) which were used in all calculations. The final *R*<sub>1</sub> was 0.0321 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.0709 (all data).

**Table S9.** Crystal data and structure refinement for 15.

Identification code	pr0124a_0m
Empirical formula	$C_{48}H_{55}AuN_2O_4$
Formula weight	920.90
Temperature/K	193.00
Crystal system	monoclinic
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Space group	P21/n
a/Å	18.4242(9)
b/Å	13.8027(7)
c/Å	18.9461(10)
α/°	90
β/°	109.094(2)
γ/°	90
Volume/Å <sup>3</sup>	4553.0(4)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.343
µ/mm <sup>-1</sup>	3.273
F(000)	1872.0
Crystal size/mm <sup>3</sup>	0.3 × 0.2 × 0.15
Radiation	ΜοΚα (λ = 0.71073)
2O range for data collection/°	4.55 to 61.064
Index ranges	$-26 \le h \le 26, -19 \le k \le 19, -26 \le l \le 27$
Reflections collected	164776
Independent reflections	13925 [ $R_{int} = 0.0865, R_{sigma} = 0.0376$ ]
Data/restraints/parameters	13925/0/507
Goodness-of-fit on F <sup>2</sup>	1.057
Final R indexes [I>=2σ (I)]	$R_1 = 0.0321$ , $wR_2 = 0.0602$
Final R indexes [all data]	$R_1 = 0.0558, wR_2 = 0.0709$
Largest diff. peak/hole / e Å-3	1.50/-1.59



Figure S86. Solid-state structure of complex 15 at the 50% probability level.

• Complex **16** (PhC=CCOOMe insertion on **7**)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The crystal was twinned, so refinement using HKLF 5 and BASF was necessary to improve the structure. Due to low diffraction intensity of the crystal and the twin, RIGU, SIMU and ISOR were used.

**Crystal Data** for C<sub>150</sub>H<sub>178</sub>Au<sub>4</sub>N<sub>8</sub>O<sub>4</sub> (*M* =2944.86 g/mol): triclinic, space group P-1 (no. 2), *a* = 13.4415(13) Å, *b* = 29.354(3) Å, *c* = 36.128(4) Å, *a* = 93.781(5)°, *β* = 94.261(4)°,  $\gamma$  = 100.703(4)°, *V* = 13921(3) Å<sup>3</sup>, *Z* = 4, *T* = 193.00 K,  $\mu$ (MoK $\alpha$ ) = 4.256 mm<sup>-1</sup>, *Dcalc* = 1.405 g/cm<sup>3</sup>, 50762 reflections measured (3.786° ≤ 2Θ ≤ 50.7°), 50762 unique (*R*<sub>int</sub> = ?, *R*<sub>sigma</sub> = 0.0601) which were used in all calculations. The final *R*<sub>1</sub> was 0.0864 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.1960 (all data).

 Table S10 Crystal data and structure refinement for 16.
 16

Identification code	pr1924a
Empirical formula	C <sub>150</sub> H <sub>178</sub> Au <sub>4</sub> N <sub>8</sub> O <sub>4</sub>
Formula weight	2944.86
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	13.4415(13)
b/Å	29.354(3)
c/Å	36.128(4)
α/°	93.781(5)
β/°	94.261(4)
γ/°	100.703(4)
Volume/Å <sup>3</sup>	13921(3)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.405
µ/mm <sup>-1</sup>	4.256
F(000)	5928.0
Crystal size/mm <sup>3</sup>	$0.5 \times 0.05 \times 0.03$
Radiation	ΜοΚα (λ = 0.71073)
2O range for data collection/°	3.786 to 50.7
Index ranges	$-16 \leq h \leq 16,  -35 \leq k \leq 35,  0 \leq l \leq$
Reflections collected	50762

43

Independent reflections50762 [Rint = ?, Rsigma = 0.0601]Data/restraints/parameters50762/3475/3167Goodness-of-fit on F21.141Final R indexes [I>=2 $\sigma$  (I)]R1 = 0.0864, wR2 = 0.1893Final R indexes [all data]R1 = 0.0993, wR2 = 0.1960Largest diff. peak/hole / e Å-32.28/-2.56



Figure S87. Solid-state structure of complex 15 at the 50% probability level.

• Complex **17** (CS<sub>2</sub> insertion on **7**)

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-4 v2021.4-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELX<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface.

The solid-state molecular structure of **17** exhibits the IPrAuS<sub>2</sub>CCC fragment on a special position in which a second fragment is generated via a rotational axis. The [S<sub>2</sub>CCC] moiety is rotationally disordered wherein each Au atom is bound to an S atom of an inserted CS<sub>2</sub> molecule or a C atom of the acetylide moiety. The relative occupancy of each part was fixed at 0.5 and EADP was used to constrain the ligating C and S atoms to the same displacement parameters. Furthermore, there are two solvent molecules of acetonitrile in the asymmetric unit cell, one of which exhibits positional disorder. Various restraints (DFIX, DANG, SIMU, RIGU) were used to model the disordered solvent molecule and to maintain physically reasonable anisotropic displacement parameters and geometries. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in

the model at geometrically calculated positions and refined using a riding model, unless otherwise noted.

