Supporting Information

Dissecting Anion Effects in Gold(I)-Catalyzed Intermolecular Cycloadditions

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Supporting Information
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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 GF234) 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. Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). If indicated, preparative TLC was performed on 20 cm x 20 cm aluminum oxide plates (0.25 mm thick, 90066, Fluka). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

NMR spectra was recorded at 298 K on a Bruker Avance 400 Ultrashield and Bruker Avance 500 Ultrashield apparatus. Mass spectra was recorded on a Waters Micromass LCT Premier (ESI), Waters Micromass GCT (EI, CI) and Bruker Daltonics Autoflex (MALDI) spectrometers. Elemental analyses were performed on a LECO CHNS 932 micro-analyzer at the Universidad Complutense de Madrid. Melting points were determined using a Büchi melting point apparatus and are uncorrected.

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.

Alkynes, alkenes, 5-methylhex-5-en-2-one as well as the silver salts, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate and catalyst A1 were used as received.
from Alfa Aesar or Aldrich. Alkene 2f and 1,4-enyne 10 were prepared according the described procedure. Catalysts B1, B2 and {phenylethynyl [(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl) di-tert-butylphosphine] gold(I)} [(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl) di-tert-butylphosphine] gold(I) hexafuloroantimonate were prepared according to the literature too.

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2. Synthesis of Gold(I) Complexes

(Acetonitrile)[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (A2)

\[
\text{Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (100.0 mg, 0.152 mmol) and acetonitrile (9.5 µl, 0.183 mmol) were dissolved in CH}_2\text{Cl}_2 (6.6 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (135.0 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH}_2\text{Cl}_2. The solvent was removed to afford a white powder (224.3 mg, 0.147 mmol, 97%).
\]

\[
1^H \text{NMR (400 MHz, CD}_2\text{Cl}_2): \delta (\text{ppm}) 7.92 - 7.85 (m, 1H), 7.75 - 7.70 (m, 8H), 7.66 - 7.58 (m, 2H), 7.56 (s, 4H), 7.32 (m, 1H), 7.16 (s, 2H), 2.94 (p, \text{J} = 6.9 \text{ Hz}, 1H), 2.33 (dt, \text{J} = 13.4, 6.7 \text{ Hz}, 2H), 2.25 (broad s, 3H), 1.41 (d, \text{J} = 6.9 \text{ Hz}, 6H), 1.25 (d, \text{J} = 6.8 \text{ Hz}, 6H), 0.93 (d, \text{J} = 6.6 \text{ Hz}, 6H).
\]

\[
13^C \text{NMR (101 MHz, CD}_2\text{Cl}_2): \delta (\text{ppm}) 162.3 (q, J^{13^C-11^B} = 50.1 \text{ Hz}), 150.4, 148.0, 147.6 (d, J^{13^C-31^P} = 12.8 \text{ Hz}), 136.7 (d, J^{13^C-31^P} = 6.1 \text{ Hz}), 135.5, 135.4, 134.7 (d, J^{13^C-31^P} = 4.6 \text{ Hz}), 132.1 (d, J^{13^C-31^P} = 2.6 \text{ Hz}), 129.5 (q, J^{13^C-19^F} = 28.6 \text{ Hz}), 128.1 (d, J^{13^C-31^P} = 8.1 \text{ Hz}), 126.0 (d, J^{13^C-31^P} = 50.2 \text{ Hz}), 125.2 (q, J^{13^C-19^F} = 272.3 \text{ Hz}), 122.5, 118.1 (p, J^{13^C-19^F} = 4.0 \text{ Hz}), 39.2 (d, J^{13^C-31^P} = 29.3 \text{ Hz}), 34.6, 31.5 (d, J^{13^C-31^P} = 4.3 \text{ Hz}), 31.5, 26.3, 24.5, 23.4, 3.3 and one carbon is missing probably because of overlapping. \text{^{31^P \{1^H\} NMR (162 MHz, CD}_2\text{Cl}_2): \delta (\text{ppm}) 58.68. \text{^{19^F \{1^H\} NMR (376 MHz, CD}_2\text{Cl}_2): \delta (\text{ppm}) -62.97. \text{^{11^B \{1^H\} NMR (128 MHz, CD}_2\text{Cl}_2): \delta (\text{ppm}) -6.68. MALDI^+: m/z \text{ calcd for C}_{31}H_{48}AuNP^+ [M-C}_{32}H_{12}BF_{24}^+: 662.3175, found: 662.3184. Anal. calcd for C}_{63}H_{60}AuBF_{24}NP: C, 49.59; H, 3.97; N, 0.92; found: C, 49.56; H, 3.94; N, 0.97.}
\]
(Acetonitrile)(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine|gold(I) tetrafluoroborate (A3)

![Chemical structure](image)

Chloro[(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine|gold(I) (100.0 mg, 0.152 mmol) and acetonitrile (9.5 µl, 0.183 mmol) were dissolved in CH₂Cl₂ (6.6 ml). Then, silver tetrafluoroborate (29.6 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 20 min. The crude was filtered through and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH₂Cl₂. The solvent was removed to afford a white powder (113.9 mg, 0.152 mmol, 100%).

$^{1}$H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.90 (td, $J = 8.9, 8.1, 2.3$ Hz, 1H), 7.69 – 7.54 (m, 2H), 7.17 (s, 2H), 2.97 (hept, $J = 6.8$ Hz, 1H), 2.39 (s, 3H), 2.33 (hept, $J = 6.7$ Hz, 2H), 1.43 (d, $J = 16.3$ Hz, 18H), 1.33 (d, $J = 6.9$ Hz, 6H), 1.27 (d, $J = 6.8$ Hz, 6H), 0.93 (d, $J = 6.6$ Hz, 6H). $^{13}$C NMR (101 MHz, CD₂Cl₂): δ (ppm) 150.5, 147.8, 147.7 (d, $J (^{13}$C-$^{31}$P) = 12.7 Hz), 136.6 (d, $J (^{13}$C-$^{31}$P) = 6.0 Hz), 135.4 (d, $J (^{13}$C-$^{31}$P) = 8.1 Hz), 134.8 (d, $J (^{13}$C-$^{31}$P) = 4.3 Hz), 132.0, 128.0 (d, $J (^{13}$C-$^{31}$P) = 7.8 Hz), 126.3 (d, $J (^{13}$C-$^{31}$P) = 47.8 Hz), 122.5, 120.0 (d, $J (^{13}$C-$^{31}$P) = 4.4 Hz), 39.2 (d, $J (^{13}$C-$^{31}$P) = 28.2 Hz), 34.5, 31.6 (d, $J (^{13}$C-$^{31}$P) = 5.8 Hz), 31.5, 26.4, 24.5, 23.4, 3.3. $^{31}$P $^{1}$H NMR (162 MHz, CD₂Cl₂): δ (ppm) 58.58. $^{19}$F $^{1}$H NMR (376 MHz, CD₂Cl₂): δ (ppm) -153.10. $^{11}$B $^{1}$H NMR (128 MHz, CD₂Cl₂): δ (ppm) -1.23. MALDI$: m/z$ calcd for C₃₁H₄₈AuNP$^+$ [M-BF₄]$^+$: 662.3184, found: 662.3180. Anal. calcd for C₆₃H₆₀AuBF₂₄NP: C, 49.68; H, 6.46; N, 1.87; found: C, 48.89; H, 6.20; N, 1.64.
(Acetonitrile)|(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine|gold(I) hexafluorophosphate (A4)

Chloro|(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine|gold(I) (350.0 mg, 0.533 mmol) and acetonitrile (33.0 µl, 0.639 mmol) were dissolved in CH₂Cl₂ (23 ml). Then, silver hexafluorophosphate (135.0 mg, 0.533 mmol) was added and the reaction mixture was stirred at room temperature for 20 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH₂Cl₂. The solvent was removed to afford a white powder (221.0 mg, 0.274 mmol, 51%).

¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.90 (ddd, J = 9.0, 7.1, 2.2 Hz, 1H), 7.60 (dq, J = 7.1, 2.0 Hz, 2H), 7.33 (td, J = 6.6, 5.7, 3.2 Hz, 1H), 7.17 (s, 1H), 2.95 (hept, J = 6.9 Hz, 1H), 2.38 – 2.27 (m, 4H), 1.43 (d, J = 16.3 Hz, 18H), 1.33 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.7 Hz, 6H), 0.93 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CD₂Cl₂): δ (ppm) 149.9, 147.8, 136.6 (d, J (¹³C-³¹P) = 7.1 Hz), 135.3 (d, J (¹³C-³¹P) = 9.3 Hz), 134.8 (d, J (¹³C-³¹P) = 4.2 Hz), 132.0, 128.0 (d, J (¹³C-³¹P) = 7.2 Hz), 122.4, 117.9, 39.2 (d, J (¹³C-³¹P) = 29.2 Hz), 34.55, 31.56 (d, J = 5.6 Hz), 26.35, 24.47, 23.39, 3.23. Two signals are missing due to overlapping. ³¹P {¹H} NMR (162 MHz, CD₂Cl₂): δ (ppm) 58.53, -139.23 (hept, J (³¹P-¹⁹F ) = 715.0 Hz). ¹⁹F {¹H} NMR (376 MHz, CD₂Cl₂): δ (ppm) -73.46 (d, J (¹⁹F-³¹P) = 710.3 Hz). ESI⁺: m/z calcd for C₃₁H₄₈AuNP⁺ [M-PF₆]⁺: 662.3184, found: 662.3176.
[2′,4′,6′-Triisopropyl-1,1′-biphenyl-2-yl]di-tert-butylphosphine(2-phenylethynyl)gold(I) (16)

Lithium bis(trimethylsilyl)amide (53.5 mg, 0.320 mmol) was dissolved in THF (4.0 ml) and cooled to 0 °C. Ethynylbenzene (35.1 µl, 0.320 mmol) was added and the solution was stirred for 30 min. Afterwards, chloro[2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl]di-tert-butylphosphine]gold(I) (200.0 mg, 0.304 mmol) dissolved in THF (3.0 ml) was added and the solution was stirred overnight at room temperature. The crude was concentrated, dissolved in CH₂Cl₂ and filtered through Teflon 0.22. The solvent was removed to afford a white powder (219.0 mg, 0.303 mmol, 99%).

¹H NMR (500 MHz, CD₂Cl₂): δ (ppm) 7.92 (td, J = 7.4, 1.8 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.30 – 7.28 (m, 3H), 7.21 – 7.18 (m, 2H), 7.15 – 7.12 (m, 3H), 2.93 (p, J = 6.9 Hz, 1H), 2.40 (p, J = 6.7 Hz, 2H), 1.43 (d, J = 14.8 Hz, 18H), 1.36 (d, J = 6.8 Hz, 6H), 1.27 (d, J = 6.9 Hz, 6H), 0.92 (d, J = 6.7 Hz, 6H). ¹³C NMR (126 MHz, CD₂Cl₂): δ (ppm) 150.0, 148.7 (d, J (¹³C-³¹P) = 15.6 Hz), 146.4, 137.3 (d, J (¹³C-³¹P) = 133.1 Hz), 136.6 (d, J (¹³C-³¹P) = 5.1 Hz), 136.1 (d, J (¹³C-³¹P) = 1.6 Hz), 135.2 (d, J (¹³C-³¹P) = 7.9 Hz), 132.2, 130.4 (d, J (¹³C-³¹P) = 2.2 Hz), 129.9 (d, J (¹³C-³¹P) = 37.0 Hz), 128.3, 127.4 (d, J (¹³C-³¹P) = 2.7 Hz), 126.9 (d, J (¹³C-³¹P) = 6.0 Hz), 126.0, 122.3, 101.5 (d, J (¹³C-³¹P) = 23.9 Hz), 38.5 (d, J (¹³C-³¹P) = 23.2 Hz), 34.5, 31.7 (d, J (¹³C-³¹P) = 6.8 Hz), 31.4, 26.5, 24.4, 23.2. ³¹P {¹H} NMR (202 MHz, CD₂Cl₂): δ (ppm) 66.89. MALDI⁺: m/z calcd for C₃₇H₅₀AuPNa⁺ [M+Na⁺]: 745.3208, found: 745.3216. Structure confirmed by X-ray crystallography: CCDC 953709.
(α-Methylstyrene)[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)]di-tert-butylphosphine|gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)

Chloro[(2’,4’,6’-triisopropyl-1,1’-biphenyl-2-yl)]di-tert-butylphosphine|gold(I) (100.0 mg, 0.152 mmol) and α-methylstyrene (30.0 µl, 0.228 mmol) were dissolved in CH₂Cl₂ (10.0 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (135.0 mg, 0.152 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH₂Cl₂. The solvent was removed to afford a white powder (210.4 mg, 0.131 mmol, 86%).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ (ppm) 7.82 (td, J = 7.8, 1.6 Hz, 1H), 7.76 – 7.70 (m, 8H), 7.63 – 7.53 (m, 6H), 7.50 – 7.39 (m, 5H), 7.29 (s, 2H), 7.21 (ddd, J = 7.3, 3.7, 1.7 Hz, 1H), 4.27 (dd, J = 4.5, 0.8 Hz, 1H), 3.95 (d, J = 4.5 Hz, 1H), 3.12 (p, J = 6.9 Hz, 1H), 2.50 (s, 3H), 2.42 – 2.19 (m, 2H), 1.43 (d, J = 6.9 Hz, 6H), 1.39 – 1.03 (m, 24H), 0.92 (d, J = 6.6 Hz, 6H).

¹³C NMR (101 MHz, CD₂Cl₂, 213 K): it was not possible to properly assign all the signals due to the broadening of some peaks because of the weak coordination of the metal to the alkene combined with the complexity of the heterocouplings with ³¹P, ¹⁹F and ¹¹B δ (ppm) 162.95, 162.55, 162.16, 161.76, 155.99, 151.76, 149.09, 147.08, 146.97, 135.95, 135.75, 135.47, 135.32, 135.04, 133.40, 132.93, 132.61, 132.26, 130.29, 129.79, 129.61, 129.36, 129.07, 128.44, 127.14, 126.67, 126.27, 124.11, 123.63, 123.12, 121.94, 118.55, 118.21, 117.88, 117.55, 89.01, 88.68, 88.61, 88.14, 32.64, 31.42, 31.11, 26.27, 26.04, 25.90, 25.02, 24.82, 24.64, 24.45, 23.82. ³¹P {¹H} NMR (162 MHz, CD₂Cl₂, 298 K): δ (ppm) 69.34. ¹⁹F {¹H} NMR (376 MHz, CD₂Cl₂, 298 K): δ (ppm) -62.83. ¹¹B {¹H} NMR (128 MHz, CD₂Cl₂, 298 K): δ (ppm) -6.67. ESI⁺: m/z calcd for C₂₉H₄₅AuP⁺ [M-C₃H₂₂BF₄]⁺: 621.2919, found: 621.2916. Structure confirmed by X-ray crystallography: CCDC 953708.
{Phenylethynyl[(2,4,6-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I)}

[(2,4,6-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)

Chloro[(2,4,6-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (68.2 mg, 0.104 mmol) and [(2,4,6-triisopropyl-1,1′-biphenyl-2-yl)di-tert-butylphosphine](2-phenylethynyl)gold(I) (75 mg, 0.104 mmol) were dissolved in CH₂Cl₂ (9.4 ml). Then, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (92 mg, 0.104 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. The crude was filtered through Celite and concentrated. Finally, it was filtered through Teflon 0.22 and washed with CH₂Cl₂. The solvent was removed to afford a white powder (223.0 mg, 0.101 mmol, 97%).

¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.95 – 7.87 (m, 2H), 7.73 (dd, J = 4.2, 2.0 Hz, 8H), 7.57 (broad s, 4H), 7.56 – 7.49 (m, 4H), 7.48 – 7.42 (m, 1H), 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.22 (m, 2H), 6.84 (s, 4H), 2.39 – 2.29 (m, 6H), 1.42 (d, J = 15.6 Hz, 36H), 1.14 (d, J = 6.8 Hz, 12H), 1.09 (d, J = 6.9 Hz, 12H), 0.85 (d, J = 6.6 Hz, 12H). ¹³C NMR (101 MHz, CD₂Cl₂): δ (ppm) 162.3 (q, J (¹³C-¹¹B) = 50.0 Hz), 150.0, 148.1 (d, J (¹³C-³¹P) = 14.3 Hz), 147.1, 136.2 (d, J (¹³C-³¹P) = 5.6 Hz), 135.5, 135.4, 135.0 (d, J (¹³C-³¹P) = 1.2 Hz), 133.1, 131.4, 130.6, 130.0 – 129.0 (m), 129.0, 127.7 (d, J (¹³C-³¹P) = 42.5 Hz), 127.6, 127.5, 125.2 (q, J (¹³C-¹⁹F) = 272.6 Hz), 122.2, 121.3, 118.2 – 118.0 (m), 39.3 (d, J (¹³C-³¹P) = 24.6 Hz), 34.0, 31.9 (d, J (¹³C-³¹P) = 6.8 Hz), 31.4, 26.4, 24.3, 23.6 and one signal missing because of overlapping. ³¹P ¹H NMR (162 MHz, CD₂Cl₂): δ (ppm) 65.09. ¹⁹F ¹H NMR (376 MHz, CD₂Cl₂): δ (ppm) -62.95. ¹¹B ¹H NMR (128 MHz, CD₂Cl₂): δ (ppm) -6.67.
MALDI$^+$: $m/z$ calcd for $\text{C}_{66}\text{H}_{95}\text{Au}_2\text{P}_2^+$: 1343.6235, found: 1343.5751. Structure confirmed by X-ray crystallography: CCDC 953710.
3. General Procedure for the Preparation of Cyclobutenes

Alkyne and alkene (2 equiv) were dissolved in dichloromethane (0.48 M) and the cationic gold (I) catalyst (3 mol%) was added. The reaction mixture was stirred at room temperature until no alkyne was observed by TLC. The reaction was quenched by adding a drop of a solution of Et₃N in cyclohexane (1M) and the solvent was removed. Preparative TLC was used to purify the resulting cyclobutenes.

1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3g)

Cyclobutene 3g was synthetized following the general procedure starting from 1-ethynyl-3-methoxybenzene (1g) (21 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 8 h and a mixture of pentane and diethyl ether (9:1) was used as eluent in the separation to obtain 33 mg (0.132 mmol) of 3g as a colorless oil in 78% yield.

1H NMR (500 MHz, CDCl₃) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.25 (td, J = 7.2, 1.4 Hz, 1H), 7.05 (dt, J = 7.7, 1.2 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.87 (dd, J = 7.8, 3.2 Hz, 1H), 6.78 (s, 1H), 3.87 (s, 3H), 3.02 (d, J = 12.7 Hz, 1H), 2.95 (d, J = 12.5 Hz, 1H), 1.68 (s, 3H). 13C NMR (126 MHz, CDCl₃) δ 159.83, 147.74, 143.86, 136.25, 134.28, 129.51, 128.26, 125.98, 125.83, 117.37, 113.77, 109.98, 55.37, 46.08, 44.46, 27.68. HRMS-APCI m/z calculated for C₁₈H₁₈O [M+H]⁺ 251.1430, found 251.1434.

1-Fluoro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3j)

Cyclobutene 3j was synthetized following the general procedure starting from 1-ethynyl-3-fluorobenzene (1j) (21 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl,
0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 31 mg (0.130 mmol) of 3j as a yellowish oil in 77% yield.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.40 - 7.35 (m, 2H), 7.34 - 7.29 (m, 2H), 7.29 - 7.24 (m, 1H), 7.21 - 7.17 (m, 1H), 7.14 (dt, J = 7.7, 1.2 Hz, 1H), 7.05 (ddd, J = 9.8, 2.6, 1.5 Hz, 1H), 6.94 (tdd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.75 (s, 1H), 2.95 (d, J = 12.6 Hz, 1H), 2.88 (d, J = 12.5 Hz, 1H), 1.62 (s, 1H). \]

\[ ^13C \text{ NMR (126 MHz, CDCl}_3 \delta 163.17 (d, J = 245.8 Hz), 147.45, 142.97 (d, J = 2.5 Hz), 137.09 (d, J = 7.6 Hz), 135.39, 129.99 (d, J = 8.3 Hz), 128.32, 125.96, 125.94, 120.48 (d, J = 2.8 Hz), 114.77 (d, J = 21.4 Hz), 111.51 (d, J = 21.4 Hz), 46.29, 44.34, 27.68. \]

HRMS-APCI m/z calculated for C_{17}H_{15}F [M+H]^+ 239.1234, found 239.1231.

1-Chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3k)

Cyclobutene 3k was synthetized following the general procedure starting from 1-ethynyl-3-chlorobenzene (1k) (21 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 36 mg (0.141 mmol) of 3k as a yellowish oil in 83% yield.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.40 - 7.35 (m, 3H), 7.35 - 7.30 (m, 2H), 7.27 - 7.17 (m, 4H), 6.77 (s, 1H), 2.96 (d, J = 12.5 Hz, 1H), 2.89 (d, J = 12.5 Hz, 1H), 1.63 (s, 3H). \]

\[ ^13C \text{ NMR (126 MHz, CDCl}_3 \delta 147.39 , 142.74 , 136.61 , 135.57 , 134.55 , 129.74 , 128.32 , 127.87 , 125.94 , 124.90 , 122.86 , 46.35 , 44.31 , 27.66. \]

HRMS-APCI m/z calculated for C_{17}H_{15}Cl [M+H]^+ 255.0935, found 255.0935.

1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3l)

1-Chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3k)

Cyclobutene 3k was synthetized following the general procedure starting from 1-ethynyl-3-chlorobenzene (1k) (21 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 36 mg (0.141 mmol) of 3k as a yellowish oil in 83% yield.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.40 - 7.35 (m, 3H), 7.35 - 7.30 (m, 2H), 7.27 - 7.17 (m, 4H), 6.77 (s, 1H), 2.96 (d, J = 12.5 Hz, 1H), 2.89 (d, J = 12.5 Hz, 1H), 1.63 (s, 3H). \]

\[ ^13C \text{ NMR (126 MHz, CDCl}_3 \delta 147.39 , 142.74 , 136.61 , 135.57 , 134.55 , 129.74 , 128.32 , 127.87 , 125.94 , 124.90 , 122.86 , 46.35 , 44.31 , 27.66. \]

HRMS-APCI m/z calculated for C_{17}H_{15}Cl [M+H]^+ 255.0935, found 255.0935.

1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3l)
Cyclobutene 3l was synthetized following the general procedure starting from 1-ethynyl-2-methoxybenzene (1l) (22 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 48 h and a mixture of pentane and diethyl ether (9:1) was used as eluent in the separation to obtain 11 mg (0.044 mmol) of 3l as a colorless oil in 24% yield.

\[ ^1H \text{NMR (300 MHz, CDCl}_3\] \( \delta \) 7.47 – 7.39 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.14 (m, 3H), 6.98 – 6.86 (m, 2H), 6.80 (s, 1H), 3.92 (s, 3H), 3.03 (d, \( J = 12.4 \text{ Hz}, 1H), 2.95 (d, \( J = 12.3 \text{ Hz}, 1H), 1.65 (s, 3H). \]

\[ ^13C \text{NMR (75 MHz, CDCl}_3\] \( \delta \) 158.63, 148.22, 140.29, 138.70, 128.91, 128.19, 127.15, 126.04, 125.65, 123.58, 120.34, 110.50, 55.29, 46.88, 45.40, 27.86. HRMS-APCI m/z calculated for C\(_{18}\)H\(_{18}\)O [M+H]\(^+\) 251.1430, found 251.1433.

**3-(3-Methyl-3-phenylcyclobut-1-en-1-yl)thiophene (3m)**

![3-(3-Methyl-3-phenylcyclobut-1-en-1-yl)thiophene (3m)](image)

Cyclobutene 3m was synthetized following the general procedure starting from 3-ethynylthiophene (1m) (17 µl, 0.169 mmol) and α-methylstyrene (2a) (44 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 24 h and a mixture of pentane and diethyl ether (90:1) was used as eluent in the separation to obtain 33 mg (0.146 mmol) of 3m as a brownish oil in 86% yield.

\[ ^1H \text{NMR (500 MHz, CDCl}_3\] \( \delta \) 7.43 – 7.39 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 (dd, \( J = 5.0, 2.9 \text{ Hz}, 1H), 7.23 – 7.19 (m, 2H), 7.17 (dd, \( J = 3.0, 1.2 \text{ Hz}, 1H), 6.51 (s, 1H), 2.97 (d, \( J = 12.5 \text{ Hz}, 1H), 2.91 (d, \( J = 12.4 \text{ Hz}, 1H), 1.65 (s, 3H). \]

\[ ^13C \text{NMR (126 MHz, CDCl}_3\] \( \delta \) 147.83, 139.38, 137.87, 132.74, 128.25, 126.04, 125.95, 125.82, 125.13, 121.14, 47.17, 45.20, 27.75z. HRMS-APCI m/z calculated for C\(_{15}\)H\(_{14}\)S [M+H]\(^+\) 239.0889, found 239.0896.

