On the Silver Effect and the Formation of Chloride-Bridged Digold Complexes

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1. General Information

Unless otherwise stated, reactions were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Analytical thin layer chromatography was carried out using TLC-aluminium sheets with 0.2 mm of silica gel (Merck GF254) using UV light as the visualizing agent and an acidic solution of vanillin in ethanol as the developing agent. Chromatography purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 mm) or automated flash chromatographer CombiFlash Companion. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. NMR spectra were recorded at 298 K on a Bruker Avance 400 Ultrasound and Bruker Avance 500 Ultrasound apparatus. Mass spectra were recorded on a Waters Micromass LCT Premier (ESI), Waters Micromass GCT (EI, CI) and Bruker Daltonics Autoflex (MALDI) spectrometers. Crystal structure determinations were carried out using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = -173 °C). Full-sphere data collection was used with w and j scans. Programs used: Data collection APEX-2, data reduction Bruker Saint V.60A and absorption correction SADABS. Structure Solution and Refinement: Crystal structure solution was achieved using direct methods as implement in SHELXTL and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Phenylacetylene, α-methylstyrene as well as the silver salts and catalyst 1 were used as received from Alfa Aesar or Aldrich. 1,6-Enynes 7a1 and 7b2 were prepared according to the described procedures.

(1) Buisine, O.; Corinne, A.; Malacria, M. Chem. Eur. J. 2001, 7, 3517–3525.
(2) Nieto-Oberhuber, C.; Pérez-Galán, P.; Herrero-Gómez, E.; Lauterbach, T.; Rodriguez, C.; López, S.; Bour, C.; Rosellón, A.; Cárdenas, D. J.; Echavarren, A. M. J. Am. Chem. Soc. 2008, 130, 269–279.
2. Synthesis of Gold(I) Complexes

Although the initial isolation of the dinuclear gold(I) complexes was achieved using 1:1 ratio of Au:Ag in CH₂Cl₂, its synthesis has been proven to be more efficient following a modified procedure of Schmidbaur.³

Complex 2a

A solution of chloro[(1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (205 mg, 0.387 mmol, 2 equiv) in dry CH₂Cl₂ (10 mL) is added dropwise to a solution of silver bis(trifluoromethanesulfonil)imide (75 mg, 0.193 mmol, 1 equiv) in 10 mL of dry THF at 23 °C. After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and the resulting colorless solution was evaporated to dryness under vacuum. White crystals were obtained after crystallization from CH₂Cl₂/n-pentane (1:1). 216.3 mg (0.166 mmol) of 2a were obtained in 86% yield.


³H NMR (400 MHz, CD₂Cl₂) δ 7.93-7.84 (m, 2H), 7.65-7.54 (m, 4H), 7.56 - 7.45 (m, 2H), 7.43 -7.35 (m, 4H), 7.42 -7.32 (m, 2H), 7.18 - 7.08 (m, 4H), 1.39 (d, J = 16.0 Hz, 36H); ¹³C NMR (126 MHz CD₂Cl₂) δ 149.65 (d, J = 12.3 Hz), 143.12 (d, J = 6.8 Hz), 133.82 (d, J = 7.2 Hz), 133.79 (d, J = 3.3 Hz), 131.91 (d, J = 2.5 Hz), 130.01, 129.28, 128.78, 128.10 (d, J = 7.4 Hz), 124.87 (d, J = 49.1 Hz), 38.68 (d, J = 26.2 Hz), 31.24 (d, J = 6.4 Hz); ³¹P NMR (202 MHz, CD₂Cl₂) δ 64.62; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -78.78; HRMS-ESI m/z calculated for C₄₀H₅₄Au₂ClP₂ + [M+-C₂F₆NO₄S₂]: 1025.2715 found 1025.2744. Structure confirmed by X-ray diffraction.

Complex 2b

A solution of chloro[(1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (205 mg, 0.389 mmol, 2 equiv) in dry CH₂Cl₂ (10 mL) is added dropwise to a solution of silver trifluoromethanesulfonate (50 mg, 0.195 mmol, 1 equiv) in 10 mL of dry THF at 23 °C. After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and the resulting colorless solution was evaporated to dryness under vacuum. White crystals were obtained after crystallization from CH₂Cl₂/n-pentane (1:1). 206 mg (0.175 mmol) of 2b were obtained in 90% yield.

¹H NMR (500 MHz, CD₂Cl₂) δ 7.92-7.85 (m, 2H), 7.63-7.56 (m, 4H), 7.55 - 7.50 (m, 2H), 7.43-7.36 (m, 4H), 7.34-7.29 (m, 2H), 7.16 - 7.11 (m, 4H), 1.40 (d, J = 16.1 Hz, 36H); ¹³C NMR (126 MHz

³ Schmidbaur, H.; Hamel, A.; Mitzel, N. W.; Schier, A.; Nogai, S. Proc. Natl. Acad. Sci. 2002, 99, 4916–4921.
CD₂Cl₂ δ 149.74 (d, J = 12.2 Hz), 143.08 (d, J = 6.9 Hz), 133.87 (d, J = 7.9 Hz), 133.79 (d, J = 4.0 Hz), 131.90 (d, J = 2.6 Hz), 130.01, 128.81, 128.05 (d, J = 7.4 Hz), 124.90 (d, J = 49.0 Hz), 38.68 (d, J = 26.0 Hz), 31.25 (d, J = 6.4 Hz); ³¹P NMR (202 MHz, CD₂Cl₂) δ 64.60; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -78.74; HRMS-ESI m/z calculated for C₄₀H₅₄Au₂ClP₂⁺ [M+-CF₃O₃S]: 1025.2715 found 1025.2704. Structure confirmed by X-ray diffraction.

Complex 2c

A solution of chloro[(1,1′-biphenyl-2-yl)diterbutylphosphine]gold(I) (205 mg, 0.380 mmol, 2 equiv) in dry CH₂Cl₂ (10 mL) is added dropwise to a solution of silver tetrafluoroborate (37 mg, 0.190 mmol, 1 equiv) in 10 mL of THF at 23 ºC. After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and the resulting colorless solution was evaporated to dryness under vacuum. White crystals were obtained after crystallization from CH₂Cl₂/n-pentane (1:1). 171 mg (0.154 mmol) of 2c were obtained in 81% yield.