Identification code	pr03123a_0m			
Empirical formula	C32.5H42AuN4S			
Formula weight	717.72			
Temperature/K	194.00			
Crystal system	monoclinic			
Space group	P21/n			
a/Å	10.7024(6)			
b/Å	27.5930(15)			
c/Å	12.0247(6)			
α/°	90			
β/°	92.657(2)			
γ/°	90			
Volume/Å <sup>3</sup>	3547.2(3)			
Z	4			
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.344			
µ/mm <sup>-1</sup>	4.230			
F(000)	1440.0			
Crystal size/mm <sup>3</sup>	0.15 × 0.08 × 0.08			
Radiation	ΜοΚα (λ = 0.71073)			
20 range for data collection/	4.086 to 56.624			
Index ranges	$-14 \le h \le 14$ , $-36 \le k \le 36$ , $-16 \le l \le 15$			
Reflections collected	96073			
Independent reflections	$8797 [R_{int} = 0.0541, R_{sigma} = 0.0234]$			
Data/restraints/parameters	8797/78/403			
Goodness-of-fit on F <sup>2</sup>	1.193			
Final R indexes [I>=2σ (I)]	$R_1 = 0.0320, wR_2 = 0.0719$			
Final R indexes [all data]	$R_1 = 0.0386$ , $wR_2 = 0.0748$			
Largest diff. peak/hole / e Å-3	1.08/-0.60			

Table S11 Crystal data and structure refinement for 17



Figure S88. Solid-state structure of complex 17 at the 50% probability level.

• Complex **19** [(IPrAu)<sub>3</sub>C<sub>2</sub>][OTf])

Low-temperature diffraction data were collected on a Bruker D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IµS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of  $\omega$  and  $\varphi$  scans using monochromatic radiation  $\lambda$ (Mo K $\alpha$ 1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX4 v2021.10-0 software. The structures were solved with SHELXT and was refined against F2 on all data by full-matrix least squares with SHELXL,<sup>[10]</sup> using Olex2<sup>[11]</sup> as graphical interface. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The unit cell contains two benzene molecules which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE.<sup>[12]</sup> The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). SIMU, DELU and RIGU restrains were used for modelling due to slight disorder.

**Crystal Data** for C<sub>84</sub>H<sub>108</sub>Au<sub>3</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>S (*M* =1929.72 g/mol): monoclinic, space group P2<sub>1</sub>/n (no. 14), *a* = 16.3416(6) Å, *b* = 20.8456(8) Å, *c* = 30.6473(12) Å,  $\beta$  = 100.380(2)°, *V* = 10269.2(7) Å<sup>3</sup>, *Z* = 4, *T* = 193.00 K, µ(MoKα) = 4.341 mm<sup>-1</sup>, *Dcalc* = 1.248 g/cm<sup>3</sup>, 397960 reflections measured (3.882° ≤ 2Θ ≤ 56.596°),

25501 unique ( $R_{int} = 0.0637$ ,  $R_{sigma} = 0.0248$ ) which were used in all calculations. The final  $R_1$  was 0.0312 (I >  $2\sigma(I)$ ) and  $wR_2$  was 0.0768 (all data).

Table S12. (	Crystal data	and structure	refinement for	<b>19</b> .
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Identification code	pr2323a_0m
Empirical formula	C84H108Au3F3N6O3S
Formula weight	1929.72
Temperature/K	193.00
Crystal system	monoclinic
Space group	P21/n
a/Å	16.3416(6)
b/Å	20.8456(8)
c/Å	30.6473(12)
α/°	90
β/°	100.380(2)
γ/°	90
Volume/Å <sup>3</sup>	10269.2(7)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.248
µ/mm⁻¹	4.341
F(000)	3832.0
Crystal size/mm <sup>3</sup>	0.4 × 0.2 × 0.18
Radiation	ΜοΚα (λ = 0.71073)
2Θ range for data collection/°	3.882 to 56.596
Index ranges	$-21 \le h \le 21,  -27 \le k \le 27,  -40 \le l \le 40$
Reflections collected	397960
Independent reflections	25501 [ $R_{int} = 0.0637$ , $R_{sigma} = 0.0248$ ]
Data/restraints/parameters	25501/303/998
Goodness-of-fit on F <sup>2</sup>	1.067
Final R indexes [I>=2σ (I)]	$R_1 = 0.0312$ , $wR_2 = 0.0657$
Final R indexes [all data]	$R_1 = 0.0503$ , $wR_2 = 0.0768$
Largest diff. peak/hole / e Å $^{-3}$	1.41/-0.93



Figure S89. Solid-state structure of complex 19 at the 50% probability level.