**Triisopropyl((1-methyl-3-phenylcyclobut-2-en-1-yl)methyl)silane (3q)**

![Triisopropyl((1-methyl-3-phenylcyclobut-2-en-1-yl)methyl)silane (3q)](image)
Cyclobutene 3q was synthetized following the general procedure starting from phenylacetylene (1a) (19 µl, 0.169 mmol) and allyltriisopropylsilane (2d) (81 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane 100% was used as eluent in the separation. 3q was isolated as a colorless oil.

\[ ^1H \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.38 \text{ – 7.28 (m, 4H), 7.25 – 7.20 (m, 1H), 6.39 (d, } J = 1.1 \text{ Hz, 1H), 3.07 – 2.94 (m, 2H), 2.31 (dd, } J = 12.4, 1.4 \text{ Hz, 1H), 1.08 (s, 23H).} \]

\[ ^13C \text{NMR (101 MHz, Chloroform-}d\text{)} \delta 143.85, 135.24, 133.78, 128.41, 127.54, 124.48, 38.60, 35.50, 19.04, 15.31, 11.41. \]

HRMS-APCI m/z calculated for C_{20}H_{32}Si [M+H]^+ 301.2346, found 301.2352.

\[ ((1\text{-methyl-3-phenylcyclobut-2-en-1-yl)methoxy} \text{triphenylsilane (3s)}) \]

\[ \text{Cyclobutene } 3r \text{ was synthetized following the general procedure starting from phenylacetylene (1a) (19 µl, 0.169 mmol) and ((2-methylallyl)oxy)benzene (2e) (52 µl, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane and diethyl ether (20:1) was used as eluent in the separation in a preparative TLC in Alumina oxide. 3r was isolated as a colorless oil.} \]

\[ ^1H \text{NMR (500 MHz, Chloroform-}d\text{)} \delta 7.39 \text{ – 7.36 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 6.96 – 6.91 (m, 3H), 6.47 (s, 1H), 3.98 (d, } J = 8.7 \text{ Hz, 1H), 3.95 (d, } J = 8.7 \text{ Hz, 1H), 2.74 (d, } J = 12.8 \text{ Hz, 1H), 2.56 (d, } J = 12.8 \text{ Hz, 1H), 1.42 (s, 3H).} \]

\[ ^13C \text{NMR (126 MHz, Chloroform-}d\text{)} \delta 159.62, 144.31, 134.84, 132.96, 129.52, 128.47, 128.00, 124.70, 120.66, 114.79, 75.46, 42.91, 38.91, 21.79. \]

HRMS-APCI m/z calculated for C_{18}H_{18}O [M+H]^+ 251.1426, found 251.1430.
Cyclobutene 3\textit{s} was synthetized following the general procedure starting from phenylacetylene (1\textit{a}) (19 µl, 0.169 mmol) and ((2-methylallyl)oxy)triphenylsilane (2\textit{f}) (112 mg, 0.338 mmol) with catalyst A2 (7.7 mg, 0.05 mmol). The reaction time was 72 h and a mixture of pentane and diethyl ether (20:1) was used as eluent in the separation in a preparative TLC in Alumina oxide. 3\textit{s} was isolated as a colorless oil.

$^1$H NMR (300 MHz, Chloroform-\textit{d}) $\delta$ 7.68 – 7.57 (m, 7H), 7.46 – 7.28 (m, 14H), 6.29 (s, 1H), 3.80 (s, 2H), 2.61 (d, $J =$ 12.7 Hz, 1H), 2.40 (d, $J =$ 12.7 Hz, 1H), 1.30 (s, 3H). $^{13}$C NMR (75 MHz, Chloroform-\textit{d}) $\delta$ 143.92, 135.60, 135.07, 134.60, 133.51, 130.07, 128.39, 127.94, 127.73, 124.62, 71.07, 44.64, 38.30, 21.51. HRMS-APCI m/z calculated for C$_{30}$H$_{28}$OSi [M+H]$^+$ 433.1982, found 433.1984.
4. Procedure for the Macrocyclization Reaction

To a solution of the 1,n-enyne (0.263 mmol) in CH₂Cl₂ (0.007 M) gold(I) complex (0.00789 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with 0.05 ml of triethylamine and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC.

5. General Procedure for the Preparation of [3.2.1]Oxabicycles

Alkyne (3.5 equiv) and oxoalkene were dissolved in 1,2-dichloroethane (0.50 M) and the cationic gold (I) catalyst (5 mol%) was added. The reaction mixture was stirred at 50 ºC untill no oxoalkene was observed by TLC. Then, the mixture was quenched by adding a drop of of Et₃N and the solvent was removed. Preparative TLC was used to purify the [3.2.1]oxabicycle product.
6. Mechanistic Study

Order of reagents

Figure S1. $^1$H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of $\alpha$-methylstyrene (0.50 mmol) and changing quantities of phenylacetylene with catalyst A2 (7.2 $\mu$mol) in CD$_2$Cl$_2$ (0.56 ml) at room temperature and using diphenylmethane as internal standard.

Figure S2. $^1$H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and changing quantities of $\alpha$-methylstyrene with catalyst A2 (7.2 $\mu$mol) in CD$_2$Cl$_2$ (0.56 mL) at room temperature and using diphenylmethane as internal standard.
Figure S3. $^1$H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and $\alpha$-methylstyrene (0.50 mmol) with changing quantities of catalyst A2 in CD$_2$Cl$_2$ (0.56 ml) at room temperature and using diphenylmethane as internal standard.

Figure S4. According to the method of the initial rates, it is possible to determine the order of the reagents by the logarithmic graph of the initial formation of the product and the concentration of the varying reagent.
Kinetics

Figure S5. $^1$H NMR monitoring of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene (0.25 mmol) and $\alpha$-methylstyrene (2 equivalents) with [LAuNCMe]X (3 mol\%, L = tBuXPhos) in CD$_2$Cl$_2$ (0.55 ml) at room temperature and using diphenylmethane as internal standard (0.5 equivalents). Spectra recorded every 10 min during 10 h and then at 15 h.

Figure S6. Initial $^{31}$P NMR spectrum of the intermolecular gold(I)-catalyzed [2+2] cycloaddition of phenylacetylene and $\alpha$-methylstyrene with A2 (3 mol\%) in CD$_2$Cl$_2$ and at room temperature shown in Figure S5.
Equilibrium Constants

The equilibrium constants between catalysts A1 and A2 and their related digold and alkene complexes were determined using the van't Hoff equation. Therefore, several samples (substrate:sample $0.5\text{ M} = 1:2$, $1:1$, $2:1$, $3.5:1$ and $5:1$) in CD$_2$Cl$_2$ (0.5 ml) were analysed immediately from $263\text{ to }278\text{, to }293\text{ and to }308\text{K}$ by $^1\text{H}$ and $^{31}\text{P}$ NMR.