¹H NMR (400 MHz, CD₂Cl₂) δ 7.92-7.85 (m, 2H), 7.63-7.56 (m, 4H), 7.55-7.49 (m, 2H), 7.40-7.35 (m, 4H), 7.34-7.28 (m, 2H), 7.17-7.10 (m, 4H), 1.39 (d, J = 16.0 Hz, 36H); ¹³C NMR (126 MHz CD₂Cl₂) δ 149.08 (d, J = 12.5 Hz), 142.55 (d, J = 6.9 Hz), 133.40 (d, J = 7.7 Hz), 133.25 (d, J = 3.6 Hz), 131.35 (d, J = 2.5 Hz), 129.45, 128.71, 128.22, 127.53 (d, J = 7.6 Hz), 124.30 (d, J = 49.2 Hz), 38.11 (d, J = 26.2 Hz), 30.67 (d, J = 6.3 Hz); ³¹P NMR (202 MHz, CD₂Cl₂) δ 64.78; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -153.56; HRMS-ESI m/z calculated for C₄₀H₅₄Au₂ClP₂⁺ [M+-BF₄]: 1025.2715 found 1025.2747. Structure confirmed by X-ray diffraction.

Complex 2d

A solution of chloro[(1,1′-biphenyl-2-yl)diterbutylphosphine]gold(I) (205 mg, 0.378 mmol, 2 equiv) in dry CH₂Cl₂ (10 mL) is added dropwise to a solution of silver hexafluoroantimonate (65 mg, 0.189 mmol, 1 equiv) in 10 mL of THF at 23 ºC. After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and the resulting colorless solution was evaporated to dryness under vacuum. White crystals were obtained after crystallization from CH₂Cl₂/n-pentane (1:1). 171 mg (0.154 mmol) of 2c were obtained in 81% yield.

¹H NMR (400 MHz, CD₂Cl₂) δ 7.92-7.85 (m, 2H), 7.63-7.56 (m, 4H), 7.55-7.49 (m, 2H), 7.40-7.35 (m, 4H), 7.34-7.28 (m, 2H), 7.17-7.10 (m, 4H), 1.39 (d, J = 16.0 Hz, 36H); ¹³C NMR (126 MHz CD₂Cl₂) δ 149.08 (d, J = 12.5 Hz), 142.55 (d, J = 6.9 Hz), 133.40 (d, J = 7.7 Hz), 133.25 (d, J = 3.6 Hz), 131.35 (d, J = 2.5 Hz), 129.45, 128.71, 128.22, 127.53 (d, J = 7.6 Hz), 124.30 (d, J = 49.2 Hz), 38.11 (d, J = 26.2 Hz), 30.67 (d, J = 6.3 Hz); ³¹P NMR (202 MHz, CD₂Cl₂) δ 64.78; ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -153.56; HRMS-ESI m/z calculated for C₄₀H₅₄Au₂ClP₂⁺ [M+-BF₄]: 1025.2715 found 1025.2747. Structure confirmed by X-ray diffraction.
26.0 Hz), 31.25 (d, J = 6.3 Hz); $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$) δ 64.80; HRMS-ESI m/z calculated for C$_{40}$H$_{54}$Au$_2$ClP$_2$ $^{+}$ [M$^+$-SbF$_6$]: 1025.2715 found 1025.2719. Structure confirmed by X-ray diffraction.

[(1,1′-Biphenyl-2-yl)di-tert-butylphosphine]gold(I) bis(trifluoromethanesulfonylimide) (3a)

Silver bis(trifluoromethanesulfonylimide)imide (181 mg, 0.471 mmol, 5 equiv) was added to a solution of chloro[(1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (50 mg, 0.094 mmol, 1 equiv) in dry CH$_2$Cl$_2$ (1 mL). After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and Teflon filters (2 x 0.22 µm). The resulting colorless solution was evaporated to dryness under vacuum to give the neutral complex as a white solid. Crystals were grown by crystallization with CH$_2$Cl$_2$/n-pentane. 58.4 mg (0.075 mmol) were obtained (80% yield).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.94-7.88 (m, 1H), 7.61-7.44 (m, 5H), 7.32-7.26 (m, 1H), 7.24-7.18 (m, 2H), 1.41 (d, J = 16.1 Hz, 18H); $^{13}$C NMR (126 MHz CD$_2$Cl$_2$) δ 150.18 (d, J = 12.0 Hz), 142.52 (d, J = 6.9 Hz), 134.03 (d, J = 7.5 Hz), 133.90 (d, J = 3.8 Hz), 129.83, 129.57, 127.75, 127.59 (d, J = 6.3 Hz); $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) δ 60.77; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -74.38; HRMS-ESI m/z calculated for C$_{40}$H$_{54}$Au$_2$ClP$_2$ $^{+}$ [M$^+$-C$_2$F$_6$NO$_3$S$_2$]: 495.1511 found 495.1512. Structure confirmed by X-ray diffraction.

[(1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) trifluoromethanesulfonate (3b)

Silver trifluoromethanesulfonate (121 mg, 0.471 mmol, 5 equiv) was added to a solution of chloro[(1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (50 mg, 0.094 mmol, 1 equiv) in dry CH$_2$Cl$_2$ (1 mL). After stirring the reaction mixture for 2 h at the same temperature, the crude was filtered through a pad of celite and cotton at the top of the pipette and Teflon filters (2 x 0.22 µm). The resulting colorless solution was evaporated to dryness under vacuum to give the neutral complex as a white solid. White crystals were grown by crystallization with CH$_2$Cl$_2$/n-pentane. 47 mg (0.073 mmol) of [(1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) trifluoromethanesulfonate (3b) were obtained in 77% yield.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.89 (td, 1H), 7.63-7.43 (m, 5H), 7.38-7.32 (m, 1H), 7.22-7.16 (m, 2H), 1.40 (d, J = 16.2 Hz, 18H); $^{13}$C NMR (126 MHz CD$_2$Cl$_2$) δ 150.13 (d, J = 11.7 Hz), 133.46 (d, J = 4.2 Hz), 131.69 (d, J = 2.4 Hz), 129.86, 129.17, 128.95, 127.75 (d, J = 7.8 Hz), 124.65, 124.24, 121.95, 119.42, 38.62 (d, J = 28.0 Hz), 31.07 (d, J = 6.1 Hz); $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) δ 60.77; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -77.69; HRMS-ESI m/z calculated for C$_{40}$H$_{54}$Au$_2$ClP$_2$ $^{+}$ [M$^+$-CF$_3$O$_3$S]: 495.1511 found 495.1512. Structure confirmed by X-ray diffraction.
Complex 5