## 9. Computational Details

### Gibbs energy profiles

Unless otherwise stated, calculations were performed using the M06-L functional including the D3 version of Grimme's dispersion correction, <sup>[13]</sup> as implemented in Gaussian 09.<sup>[14]</sup> Geometry optimizations were performed in solution (solvent = benzene.  $\varepsilon = 2.27$ ) using the continuum SMD model<sup>[15]</sup> and basis set 1 (BS1). BS1 uses the double- $\zeta$  6-31G(d,p)<sup>[16]</sup> basis set for the H, C, N and O atoms and the scalar relativistic Stuttgart-Dresden SDD pseudopotential<sup>[17]</sup> and its associated double- $\zeta$  basis set, complemented with a set of polarization functions, for the Au atoms.<sup>[18]</sup> The nature of the stationary points was confirmed by frequency analysis. Connections between the transition states and the minima were checked by perturbing the transition state geometry along the TS coordinate and optimizing until the corresponding minima. All energies in solution were corrected by single-point calculations with the larger basis set 2 (BS2) including triple-ζ def2TZVP basis set for the H, C, N, O and Au atoms.<sup>[19]</sup> The scalar relativistic Stuttgart-Dresden SDD pseudopotential and its associated basis set for Au was used in the energy profile calculations. Gibbs energies in benzene were calculated at 298.15 K. Gibbs energy corrections were obtained based on vibrational frequencies of the BS1- optimized structures using the quasi-harmonic approximation. Thermal contributions to the Gibbs energies were corrected by employing the approximation described by Grimme, where entropic terms for frequencies below a cut-off of 100 cm-1 were calculated using the free-rotor approximation.<sup>[20]</sup> The GoodVibes program developed by Paton and Funes-Ardoiz was employed to introduce these corrections.<sup>[21]</sup> All reported energies in the main text correspond to M06-L-D3/BS2 Gibbs energies in benzene solvent (1 M) at 298.15 K in kcal mol<sup>-1</sup>. Structure visualization was performed with Chemcraft software.<sup>[22]</sup>

# Activation Strain Model (ASM) of Reactivity and Energy Decomposition Analysis (EDA)

Within the ASM method, <sup>[23]</sup> also known as the distortion/interaction model, <sup>[23c]</sup> the potential energy surface  $\Delta E(\zeta)$  is decomposed along the reaction coordinate,  $\zeta$ , into two contributions, namely the strain  $\Delta E_{strain}(\zeta)$  associated with the deformation (or distortion) required by the individual reactants during the process and the interaction  $\Delta E_{int}(\zeta)$  between these increasingly deformed reactants:

$$\Delta \mathsf{E}(\zeta) = \Delta \mathsf{E}_{\mathsf{strain}}(\zeta) + \Delta \mathsf{E}_{\mathsf{int}}(\zeta)$$

Within the EDA method,<sup>[24]</sup> the interaction energy can be further decomposed into the following chemically meaningful terms:

$$\Delta \mathsf{E}_{int}(\zeta) = \Delta \mathsf{V}_{elstat}(\zeta) + \Delta \mathsf{E}_{Pauli}(\zeta) + \Delta \mathsf{E}_{orb}(\zeta) + \Delta \mathsf{E}_{disp}(\zeta)$$

The term  $\Delta V_{elstat}$  corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants and is usually attractive. The Pauli repulsion  $\Delta E_{Pauli}$  comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. The orbital interaction  $\Delta E_{orb}$  accounts for bond pair formation, charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals on the other, including HOMO-LUMO interactions), and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). Finally, the  $\Delta E_{disp}$  term takes into account interactions coming from dispersion forces. Moreover, the NOCV (Natural Orbital for Chemical Valence)<sup>[25]</sup> extension of the EDA method has been also used to further partition the  $\Delta E_{orb}$  term. The EDA-NOCV approach provides pairwise energy contributions for each pair of interacting orbitals to the total bond energy.

The program package ADF<sup>[26]</sup> was used for ASM and EDA(NOCV) calculations using the optimized /SMD-M06L-D3/6-31G(d,p)&SDD(+f) geometries at the same M06L-D3 level in conjunction with a double-ζ-quality basis set using uncontracted Slater-type orbitals (STOs) augmented by polarization functions.<sup>[27]</sup> Auxiliary sets of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.<sup>[28]</sup> Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA).<sup>[29]</sup> This level of theory is denoted ZORA-M06L-D3/DZP//SMD-M06L-D3/6-31G(d,p)&SDD(+f).

### 10. Calculated energy profiles



**Figure S90.** Gibbs energy profile in benzene for the reaction between **7** + DMAD. Gibbs energies at 298 K in kcal mol<sup>-1</sup>. Enthalpy values highlighted in green.



**Figure S91.** Migration of [IPrAu]<sup>+</sup> from **Int1-***trans*, leading to **10**-*trans*. Gibbs energies at 298 K in kcal mol<sup>-1</sup>.



**Figure S92.** Gibbs energy profile in benzene for the reaction between **12** + DMAD. Gibbs energies at 298 K in kcal mol<sup>-1</sup>.



**Figure S93.** Calculated isomerization of complex **19**. Gibbs energies at 298 K in kcal mol<sup>-1</sup> using PBE0-D3BJ<sup>[30]</sup> and BS1.



**Figure S94.** Calculated transition state (analogue to **TS1**) for the interaction between PhC=CCOOMe and complex **7**, leading to complex **16** or its regioisomer.

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