Figure S7. Correlation between the equilibrium constant of A1 and the digold complex with the temperature was already reported ($\Delta H^\circ>0$).\textsuperscript{5}

![Figure S7](image)

Figure S8. Correlation between the equilibrium constant of A1 and the alkene complex with the temperature ($\Delta H^\circ<0$).

\[ LAuNCMe^+ + \begin{array}{c} \text{Ph} \\ \end{array} \rightleftharpoons LAu^+ + MeCN + \begin{array}{c} \text{Ph} \\ \end{array} \]

\[ K_{eq} = \frac{[15] \cdot [MeCN]}{[A] \cdot [Alkene]} = \frac{[15]^2}{([A]_0 - [15]) \cdot ([Alkene]_0 - [15])} \]

Integrals ratio $= \frac{[15]}{([A]_0 - [15])}$

| Substrate:sample | 263 K | 278 K | 293 K | 308 K |
|------------------|-------|-------|-------|-------|
| 1:2              | 5.93  | 5.96  | 6.41  | 6.90  |
| 1:1              | 4.01  |       | 4.77  | 5.91  |
| 2:1              | 2.76  | 2.78  | 2.77  | 3.63  |
Figure S9. Correlation between the equilibrium constant of A2 and the digold complex with the temperature ($\Delta H^\circ$>0).

\[
\begin{align*}
\text{LAuNCMe}^+ + \text{Ph} & \rightleftharpoons \text{LAu}^+ + \text{MeCN} \\
\text{LAu}^+ + \text{Ph} & \rightleftharpoons \text{Ph} + \text{Au}^+ + \text{H}^+
\end{align*}
\]

\[
\text{Keq} = \frac{[9] \cdot [H^+] \cdot [\text{MeCN}]^2}{[A]^2 \cdot [\text{Alkyne}]} = \frac{4 \cdot [9]^4}{([A]_0 - 2 \cdot [9])^2 \cdot ([\text{Alkyne}] - [9])}
\]

\[
\text{Integrals ratio} = \frac{[9]}{([A]_0 - 2 \cdot [9])}
\]

| Substrate:sample | 263 K | 278 K | 293 K | 308 K |
|------------------|------|------|------|------|
| 1:2              | 160.29 | 103.04 | 86.90 | 56.60 |
Figure S10. Correlation between the equilibrium constant of A1 and the alkene complex with the temperature ($\Delta H^\circ < 0$).

| Substrate:sample | 263 K | 278 K | 293 K | 308 K |
|------------------|-------|-------|-------|-------|
| 1:2              | 4.84  | 4.90  | 4.97  | 5.05  |
| 1:1              | 3.01  | 3.03  | 3.32  | 3.53  |
| 2:1              | 1.85  | 1.98  | 2.04  | 2.19  |
| 3.5:1            | 1.32  | 1.36  | 1.46  | 1.57  |
| 5:1              | 0.98  | 1.06  | 1.12  | 1.32  |
\[
y = 518.25x - 4.1513
\]

\[
R^2 = 0.96362
\]
Low temperature NMR experiments

Figure S11. $^{31}$P NMR spectrum of a mixture of phenylacetylene and complex A1 (10:1) in CD$_2$Cl$_2$ from 213 – 298 K already reported.$^5$

Figure S12. $^{31}$P NMR spectrum of a mixture of phenylacetylene and 25 mg of complex A2 (10:1) in CD$_2$Cl$_2$ (0.5 ml) from 213 – 298 K.
**Electron density Surfaces**

Total SCF density mapped with ESP ($r = 0.03 \text{ e/Å}^3$). Structures calculated with Gaussian 09 using M06 with 6-31G(d) (C, H, P, B, F) and SDD (Au, Sb) in CH$_2$Cl$_2$.

*Figure S13.* (tBuXPhosAu($\eta^2$-phenylacetylene)SbF$_6$ (8a).

*Figure S14.* (tBuXPhosAu($\eta^2$-phenylacetylene)BAr$_4$F$^-$ (8b).
Additional Experiments

We also performed some additional catalytic tests to exclude any other mechanistic pathways. We started reacting the isolable intermediates stoichiometrically with \( \alpha \)-methylstyrene and none of them reacted at all.

Scheme S1. Stoichiometric reaction between 16 or 9b and \( \alpha \)-methylstyrene under the optimized conditions (L = \( \text{tBuXPhos} \)).
Scheme S2. Intermolecular gold(I)-catalyzed reaction between phenylacetylene and α-methylstyrene with 16 or 9b under the optimized conditions (L = tBuXPhos).

\[
\text{Ph} = \text{Ph} + \text{Me} \xrightarrow{\text{LAu}^+\text{Ph}} \text{Ph} \quad \text{No reaction}
\]

DCM, r.t. 8 h (3 mol%)

\[
\text{Ph} = \text{Ph} + \text{Me} \xrightarrow{\text{LAu}^+\text{Ph}} \text{Ph} \quad \text{(13 %)}
\]

DCM, r.t. 8 h (1.5 mol%)

\[
\text{Ph} = \text{Ph} + \text{Me} \xrightarrow{\text{LAu}^+\text{Ph}} \text{Ph} \quad \text{(13 %)}
\]

DCM, r.t. 8 h (1.5 mol%)

Scheme S3. Intermolecular gold(I)-catalyzed reaction between phenylacetylene and α-methylstyrene with 16 or 9a and substoichiometric amounts of HSbF$_6\cdot$6H$_2$O under the optimized conditions (L = tBuXPhos). The activity increases as a result of the reestablishment of the equilibrium to the monogold complex 8a.

\[
\text{Ph} = \text{Ph} + \text{Me} \xrightarrow{\text{LAu}^+\text{Ph}} \text{Ph} \quad \text{(75 %)}
\]

DCM, r.t. 8 h (3 mol%)

\[
\text{Ph} = \text{Ph} + \text{Me} \xrightarrow{\text{LAu}^+\text{Ph}} \text{Ph} \quad \text{(79 %)}
\]

DCM, r.t. 8 h (1.5 mol%)
Scheme S4. Intermolecular gold(I)-catalyzed reaction between 15b and 16 or phenylacetylene under the optimized conditions \((L = \text{tBuXPhos})\). We also tried to add other carbonucleophiles, for example, allyltrimethylsilane, indole, 1,3,5-trimethoxybenzene or 1,3-diphenylpropane-1,3-dione to the alkene using A2.

\[
\begin{align*}
&\text{Me, } \text{Ph} \quad \text{Ph} \\
&\text{Ph} \\
&\text{LAu}^{+}\text{BArF}_4^- \\
\end{align*}
\[
\begin{align*}
&\text{LAu}^{+}\text{Ph} \\
&\text{Ph} \\
&\text{DCM, r.t.} \\
&8 \text{ h} \\
\end{align*}
\]

No reaction

\[
\begin{align*}
&\text{Ph} \\
&\text{HNu} + \text{Me} \\
&\text{Ph} \\
&\text{LAu}^{+}\text{NCMe}^{+}\text{BArF}_4^- \\
&\text{DCM, r.t.} \\
&8 \text{ h} \\
&\text{(3 mol\%)} \\
\end{align*}
\]

No reaction

\[
\begin{align*}
&\text{Ph} \\
&\text{Me, } \text{Ph} \\
&\text{Ph} \\
&\text{LAu}^{+}\text{BArF}_4^- \\
\end{align*}
\[
\begin{align*}
&\text{Ph} \\
&\text{Ph} \\
&\text{DCM, r.t.} \\
&8 \text{ h} \\
\end{align*}
\]

(72 \%)
7. X-Ray Crystallographic Data

\[ [(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-\textit{tert}-butylphosphine](2-phenylethynyl)gold(I)] (16) 

![Crystal Structure Diagram](image)

Table S1. Crystal data and structure refinement for CCDC 953709.

| Property                                           | Value                      |
|----------------------------------------------------|----------------------------|
| Empirical formula                                  | \text{C}_{36}\text{H}_{50}\text{AuN}_{\text{P}}             |
| Formula weight                                     | 724.71                     |
| Temperature                                        | 100(2) K                   |
| Wavelength                                         | 0.71073 Å                  |
| Crystal system                                     | Triclinic                  |
| Space group                                        | P-1                        |
| Unit cell dimensions                               | 
| \(a\)                                             | 10.8245(8) Å               |
| \(b\)                                             | 12.6401(9) Å               |
| \(c\)                                             | 13.3697(10) Å              |
| \(a\) angle                                       | 101.506(2) °               |
| \(b\) angle                                       | 95.285(2) °                |
| \(g\) angle                                       | 112.126(2) °               |
| Volume                                             | 1632.1(2) Å³               |
| \(Z\)                                             | 2                          |
| Density (calculated)                               | 1.475 Mg/m³                |
| Absorption coefficient                             | 4.580 mm\(^{-1}\)          |
| \(F(000)\)                                        | 734                        |
| Crystal size                                       | 0.25 x 0.12 x 0.10 mm³     |
| Theta range for data collection                    | 1.80 to 30.39 °            |
| Index ranges                                       | -14 <= \(h\) <= 13, -14 <= \(k\) <= 17, -17 <= \(l\) <= 17 |
| Reflections collected                              | 26200                      |
| Independent reflections                            | 8605 [R(int) = 0.0279 ]    |
| Completeness to theta =30.39 °                      | 87.1%                      |
| Absorption correction                              | Empirical                  |
| Max. and min. transmission                         | 0.6573 and 0.3939          |
| Refinement method                                  | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters                     | 8605 / 0 / 364             |
Goodness-of-fit on F²  
Final R indices [I>2sigma(I)]  
R indices (all data)  
Largest diff. peak and hole