This complex was prepared according to the procedure used for the synthesis of [(JohnPhosAu)(OH)]SbF₆. 

$^1$H NMR (500 MHz, CDCl₃) $\delta$ 7.91-7.77 (m, 2H), 7.61-7.52 (m, 6H), 7.47 (t, $J = 7.6$ Hz, 4H), 7.34-7.27 (m, 2H), 7.24-7.17 (m, 4H), 1.38 (d, $J = 15.9$ Hz, 36H). 

$^{31}$P NMR (202 MHz, CDCl₃) $\delta$ 60.57. Structure confirmed by X-ray diffraction.

(4) Adriaenssens, L.; Escribano-Cuesta, A.; Homs, A.; Echavarren, A. M.; Ballester, P. Eur. J. Org. Chem. 2013, 1494–1500.
3. General Procedures

a) \( [2+2] \) Intermolecular Cycloaddition Reaction

Product 6

This compound was prepared according to the previous described procedure. \(^5\) \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.39 (d, \( J = 7.2 \) Hz, 4H), 7.32 (dd, \( J = 13.7, 7.2 \) Hz, 4H), 7.27-7.22 (m, 1H), 7.21-7.15 (m, 1H), 6.72 (s, 1H), 2.93 (q, \( J = 12.5 \) Hz, 2H), 1.62 (s, 3H).

Conditions A: Phenylacetylene (19 µL, 0.169 mmol, 1 equiv), \( \alpha \)-methylstyrene (44 µL, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 µL, 0.085 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. JohnPhosAuCl (I) (4.5 mg, 8.45 µmol, 0.05 equiv) and AgX (8.45 µmol, 0.05 equiv) were then added and the resulting mixture was stirred for 8 h at 23 ºC. The reaction was monitored by \( ^1 \)H NMR and \( ^{31} \)P NMR.

Conditions B: JohnPhosAuCl (I) (4.5 mg, 8.45 µmol, 0.05 equiv) and AgX (8.45 µmol, 0.05 equiv) were dissolved in 0.6 mL CD\(_2\)Cl\(_2\) and introduced in a NMR tube. After 10 min stirring, phenylacetylene (19 µL, 0.169 mmol, 1 equiv), \( \alpha \)-methylstyrene (44 µL, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 µL, 0.085 mmol) were added. The resulting mixture was stirred for 8 h at 23 ºC and monitored by \( ^1 \)H NMR and \( ^{31} \)P NMR.

Conditions C: In a vial, JohnPhosAuCl (I) (4.5 mg, 8.45 µmol, 0.05 equiv) and AgX (8.45 µmol, 0.05 equiv) were dissolved in 0.6 mL CD\(_2\)Cl\(_2\). After 10 min stirring, the slurry mixture was filtered through a pipette containing Celite and cotton (top and bottom). The resulting solution was introduced in a NMR tube along with phenylacetylene (19 µL, 0.169 mmol, 1 equiv), \( \alpha \)-methylstyrene (44 µL, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 µL, 0.085 mmol). The resulting mixture was stirred for 8 h at 23 ºC and monitored by \( ^1 \)H NMR and \( ^{31} \)P NMR.

Reaction with 2c or 2d: Phenylacetylene (19 µL, 0.169 mmol, 1 equiv), \( \alpha \)-methylstyrene (44 µL, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 µL, 0.085 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. Complex 2 (4.23 µmol, 0.025 equiv) was then added and the resulting mixture was stirred for 8 h at 23 ºC. The reaction was monitored by \( ^1 \)H NMR and \( ^{31} \)P NMR.

Reactions with 2c or 2d and AgX: Phenylacetylene (19 µL, 0.169 mmol, 1 equiv), \( \alpha \)-methylstyrene (44 µL, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 µL, 0.085 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. Complex 2 (4.23 µmol, 0.025 equiv) and AgX (4.23 µmol, 0.025 equiv) were then added and the resulting mixture was stirred for 8 h at 23 ºC. The reaction was monitored by \( ^1 \)H NMR and \( ^{31} \)P NMR.

\(^4\) López-Carrillo, V.; Echavarren, A. M. J. Am. Chem. Soc. 2010, 132, 9292–9294.
b) Cycloisomerization of 1,6-enyne 7a

Product 8

This complex was prepared according to the previous described procedure.\(^6\)\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.25 (m, 4H), 7.21-7.15 (m, 1H), 3.68 (s, 3H), 3.50-3.45 (m, 1H), 3.22 (s, 3H), 3.15-3.11 (m, 1H), 2.72 (dd, \(J = 28.8, 13.3\) Hz, 1H), 2.02 (dd, \(J = 13.4, 7.2\) Hz, 1H), 1.86 (dd, \(J = 13.2, 7.6\) Hz, 1H), 1.85 (dd, \(J = 2.8, 1.4\) Hz, 3H).

Conditions A: Enyne 7a (30 mg, 0.1 mmol, 1 equiv) and the internal standard (diphenylmethane; 8.3 \(\mu\)L, 0.05 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. JohnPhosAuCl (I) (1.6 mg, 3 \(\mu\)mol, 0.03 equiv) and AgX (3 \(\mu\)mol, 0.03 equiv) were then added and the resulting mixture was stirred for 2 h at 23 ºC. The reaction was monitored by \(^1\)H NMR and \(^{31}\)P NMR.