1.039  
R1 = 0.0196 , wR2 = 0.0483  
R1 = 0.0213 , wR2 = 0.0490  
1.618 and -1.437 e.Å⁻³

(α-Methylstyrene)((2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)di-tert-
butylphosphine|gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)

Table 2. Crystal data and structure refinement for CCDC 953708.

| Property                              | Value                                |
|---------------------------------------|--------------------------------------|
| Empirical formula                     | C70 H67 Au B F24 P                   |
| Formula weight                        | 1602.98                              |
| Temperature                           | 100(2) K                             |
| Wavelength                            | 0.71073 Å                            |
| Crystal system                        | Monoclinic                           |
| Space group                           | P2(1)/n                              |
| Unit cell dimensions                  | a = 12.876(11) Å, b = 14.771(3) Å, c = 36.339(8) Å |
|                                       | a= 90.00 °, b = 90.39(2) °, g = 90.00 °. |
| Volume                                | 6911(6) Å                            |
| Z                                      | 4                                    |
| Density (calculated)                  | 1.541 Mg/m³                          |
| Absorption coefficient                | 2.257 mm⁻¹                           |
| F(000)                                | 3208                                 |
| Crystal size                          | 0.20 x 0.20 x 0.20 mm³               |
| Theta range for data collection       | 2.37 to 36.40 °.                     |
| Index ranges                          | -20 <=h<=21, 0 <=k<=24, 0 <=l<=59    |
Reflections collected

Independent reflections

Completeness to theta =36.40 °

Absorption correction

Max. and min. transmission

Refinement method

Data / restraints / parameters

Goodness-of-fit on F^2

Final R indices [I>2sigma(I)]

R indices (all data)

Largest diff. peak and hole

\{Phenylethynyl\[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]\gold(I)\}

\[(2´,4´,6´-triisopropyl-1,1´-biphenyl-2-yl)di-tert-butylphosphine]\gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)

Table S3. Crystal data and structure refinement for CCDC 953710.

| Property                      | Value                  |
|-------------------------------|------------------------|
| Empirical formula             | C98.25 H108.50 Au2 B Cl0.50 F24 P2 |
| Formula weight                | 2229.76                |
| Temperature                   | 100(2) K               |
| Wavelength                    | 0.71073 Å              |
Crystal system: Triclinic
Space group: P-1
Unit cell dimensions:
- \(a = 12.7748(13) \text{ Å}\)
- \(b = 17.3827(17) \text{ Å}\)
- \(c = 22.973(2) \text{ Å}\)
- \(a = 107.801(3)^\circ\)
- \(b = 95.994(4)^\circ\)
- \(g = 93.979(3)^\circ\)
Volume: \(4802.8(8) \text{ Å}^3\)
Z: 2
Density (calculated): 1.542 Mg/m³
Absorption coefficient: 3.190 mm⁻¹
\(F(000)\): 2231
Crystal size: 0.20 x 0.12 x 0.02 mm³
Theta range for data collection: 0.94 to 26.48°
Index ranges:
- \(-15 \leq h \leq 15\)
- \(-21 \leq k \leq 21\)
- \(-28 \leq l \leq 28\)
Reflections collected: 138270
Independent reflections: 19731 [R(int) = 0.0485]
Completeness to theta =26.48°: 99.4%
Absorption correction: Empirical
Max. and min. transmission: 0.9390 and 0.5679
Refinement method: Full-matrix least-squares on \(F^2\)
Data / restraints / parameters: 19731 / 108 / 1263
Goodness-of-fit on \(F^2\): 1.046
Final R indices [I>2sigma(I)]:
- \(R1 = 0.0275\)
- \(wR2 = 0.0615\)
R indices (all data):
- \(R1 = 0.0397\)
- \(wR2 = 0.0670\)
Largest diff. peak and hole: 1.871 and -0.734 e./Å³
8. NMR Spectra

(Acetonitrile)(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine|gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (A2)
(Acetonitrile)(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylyphosphine|gold(I) tetrafluoroborate (A3)
(Acetonitrile)[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I) hexafluorophosphate (A4)
[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine](2-phenylethynyl)gold(I) (16)
(α-Methylstyrene)[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (15b)
{Phenylethynyl[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I)}

[(2',4',6'-triisopropyl-1,1'-biphenyl-2-yl)di-tert-butylphosphine]gold(I)
tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (9b)

\[ ^{+} \text{BAR}_{4}^{F^-} \]
Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3g)
1-Fluoro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3j)
1-Chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3k)
1-Methoxy-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (3l)
3-(3-Methyl-3-phenylcyclobut-1-en-1-yl)thiophene (3m)
Triisopropyl((1-methyl-3-phenylcyclobut-2-en-1-yl)methyl)silane (3q)
(3-Methyl-3-(phenoxyethyl)cyclobut-1-en-1-yl)benzene (3r)
((1-methyl-3-phenylcyclobut-2-en-1-yl)methoxy)triphenylsilane (3s)
9. DFT's Data

Calculations were carried out with DFT using the M06 functional\(^6\) as implemented in Gaussian 09.\(^7\) The 6-31G(d) basis set\(^8\) was used for all atoms except gold and antimony, which were treated with SDD and the associated effective core potential.\(^9\) Frequency calculations were performed to characterize the stationary points as minima. The solvent effect was taken into account by single-point calculations using the polarizable continuum model (PCM),\(^10, 11, 12, 13\) in particular IEF-PCM as implemented in Gaussian 09. Default options were used, except that individual spheres were placed on all hydrogen atoms to get a more accurate cavity. The calculations were performed using CH\(_2\)Cl\(_2\) (\(\varepsilon = 8.93\)) as solvent. The standard Gibbs energies in dichloromethane (\(\Delta G_{\text{DCM}}\)) were obtained by adding the solvation energies to the gas phase Gibbs energies computed at 298 K. The same procedure was employed to calculate zero-point corrected energies in CH2Cl2.

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Table S4. \( t\text{BuXPhosAu}(\eta^2\text{-phenylacetylene})\text{SbF}_6\) complex 8a.

![Diagram of the complex](image)

| Center Number | Atomic Number | Cartesian Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|----------------------------------|-------|-------|-------|
| 1             | 15            | -1.422089 -2.087430 -0.406163     |       |       |       |
| 2             | 6             | 0.178809 -2.717519 -1.210447      |       |       |       |
| 3             | 6             | -2.315312 -3.445661 0.587625      |       |       |       |
| 4             | 79            | -0.943476 -0.292388 1.039915      |       |       |       |
| 5             | 6             | 1.395771 -1.236041 4.094960       |       |       |       |
| 6             | 6             | 2.476061 -2.083819 4.289297       |       |       |       |
| 7             | 6             | 3.632799 -1.930782 3.521641       |       |       |       |
| 8             | 6             | 3.722800 -0.923044 2.564055       |       |       |       |
| 9             | 6             | 2.653997 -0.059505 2.371179       |       |       |       |
| 10            | 6             | 1.487414 -0.218565 3.131894       |       |       |       |
| 11            | 1             | 0.478428 -1.352080 4.670298       |       |       |       |
| 12            | 1             | 2.415871 -2.873741 5.034892       |       |       |       |
| 13            | 1             | 4.468896 -2.611566 3.670334       |       |       |       |
| 14            | 1             | 4.606758 -0.815782 1.938790       |       |       |       |
| 15            | 1             | 2.713905 0.719084 1.614445        |       |       |       |
| 16            | 6             | 0.372543 0.619682 2.843818        |       |       |       |
| 17            | 6             | -0.578118 1.336872 2.511143       |       |       |       |
| 18            | 1             | -1.250210 2.179512 2.482791       |       |       |       |
| 19            | 6             | -2.521079 -1.508618 -1.757237     |       |       |       |
| 20            | 6             | -2.942910 -2.458642 -2.701747     |       |       |       |
| 21            | 6             | -2.929185 -0.160041 -1.913783     |       |       |       |
| 22            | 6             | -3.710865 -2.111878 -3.804066     |       |       |       |
| 23            | 1             | -2.670454 -3.504659 -2.572889     |       |       |       |
| 24            | 6             | -3.686360 0.165755 -3.048736      |       |       |       |
| 25            | 6             | -4.069048 -0.782332 -3.987926     |       |       |       |
| 26            | 1             | -4.021493 -2.876278 -4.512846     |       |       |       |
| 27            | 1             | -3.995633 1.203495 -3.177013      |       |       |       |
| 28            | 1             | -4.659754 -0.483181 -4.851463     |       |       |       |
| 29            | 6             | -2.207064 -4.857154 0.012100      |       |       |       |
| 30            | 1             | -2.837262 -5.519614 0.623347      |       |       |       |
| 31            | 1             | -2.569657 -4.934737 -1.020190     |       |       |       |
| 32            | 1             | -1.186320 -5.255319 0.060004      |       |       |       |
| 33            | 6             | -1.731936 -3.455204 2.006044      |       |       |       |
| 34            | 1             | -0.648582 -3.630968 2.021887      |       |       |       |
| 35            | 1             | -1.929286 -2.511627 2.534066      |       |       |       |
| 36            | 1             | -2.209893 -4.265366 2.576326      |       |       |       |
| 37            | 6             | -3.790507 -3.061358 0.676080      |       |       |       |
|   |   |          |          |          |
|---|---|----------|----------|----------|
| 38| 1 | -4.296538| -3.764915| 1.352881 |
| 39| 1 | -3.924961| -2.053866| 1.089104 |
| 40| 1 | -4.294554| -3.109209| -0.298016|
| 41| 6 | 0.012396 | -3.843504| -2.231236|
| 42| 1 | 1.013628 | -4.103974| -2.603638|
| 43| 1 | -0.427729| -4.756061| -1.819504|
| 44| 1 | -0.577633| -3.525609| -3.099561|
| 45| 6 | 1.121940 | -3.164539| -0.091453|
| 46| 1 | 2.108412 | -3.373523| -0.529670|
| 47| 1 | 1.263171 | -2.384428| 0.671898 |
| 48| 1 | 0.782432 | -4.084595| 0.402380 |
| 49| 6 | 0.800560 | -1.530728| -1.941707|
| 50| 1 | 0.996365 | -0.682804| -1.276899|
| 51| 1 | 1.772654 | -1.841260| -2.350582|
| 52| 1 | 0.175829 | -1.200321| -2.782974|
| 53| 6 | -2.732826| 0.990198 | -0.961387|
| 54| 6 | -3.752055| 1.274863 | -0.022731|
| 55| 6 | -1.683198| 1.922320 | -1.142118|
| 56| 6 | -3.688261| 2.454369 | 0.722956 |
| 57| 6 | -1.667842| 3.084627 | -0.371356|
| 58| 6 | -2.657280| 3.376182 | 0.565478 |
| 59| 1 | -4.484595| 2.661317 | 1.438467 |
| 60| 1 | -0.855194| 3.801743 | -0.509693|
| 61| 6 | -0.590425| 1.722098 | -2.169257|
| 62| 1 | -0.655685| 0.687509 | -2.536201|
| 63| 6 | -2.613568| 4.688707 | 1.318162 |
| 64| 1 | -1.550090| 4.927528 | 1.490957 |
| 65| 6 | -3.315862| 4.651396 | 2.669455 |
| 66| 1 | -2.957929| 3.829624 | 3.305337 |
| 67| 1 | -3.147305| 5.592218 | 3.208310 |
| 68| 1 | -4.402896| 4.535367 | 2.553696 |
| 69| 6 | -3.205963| 5.798210 | 0.447231 |
| 70| 1 | -3.150128| 6.769435 | 0.956727 |
| 71| 1 | -2.679217| 5.882823 | -0.512046|
| 72| 1 | -4.263941| 5.586244 | 0.232854 |
| 73| 6 | 0.804760 | 1.930955 | -1.582795|
| 74| 1 | 0.929571 | 1.414150 | -0.617706|
| 75| 1 | 1.583386 | 1.552963 | -2.256434|
| 76| 1 | 1.016572 | 2.996283 | -1.413388|
| 77| 6 | -0.806861| 2.636186 | -3.375870|
| 78| 1 | -0.777328| 3.694160 | -3.078118|
| 79| 1 | -0.019419| 2.477086 | -4.124778|
| 80| 1 | -1.776795| 2.450164 | -3.856526|
| 81| 6 | -4.958583| 0.375415 | 0.157931 |
| 82| 1 | -4.740195| -0.591425| -0.318854|
| 83| 6 | -5.279072| 0.112976 | 1.628509 |
| 84| 1 | -5.690201| 1.005410 | 2.119980 |
| 85| 1 | -6.032370| -0.681361| 1.719203 |
| 86| 1 | -4.386530| -0.192047| 2.195156 |
| 87| 6 | -6.178952| 0.965784 | -0.550559 |
Table S5. \( t\text{BuXPhosAu}(\eta^2\text{-phenylacetylene})\text{BAR}_4^- \) complex 8b.

\[
\begin{array}{c}
\text{Center}\
\text{Atomic Number} \\
\text{Number} \\
\text{Cartesian Coordinates (Angstroms)} \\
X \quad Y \quad Z
\end{array}
\]