Conditions B: JohnPhosAuCl (I) (1.6 mg, 3 \(\mu\)mol, 0.03 equiv) and AgX (3 \(\mu\)mol, 0.03 equiv) were dissolved in 0.6 mL CD\(_2\)Cl\(_2\) and introduced in a NMR tube. After 10 min stirring, enyne 7a (30 mg, 0.1 mmol, 1 equiv) and the internal standard (diphenylmethane; 8.3 \(\mu\)L, 0.05 mmol) were added. The resulting mixture was stirred for 2 h at 23 ºC and monitored by \(^1\)H NMR and \(^{31}\)P NMR.

Conditions C: In a vial, JohnPhosAuCl (I) (1.6 mg, 3 \(\mu\)mol, 0.03 equiv) and AgX (3 \(\mu\)mol, 0.03 equiv) were dissolved in 0.6 mL CD\(_2\)Cl\(_2\). After 10 min stirring, the slurry mixture was filtered through a pipette containing Celite and cotton (top and bottom). The resulting solution was introduced in a NMR tube along with enyne 7a (30 mg, 0.1 mmol, 1 equiv) and the internal standard (diphenylmethane; 8.3 \(\mu\)L, 0.05 mmol). The resulting mixture was stirred for 2 h at 23 ºC and monitored by \(^1\)H NMR and \(^{31}\)P NMR.

Reaction with 2c or 2d: Enyne 7a (30 mg, 0.1 mmol, 1 equiv) and the internal standard (diphenylmethane; 8.3 \(\mu\)L, 0.05 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. Complex 2 (4.23 \(\mu\)mol, 0.025 equiv) was then added and the resulting mixture was stirred for 8 h at 23 ºC. The reaction was monitored by \(^1\)H NMR and \(^{31}\)P NMR.

Reactions with 2c or 2d and AgX: Phenylacetylene (19 \(\mu\)L, 0.169 mmol, 1 equiv), \(\alpha\)-methylstyrene (44 \(\mu\)L, 0.338 mmol, 2 equiv) and the internal standard (diphenylmethane; 14 \(\mu\)L, 0.085 mmol) dissolved in 0.6 mL of CD\(_2\)Cl\(_2\) were introduced in a NMR tube. Complex 2 (4.23 \(\mu\)mol, 0.025 equiv) and AgX (4.23 \(\mu\)mol, 0.025 equiv) were then added and the resulting mixture was stirred for 8 h at 23 ºC. The reaction was monitored by \(^1\)H NMR and \(^{31}\)P NMR.

(5) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. J. Am. Chem. Soc. 2005, 127, 6178–6179.
c) Cycloisomerization of 1,6-ene 7b

Product 9

This compound was prepared according to the previous described procedure. $^{1}$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, $J = 2.2$ Hz, 1H), 8.02 (dd, $J = 8.4, 2.3$ Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.45 (bs, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.34 (d, $J = 18.7$ Hz, 1H), 3.03 (dt, $J = 18.6, 3.0$ Hz, 1H), 2.80-2.71 (m, 1H), 2.63 (ddd, $J = 12.6, 7.6, 1.3$ Hz, 1H), 2.18 (t, $J = 12.6$ Hz, 1H), 1.49 (s, 3H), 0.95 (s, 3H).

I: Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. JohnPhosAuCl 1 (1.8 mg, 3.34 mmol, 0.03 equiv) was then added and the resulting mixture was monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h.

II: Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ in a vial. JohnPhosAuCl 1 (1.8 mg, 3.34 mmol, 0.03 equiv) was then added and the mixture was introduced in a NMR tube. AgSbF$_6$ (1.2 mg, 3.34 mmol, 0.03 equiv) was then added and the resulting mixture was monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h. Then the sample was analyzed again after 6 h and 24h.

III: JohnPhosAuCl 1 (1.8 mg, 3.34 mmol, 0.03 equiv) was dissolved in 0.7 mL CD$_2$Cl$_2$ in a vial and added to AgSbF$_6$ (1.2 mg, 3.34 µmol, 0.03 equiv). The resulting mixture was shaken during 3 min and added to enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol). The mixture resulting mixture was introduced in a NMR tube and monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h. Then the sample was analyzed again after 9 h and 24h.

IV: Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. Complex 2d (2.1 mg, 1.670 µmol, 0.015 equiv) was then added and the resulting mixture was monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h. Then the sample was analyzed again after 23 h.

V: Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. Complex 2c (1.8 mg, 1.670 µmol, 0.015 equiv) was then added and the resulting mixture was monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h. Then the sample was analyzed again after 9 h and 24h.

VI: Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and the internal standard (diphenylmethane; 9.3 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. Complex 2d (4.2 mg, 3.34 µmol, 0.03 equiv) was then added and the resulting mixture was monitored by $^{1}$H NMR at 23 °C every 5 min during 2.5 h. Then the sample was analyzed again after 9h and 25h.
**VII:** Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and diphenylmethane (9.31 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. Complex 2d (2.1 mg, 1.670 µmol, 0.015 equiv) was then added and the resulting mixture was shaken for 3 min. After that, AgSbF$_6$ (0.5 mg, 1.670 µmol, 0.015 equiv) was added and the resulting mixture was monitored by $^1$H NMR at 23 ºC every 5 min during 2 h. Then the sample was analyzed again after 6 h and 21 h.

**VIII:** Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and diphenylmethane (9.31 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. [JohnPhosAuNCMe]$^+$SbF$_6$ cationic complex (2.6 mg, 3.34 mmol, 0.03 equiv) was then added and the resulting mixture was monitored by $^1$H NMR at 23 ºC every 5 min during 2.5 h. Then the sample was analyzed again after 6 h and 24 h.

**IX:** Enyne 7b (40 mg, 0.111 mmol, 1 equiv) and diphenylmethane (9.31 µL, 0.056 mmol) were dissolved in 0.7 mL CD$_2$Cl$_2$ and introduced in a NMR tube. [tBuXPhosAuNCMe]$^+$SbF$_6$ cationic complex (3.0 mg, 3.34 mmol, 0.03 equiv) was then added and the resulting mixture was monitored by $^1$H NMR at 23 ºC every 5 min during 2.5 h. Then the sample was analyzed again after 4 h and 24 h.
Yields given in the cycloisomerization of 7b:

\[
\text{[Au] (3 mol %)} \quad \text{CDCl}_2 (0.1 \text{ M}), 2.5 \text{ h}, 23 \degree \text{ C}
\]

\(7b: \text{Ar} = \text{p-C}_6\text{H}_4\text{NO}_2, \text{E} = \text{CO}_2\text{Me}\)

| Time (min) | Yield % |
|------------|---------|
| 7.35       | 0       |
| 12.35      | 0       |
| 17.35      | 0       |
| 22.35      | 0       |
| 27.35      | 0       |
| 32.35      | 0       |
| 37.35      | 0       |
| 42.35      | 0       |
| 47.35      | 0       |
| 52.35      | 0       |
| 57.35      | 0       |
| 62.35      | 0       |
| 67.35      | 0       |
| 72.35      | 0       |
| 77.35      | 0       |
| 82.35      | 0       |
| 87.35      | 0       |
| 92.35      | 0       |
| 97.35      | 0       |
| 102.35     | 0       |
| 107.35     | 0       |
| 112.35     | 0       |
| 117.35     | 0       |

| Time (min) | Yield % |
|------------|---------|
| 7.58       | 36      |
| 12.58      | 49      |
| 17.58      | 57      |
| 22.58      | 62      |
| 27.58      | 62      |
| 32.58      | 62      |
| 37.58      | 62      |
| 42.58      | 62      |
| 47.58      | 62      |
| 52.58      | 62      |
| 57.58      | 62      |
| 62.58      | 62      |
| 67.58      | 62      |
| 72.58      | 62      |
| 77.58      | 62      |
| 82.58      | 62      |
| 87.58      | 62      |
| 92.58      | 62      |
| 97.58      | 63      |
| 102.58     | 63      |
| 107.58     | 63      |
| 112.58     | 63      |
| 117.58     | 63      |
| 122.58     | 63      |
| 127.58     | 63      |
| 132.58     | 63      |
| 137.58     | 63      |
| 142.58     | 63      |
| 147.58     | 63      |
| 360        | 65      |
| 1440       | 68      |

| Time (min) | Yield % |
|------------|---------|
| 9.84       | 8       |
| 14.84      | 16      |
| 19.84      | 32      |
| 24.84      | 32      |
| 29.84      | 32      |
| 34.84      | 32      |
| 39.84      | 32      |
| 44.84      | 32      |
| 49.84      | 32      |
| 54.84      | 32      |
| 59.84      | 32      |
| 64.84      | 32      |
| 69.84      | 32      |
| 74.84      | 32      |
| 79.84      | 32      |
| 84.84      | 32      |
| 89.84      | 32      |
| 94.84      | 32      |
| 99.84      | 32      |
| 104.84     | 32      |
| 109.84     | 32      |
| 114.84     | 32      |
| 119.84     | 32      |
| 124.84     | 32      |
| 129.84     | 32      |
| 134.84     | 32      |
| 139.84     | 32      |
| 144.84     | 32      |
| 149.84     | 32      |
| 660        | 70      |
| 1440       | 70      |
| IV | Time (min) | Yield % |
|----|------------|---------|
|    | 5.98       | 0       |
|    | 10.98      | 0.5     |
|    | 15.98      | 1       |
|    | 20.98      | 1       |
|    | 25.98      | 2       |
|    | 30.98      | 2       |
|    | 35.98      | 3       |
|    | 40.98      | 3       |
|    | 45.98      | 4       |
|    | 50.98      | 4       |
|    | 55.98      | 5       |
|    | 60.98      | 5       |
|    | 65.98      | 6       |
|    | 70.98      | 6       |
|    | 75.98      | 7       |
|    | 80.98      | 7       |
|    | 85.98      | 8       |
|    | 90.98      | 8       |
|    | 95.98      | 8       |
|    | 100.98     | 9       |
|    | 105.98     | 10      |
|    | 110.98     | 10      |
|    | 115.98     | 10      |
|    | 120.98     | 11      |
|    | 125.98     | 11      |
|    | 1380       | 52      |

| V  | Time (min) | Yield % |
|----|------------|---------|
|    | 3.89       | 0       |
|    | 8.89       | 0       |
|    | 13.89      | 1       |
|    | 18.89      | 1       |
|    | 23.89      | 1       |
|    | 28.89      | 1       |
|    | 33.89      | 1       |
|    | 38.89      | 1       |
|    | 43.89      | 2       |
|    | 48.89      | 2       |
|    | 53.89      | 2       |
|    | 58.89      | 2       |
|    | 63.89      | 2       |
|    | 68.89      | 2       |
|    | 73.89      | 2       |
|    | 78.89      | 2       |
|    | 83.89      | 2       |
|    | 88.89      | 2       |
|    | 93.89      | 2       |
|    | 98.89      | 2       |
|    | 103.89     | 3       |
|    | 108.89     | 3       |
|    | 113.89     | 3       |
|    | 118.89     | 3       |
|    | 123.89     | 3       |
|    | 128.89     | 3       |
|    | 133.89     | 3       |
|    | 138.89     | 3       |
|    | 143.89     | 3       |
|    | 540        | 7       |
|    | 1440       | 8       |

| VI | Time (min) | Yield % |
|----|------------|---------|
|    | 7.08       | 2       |
|    | 12.08      | 3       |
|    | 17.08      | 4       |
|    | 22.08      | 5       |
|    | 27.08      | 6       |
|    | 32.08      | 6       |
|    | 37.08      | 7       |
|    | 42.08      | 8       |
|    | 47.08      | 10      |
|    | 52.08      | 11      |
|    | 57.08      | 12      |
|    | 62.08      | 13      |
|    | 67.08      | 14      |
|    | 72.08      | 14      |
|    | 77.08      | 16      |
|    | 82.08      | 16      |
|    | 87.08      | 17      |
|    | 92.08      | 18      |
|    | 97.08      | 19      |
|    | 102.08     | 20      |
|    | 107.08     | 21      |
|    | 112.08     | 22      |
|    | 117.08     | 23      |
|    | 122.08     | 23      |
|    | 127.08     | 24      |
|    | 132.08     | 25      |
|    | 137.08     | 26      |
|    | 142.08     | 26      |
|    | 147.08     | 27      |
|    | 540        | 65      |
|    | 1500       | 69      |
### VII
| Time (min) | Yield % |
|------------|---------|
| 7.92       | 7       |
| 12.92      | 9       |
| 17.92      | 11      |
| 22.92      | 14      |
| 27.92      | 15      |
| 32.92      | 17      |
| 37.92      | 19      |
| 42.92      | 20      |
| 47.92      | 22      |
| 52.92      | 24      |
| 57.92      | 25      |
| 62.92      | 26      |
| 67.92      | 28      |
| 72.92      | 28      |
| 77.92      | 30      |
| 82.92      | 32      |
| 87.92      | 32      |
| 92.92      | 34      |
| 97.92      | 35      |
| 102.92     | 35      |
| 107.92     | 36      |
| 112.92     | 37      |
| 117.92     | 38      |
| 122.92     | 39      |
| 127.92     | 39      |
| 480        | 47      |
| 1440       | 49      |

### VIII
| Time (min) | Yield % |
|------------|---------|
| 9.26       | 14      |
| 14.26      | 15      |
| 19.26      | 20      |
| 24.26      | 26      |
| 29.26      | 31      |
| 34.26      | 36      |
| 39.26      | 40      |
| 44.26      | 43      |
| 49.26      | 45      |
| 54.26      | 48      |
| 59.26      | 52      |
| 64.26      | 53      |
| 69.26      | 54      |
| 74.26      | 55      |
| 79.26      | 55      |
| 84.26      | 55      |
| 89.26      | 56      |
| 94.26      | 57      |
| 99.26      | 57      |
| 104.26     | 58      |
| 109.26     | 58      |
| 114.26     | 58      |
| 119.26     | 58      |
| 124.26     | 58      |
| 129.26     | 58      |
| 134.26     | 58      |
| 139.26     | 58      |
| 144.26     | 59      |
| 149.26     | 59      |
| 154.26     | 59      |
| 159.26     | 60      |
| 180        | 60      |
| 360        | 68      |
| 1440       | 68      |

### IX
| Time (min) | Yield % |
|------------|---------|
| 6.88       | 0       |
| 11.88      | 1       |
| 16.88      | 2       |
| 21.88      | 2       |
| 26.88      | 2       |
| 31.88      | 3       |
| 36.88      | 4       |
| 41.88      | 4       |
| 46.88      | 4       |
| 51.88      | 5       |
| 56.88      | 5       |
| 61.88      | 6       |
| 66.88      | 6       |
| 71.88      | 7       |
| 76.88      | 7       |
| 81.88      | 7       |
| 86.88      | 8       |
| 91.88      | 8       |
| 96.88      | 8       |
| 101.88     | 9       |
| 106.88     | 9       |
| 111.88     | 10      |
| 116.88     | 10      |
| 121.88     | 10      |
| 126.88     | 11      |
| 131.88     | 11      |
| 136.88     | 12      |
| 141.88     | 12      |
| 146.88     | 15      |
| 240        | 18      |
| 1440       | 60      |
$^1$H NMR monitoring of the gold(I)-catalyzed cycloisomerization of enyne 7b. Spectra recorded every 5 min during 3 h and then after 12 and 24 h.
4. X-Ray Diffraction Data

Complex 2a

Table 1. Crystal data and structure refinement for mo_AI046Fb_1_0m.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | mo_AI046Fb_1_0m                            |
| Empirical formula               | C43 H56 Au2 Cl3 F6 N O4 P2 S2             |
| Formula weight                  | 1391.23                                    |
| Temperature                     | 100(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Triclinic                                  |
| Space group                     | P-1                                        |
| Unit cell dimensions            | a = 11.4925(5) Å, b = 14.9454(6) Å, c = 16.7159(8) Å |
|                                | a = 65.585(2) °, b = 81.287(2) °, g = 72.405(2) ° |
| Volume                          | 2490.90(19) Å                             |
| Z                               | 2                                          |
| Density (calculated)            | 1.855 Mg/m³                                |
| Absorption coefficient          | 6.255 mm⁻¹                                 |
| F(000)                          | 1356                                       |
| Crystal size                    | 0.3 x 0.1 x 0.03 mm³                       |
| Theta range for data collection | 1.34 to 30.30 °                            |
| Index ranges                    | -15 <=h<=15, -13 <=k<=21, -19 <=l<=23     |
| Reflections collected           | 19961                                      |
| Independent reflections         | 12629 [R(int) = 0.0355 ]                   |
| Completeness to theta = 30.30 ° | 84.5%                                      |
| Absorption correction           | Empirical                                  |
| Max. and min. transmission      | 0.8345 and 0.2555                          |
Refinement method       Full-matrix least-squares on $F^2$
Data / restraints / parameters    12629 / 0 / 580
Goodness-of-fit on $F^2$       1.022
Final R indices [I>2sigma(I)]    R1 = 0.0405 , wR2 = 0.0821
R indices (all data)    R1 = 0.0656 , wR2 = 0.1020
Largest diff. peak and hole    1.071 and -1.092 eÅ$^{-3}$

Complex 2b

Table 1. Crystal data and structure refinement for mo_AI002512B_0m.

| Identification code    | mo_AI002512B_0m       |
|------------------------|-----------------------|
| Empirical formula      | C44 H61 Au2 Cl2 F3 O3 P2 S |
| Formula weight         | 1253.76               |
| Temperature            | 100(2) K              |
| Wavelength             | 0.71073 Å             |
| Crystal system         | Triclinic             |
| Space group            | P-1                   |
| Unit cell dimensions   | a = 11.5811(13) Å, a = 68.918(2) °,  |
|                        | b = 15.0678(16) Å, b = 77.341(2) °,  |
|                        | c = 15.1920(17) Å, g = 72.311(2) °,  |
| Volume                 | 2338.6(4) Å$^3$       |
| Z                      | 2                     |
| Density (calculated)   | 1.781 Mg/m$^3$        |
Absorption coefficient 6.543 mm$^{-1}$
F(000) 1228
Crystal size 0.40 x 0.001 x 0.001 mm$^3$
Theta range for data collection 2.88 to 35.10 °.
Index ranges -18 <=h<=18 , -24 <=k<=19 , -24 <=l<=24
Reflections collected 27698
Independent reflections 18809 [R(int) = 0.0285 ]
Completeness to theta =35.10 ° 90.7%
Absorption correction Empirical
Max. and min. transmission 0.9935 and 0.1794
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 18809 / 86 / 564
Goodness-of-fit on F$^2$ 1.035
Final R indices [I>2sigma(I)] R1 = 0.0488 , wR2 = 0.1270
R indices (all data) R1 = 0.0803 , wR2 = 0.1518
Largest diff. peak and hole 3.185 and -4.483 e.Å$^{-3}$

Complex 2c

Table 1. Crystal data and structure refinement for AI0047_0m.

| Identification code | AI0047_0m |
|---------------------|-----------|
| Empirical formula   | C42 H56 Au2 B Cl7 F4 P2 |
| Formula weight      | 1351.70   |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
Crystal system: Monoclinic
Space group: P2(1)/c
Unit cell dimensions:
\[ a = 11.4730(5) \text{ Å} \]
\[ b = 16.4087(8) \text{ Å} \]
\[ c = 26.3794(11) \text{ Å} \]
\[ \alpha = 90.00^\circ \]
\[ \beta = 95.4410(10)^\circ \]
\[ \gamma = 90.00^\circ \]
Volume: 4943.7(4) Å³
Z: 4
Density (calculated): 1.816 Mg/m³
Absorption coefficient: 6.416 mm⁻¹
F(000): 2624
Crystal size: 0.18 x 0.08 x 0.04 mm³
Theta range for data collection: 2.48 to 39.50 °
Index ranges: -6 ≤ h ≤ 20, -28 ≤ k ≤ 29, -46 ≤ l ≤ 22
Reflections collected: 52894
Independent reflections: 23036 [R(int) = 0.0201]
Completeness to theta = 39.50 °: 77.5%
Absorption correction: Empirical
Max. and min. transmission: 0.7834 and 0.3913
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 23036 / 122 / 571
Goodness-of-fit on F²: 0.938
Final R indices [I>2σ(I)]: R1 = 0.0229, wR2 = 0.0576
R indices (all data): R1 = 0.0306, wR2 = 0.0609
Largest diff. peak and hole: 2.659 and -1.124 eÅ⁻³

**Complex 2d**

![Complex 2d diagram](image)
Table 1. Crystal data and structure refinement for AHR30022_0m.

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Identification code                           | AHR30022_0m                  |
| Empirical formula                             | C41.50 H55.50 Au2 Cl5.50 F6 P2 Sb |
| Formula weight                                | 1440.96                      |
| Temperature                                   | 100(2) K                     |
| Wavelength                                    | 0.71073 Å                    |
| Crystal system                                | Triclinic                    |
| Space group                                   | P-1                          |
| Unit cell dimensions                          | a = 11.5465(4) Å             |
|                                               | b = 14.7971(5) Å             |
|                                               | c = 15.8602(6) Å             |
|                                               | a= 69.5680(10) °.            |
|                                               | b = 80.2880(10) °.           |
|                                               | g= 72.5010(10) °.            |
| Volume                                        | 2415.63(15) Å³               |
| Z                                             | 2                            |
| Density (calculated)                          | 1.981 Mg/m³                  |
| Absorption coefficient                        | 7.037 mm⁻¹                   |
| F(000)                                        | 1382                         |
| Crystal size                                  | 0.15 x 0.05 x 0.03 mm³       |
| Theta range for data collection               | 1.52 to 29.96 °.             |
| Index ranges                                  | -16 <=h<=15 , -20 <=k<=20 , -22 <=l<=22 |
| Reflections collected                         | 89373                        |
| Independent reflections                       | 12847 [R(int) = 0.0336 ]     |
| Completeness to theta =29.96 °                 | 0.914 %                      |
| Absorption correction                         | Empirical                    |
| Max. and min. transmission                    | 0.8166 and 0.4183            |
| Refinement method                             | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 12847 / 150 / 650            |
| Goodness-of-fit on F²                          | 1.166                        |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0305 , wR2 = 0.0689   |
| R indices (all data)                           | R1 = 0.0394 , wR2 = 0.0723   |
| Largest diff. peak and hole                    | 2.418 and -1.354 e.Å⁻³       |
[(1,1'-Biphenyl-2-yl)di-tert-butylphosphine]gold(I) bis(trifluoromethanesulfonyl)imide (3a)

Table 1. Crystal data and structure refinement for mo_AI0035_0m.

| Identification code         | mo_AI0035_0m                  |
|-----------------------------|-------------------------------|
| Empirical formula           | C22 H27 Au F6 N O4 P S2       |
| Formula weight              | 775.50                        |
| Temperature                 | 100(2) K                      |
| Wavelength                  | 0.71073 Å                     |
| Crystal system              | Triclinic                     |
| Space group                 | P1                            |
| Unit cell dimensions        | a = 9.5483(8) Å , a= 98.149(4) °. |
|                            | b = 10.0082(12) Å , b = 96.743(3) °. |
|                            | c = 15.3039(14) Å , g = 107.426(4) °. |
| Volume                      | 1361.3(2) Å³                  |
| Z                           | 2                             |
| Density (calculated)        | 1.892 Mg/m³                   |
| Absorption coefficient      | 5.686 mm⁻¹                    |
| F(000)                      | 756                           |
| Crystal size                | 0.30 x 0.20 x 0.10 mm³        |
| Theta range for data collection | 1.36 to 30.29 °.             |
| Index ranges                | -13 <=h<=13 , -13 <=k<=14 , -21 <=l<=20 |
| Reflections collected       | 16807                         |
| Independent reflections     | 7077 [R(int) = 0.0685 ]       |
| Completeness to theta       | 86.799999%                    |
| Absorption correction       | Empirical                     |
Max. and min. transmission 0.6002 and 0.2803
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 7077 / 0 / 340
Goodness-of-fit on F^2 1.078
Final R indices [I>2sigma(I)] R1 = 0.0319, wR2 = 0.0795
R indices (all data) R1 = 0.0345, wR2 = 0.0803
Largest diff. peak and hole 2.945 and -4.094 e.Å^{-3}

|(1,1'-biphenyl-2-yl)di-tert-butylphosphine|gold(I) trifluoromethanesulfonate (3b)

Table 1. Crystal data and structure refinement for mo_AI002512_0m.

| Identification code   | mo_AI002512_0m |
|-----------------------|----------------|
| Empirical formula     | C21 H27 Au F3 O3 P S |
| Formula weight        | 644.42         |
| Temperature           | 100(2) K      |
| Wavelength            | 0.71073 Å     |
| Crystal system        | Monoclinic    |
| Space group           | P2(1)/c       |
| Unit cell dimensions  | a = 14.2158(12) Å, b = 9.9549(9) Å, c = 16.0881(13) Å |
|                       | a = 90.00 °, b = 97.068(3) °, g = 90.00 ° |
| Volume                | 2259.4(3) Å³   |
| Z                     | 4              |
| Density (calculated)  | 1.894 Mg/m³    |
| Absorption coefficient| 6.719 mm⁻¹     |
Table 1. Crystal data and structure refinement for mo_AHR30016_0m.

| Parameter                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Identification code                           | mo_AHR30016_0m               |
| Empirical formula                             | C42.50 H57.50 Au2 B Cl7.50 F4 O P2 |
| Formula weight                                 | 1392.94                      |
| Temperature                                    | 100(2) K                     |
| Wavelength                                     | 0.71073 Å                    |
| Crystal system                                 | Monoclinic                   |
| Space group                                    | P2(1)/n                      |
| Unit cell dimensions                           | a = 11.9239(16) Å            |
|                                              | a= 90.00 °                   |

Complex 5

![Complex 5 Image]

Table 1. Crystal data and structure refinement for mo_AHR30016_0m.
| Property                        | Value                          |
|--------------------------------|--------------------------------|
| b = 26.260(3) Å                | b = 92.182(4) °               |
| c = 16.336(2) Å                | g = 90.00 °                   |
| Volume                         | 5111.4(11) Å³                 |
| Z                              | 4                              |
| Density (calculated)           | 1.810 Mg/m³                   |
| Absorption coefficient         | 6.235 mm⁻¹                    |
| F(000)                         | 2708                           |
| Crystal size                   | 0.30 x 0.05 x 0.03 mm³        |
| Theta range for data collection| 1.88 to 25.44 °               |
| Index ranges                   | -14 <= h <= 14, -31 <= k <= 31, -19 <= l <= 19 |
| Reflections collected          | 47708                          |
| Independent reflections        | 9380 [R(int) = 0.0811]         |
| Completeness to theta = 25.44 °| 0.992 %                       |
| Absorption correction          | Empirical                     |
| Max. and min. transmission     | 0.8350 and 0.2563             |
| Refinement method              | Full-matrix least-squares on F²|
| Data / restraints / parameters | 9380 / 90 / 625               |
| Goodness-of-fit on F²          | 1.184                          |
| Final R indices [I>2σ(I)]      | R1 = 0.0753, wR2 = 0.1865     |
| R indices (all data)           | R1 = 0.0891, wR2 = 0.1920      |
| Largest diff. peak and hole    | 3.106 and -2.321 e.Å⁻³        |
5. NMR Spectra

Complex 2a

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (126 MHz CD$_2$Cl$_2$)
$^{31}$P NMR (202 MHz, CD$_2$Cl$_2$)

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$)
Complex 2b

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (126 MHz CD$_2$Cl$_2$)
$^{31}$P NMR (202 MHz, CD$_2$Cl$_2$)

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$)
Complex 2c

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (126 MHz CD$_2$Cl$_2$)
$^{31}$P NMR (202 MHz, CD$_2$Cl$_2$)

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$)
Complex 2d

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)

$^{13}$C NMR (126 MHz CD$_2$Cl$_2$)
$^{31}$P NMR (202 MHz, CD$_2$Cl$_2$)

[1,1'-biphenyl-2-yl]di-tert-butylphosphine]gold(I) bis(trifluoromethanesulfonyle)imide (3a)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)
$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$)

1,1'-Biphenyl-2-yl)di-tert-butylphosphine|gold(I) trifluoromethanesulfonate (3b)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$)
$^{13}$C NMR (126 MHz CD$_2$Cl$_2$)

$^{31}$P NMR (162 MHz, CD$_2$Cl$_2$)
19F NMR (376 MHz, CD$_2$Cl$_2$)

Complex 5

1H NMR (500 MHz, CDCl$_3$)
$^{31}$P NMR (202 MHz, CDCl₃)

**Formation of product 6:** [2+2] Intermolecular cycloaddition of phenylacetylene and α-methylstyrene monitored by $^1$H NMR. Singlet at 4.00 ppm corresponding to the benzylic protons of diphenylmethane (internal standard) and singlet at 6.72 ppm to quantify the formation of product 6.
**Product 8:** [2+2] intramolecular cycloaddition of enyne 7a monitored by $^1$H NMR. Singlet at 4.02 ppm corresponding to the benzylic protons of diphenylmethane (internal standard). Multiplet at 3.54-3.51 ppm and at 3.20-3.16 ppm used to quantify the formation of product 8.

**Product 9:** [4+2] intramolecular cycloaddition of enyne 7b monitored by $^1$H NMR. Singlet at 4.01 ppm corresponding to the benzylic protons of diphenylmethane (internal standard). Singlet at 6.50 ppm used to quantify the formation of product 9.