| Center Number | Atomic Number | X         | Y         | Z         |
|---------------|---------------|-----------|-----------|-----------|
| 1             | 15            | 3.641376  | 0.755852  | 1.739381  |
| 2             | 6             | 4.916324  | 1.995204  | 2.424096  |
| 3             | 6             | 1.848076  | 1.268603  | 2.087464  |
| 4             | 79            | 3.950976  | 0.645668  | -0.591248 |
| 5             | 6             | 3.784318  | 4.113133  | -2.484423 |
| 6             | 6             | 4.011281  | 5.445271  | -2.172235 |
| 7             | 6             | 5.279575  | 5.857811  | -1.766556 |
| 8             | 6             | 6.326712  | 4.940908  | -1.675916 |
| 9             | 6             | 6.109219  | 3.604323  | -1.978139 |
| 10            | 6             | 4.831427  | 3.185986  | -2.379969 |
| 11            | 1             | 2.801351  | 3.775331  | -2.803879 |
| 12            | 1             | 3.196793  | 6.162855  | -2.245709 |
| 13            | 1             | 5.455620  | 6.903334  | -1.521771 |
| 14            | 1             | 7.315097  | 5.270962  | -1.364086 |
| 15            | 1             | 6.914328  | 2.875095  | -1.900986 |
| 16            | 6             | 4.570481  | 1.805394  | -2.627195 |
| 17            | 6             | 4.329609  | 0.607196  | -2.800594 |
| 18            | 1             | 4.207555  | -0.353705 | -3.272789 |
| 19            | 6             | 3.963634  | -0.862643 | 2.556692  |
| 20            | 6             | 3.875641  | -0.903891 | 3.958845  |
| 21            | 6             | 4.331589  | -2.045996 | 1.868670  |
| 22            | 6             | 4.172136  | -2.047551 | 4.686718  |
| 23            | 1             | 3.575813  | -0.015903 | 4.508344  |
| 24            | 6             | 4.659037  | -3.176066 | 2.629729  |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 25 | 6 | 4.586886 | -3.190029 | 4.015366 |
| 26 | 1 | 4.086564 | -2.036865 | 5.770980 |
| 27 | 1 | 4.959224 | -4.079522 | 2.098446 |
| 28 | 1 | 4.842821 | -4.093881 | 4.564575 |
| 29 | 6 | 1.540690 | 1.609276 | 3.543081 |
| 30 | 1 | 0.480108 | 1.886354 | 3.613879 |
| 31 | 1 | 1.696768 | 0.762253 | 4.222365 |
| 32 | 1 | 2.114988 | 2.471529 | 3.903443 |
| 33 | 6 | 1.472820 | 2.465486 | 1.211921 |
| 34 | 1 | 1.987563 | 3.391321 | 1.490173 |
| 35 | 1 | 1.661735 | 0.762253 | 4.222365 |
| 36 | 1 | 0.391991 | 2.641005 | 1.333667 |
| 37 | 6 | 1.543079 | 1.609276 | 3.543081 |
| 38 | 1 | -0.072745 | 0.366362 | 1.733996 |
| 39 | 1 | 1.167293 | -0.162903 | 0.586082 |
| 40 | 1 | 1.152440 | -0.807351 | 2.253944 |
| 41 | 6 | 5.017016 | 2.069411 | 3.948653 |
| 42 | 1 | 5.700223 | 2.893347 | 4.200951 |
| 43 | 1 | 4.062303 | 2.278136 | 4.444497 |
| 44 | 1 | 5.443771 | 1.154961 | 4.375964 |
| 45 | 6 | 4.591415 | 3.387814 | 1.876945 |
| 46 | 1 | 5.459744 | 4.040123 | 2.051462 |
| 47 | 1 | 4.392970 | 3.388598 | 0.794322 |
| 48 | 1 | 3.737271 | 3.844304 | 2.391530 |
| 49 | 6 | 6.284199 | 1.569365 | 1.893030 |
| 50 | 1 | 6.332535 | 1.599401 | 0.796438 |
| 51 | 1 | 7.041504 | 2.266175 | 2.281029 |
| 52 | 1 | 6.561979 | 0.561233 | 2.229074 |
| 53 | 6 | 4.340109 | -2.281352 | 0.383114 |
| 54 | 6 | 3.200022 | -2.869277 | -0.216575 |
| 55 | 6 | 5.522384 | -2.131121 | -0.373623 |
| 56 | 6 | 3.251533 | -3.229267 | -1.563628 |
| 57 | 6 | 5.518501 | -2.504175 | -1.720642 |
| 58 | 6 | 4.392733 | -3.036589 | -2.341410 |
| 59 | 1 | 2.361391 | -3.657442 | -2.021349 |
| 60 | 1 | 6.432936 | -2.387410 | -2.306339 |
| 61 | 6 | 6.823333 | -1.671882 | 0.252355 |
| 62 | 1 | 6.590306 | -1.224151 | 1.229455 |
| 63 | 6 | 4.439518 | -3.458420 | -3.793625 |
| 64 | 1 | 5.371727 | -3.050717 | -4.220084 |
| 65 | 6 | 3.272116 | -2.916484 | -4.614685 |
| 66 | 1 | 3.186939 | -1.822486 | -4.554566 |
| 67 | 1 | 3.393996 | -3.185136 | -5.672046 |
| 68 | 1 | 2.313977 | -3.353310 | -4.278397 |
| 69 | 6 | 4.502854 | -4.981672 | -3.903353 |
| 70 | 1 | 4.592358 | -5.294923 | -4.952162 |
| 71 | 1 | 5.358981 | -5.387052 | -3.348719 |
| 72 | 1 | 3.589630 | -5.437625 | -3.494104 |
| 73 | 6 | 7.558163 | -0.623382 | -0.579589 |
| 74 | 1 | 6.895822 | 0.207924 | -0.865150 |

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|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 75 | 1 | 8.399949 | -0.208037 | -0.008796 |
| 76 | 1 | 7.970824 | -1.051907 | -1.503560 |
| 77 | 6 | 7.734952 | -2.872179 | 0.513150 |
| 78 | 1 | 7.984612 | -3.383008 | -0.427800 |
| 79 | 1 | 8.674674 | -2.550042 | 0.981983 |
| 80 | 1 | 7.257626 | -3.605545 | 1.176469 |
| 81 | 6 | 1.954025 | -2.872179 | 0.513150 |
| 82 | 1 | 1.969605 | -2.644236 | 1.516442 |
| 83 | 6 | 0.654621 | -2.876481 | -0.146845 |
| 84 | 1 | 0.470886 | -3.547154 | 0.998095 |
| 85 | 1 | -0.191968 | -2.993370 | 0.543031 |
| 86 | 1 | 0.648428 | -1.848483 | 1.176469 |
| 87 | 6 | 1.948775 | -4.700265 | 0.948795 |
| 88 | 1 | 1.941811 | -5.324211 | 0.043144 |
| 89 | 1 | 1.941811 | -5.324211 | 0.043144 |
| 90 | 1 | 2.826871 | -4.981884 | 1.534044 |
| 91 | 5 | -3.570401 | 0.020412 | -0.032033 |
| 92 | 6 | -4.243384 | -1.312157 | -2.503560 |
| 93 | 6 | -4.341034 | -1.477500 | -2.089673 |
| 94 | 6 | -4.903964 | -2.277345 | 0.068836 |
| 95 | 6 | -5.028682 | -2.541744 | -2.669380 |
| 96 | 1 | -3.872576 | -0.747601 | -2.753700 |
| 97 | 6 | -5.590141 | -3.348094 | -0.501147 |
| 98 | 1 | -4.893747 | -2.196225 | 1.158019 |
| 99 | 6 | -5.656470 | -3.497658 | -1.880479 |
| 100 | 1 | -6.187636 | -4.331936 | -2.329514 |
| 101 | 6 | -4.806890 | 1.094873 | -0.003444 |
| 102 | 6 | -5.730068 | 1.143888 | 1.048543 |
| 103 | 6 | -5.095530 | 1.914822 | -1.102033 |
| 104 | 6 | -6.854588 | 1.967366 | 1.016560 |
| 105 | 1 | -5.574022 | 0.515550 | 1.928842 |
| 106 | 6 | -6.217727 | 2.738565 | -1.144214 |
| 107 | 1 | -4.426770 | 1.914017 | -1.965906 |
| 108 | 6 | -7.110707 | 2.780068 | -0.080604 |
| 109 | 1 | -7.984201 | 3.425254 | -0.110626 |
| 110 | 6 | -2.941562 | -0.259075 | 1.453357 |
| 111 | 6 | -2.829911 | 0.758855 | 2.405072 |
| 112 | 6 | -2.338674 | -1.482401 | 1.791186 |
| 113 | 6 | -2.177539 | 0.573327 | 3.625262 |
| 114 | 1 | -3.261099 | 1.740418 | 2.196325 |
| 115 | 6 | -1.693805 | -1.678274 | 3.008430 |
| 116 | 1 | -2.382347 | -2.308092 | 1.079658 |
| 117 | 6 | -1.608390 | -0.649843 | 3.944530 |
| 118 | 1 | -1.101413 | -0.803519 | 4.895283 |
| 119 | 6 | -2.287863 | 0.590156 | -0.877530 |
| 120 | 6 | -1.430420 | -0.239197 | -1.614398 |
| 121 | 6 | -1.917153 | 1.938595 | -0.797562 |
| 122 | 6 | -0.296743 | 0.256252 | -2.255239 |
| 123 | 1 | -1.659149 | -1.302133 | -1.703598 |
| 124 | 6 | -0.775248 | 2.440005 | -1.418935 |
|   |   |         |         |         |
|---|---|---------|---------|---------|
| 125 | 1 | -2.540625 | 2.628672 | -0.226981 |
| 126 | 6 | 0.046490  | 1.602493 | -2.163136 |
| 127 | 1 | 0.936707  | 1.982596 | -2.665728 |
| 128 | 6 | -5.045265 | -2.640231 | -4.161014 |
| 129 | 6 | -6.215547 | -4.348490 | 0.416754 |
| 130 | 6 | -7.768812 | 1.956275 | 2.199474 |
| 131 | 6 | -6.410794 | 3.609177 | -2.343936 |
| 132 | 6 | -1.024309 | -2.972262 | 3.346951 |
| 133 | 6 | -2.124187 | 1.729703 | 4.572409 |
| 134 | 6 | -0.488844 | 3.906864 | -1.348454 |
| 135 | 6 | 0.596572  | -0.633771 | -3.057949 |
| 136 | 9 | -8.235921 | 0.724035 | 2.451865 |
| 137 | 9 | -7.135073 | 2.354167 | 3.313907 |
| 138 | 9 | -8.829783 | 2.755891 | 2.042150 |
| 139 | 9 | -7.606139 | 4.210702 | -2.360216 |
| 140 | 9 | -5.481058 | 4.577233 | -2.399473 |
| 141 | 9 | -6.298567 | 2.913868 | -3.485245 |
| 142 | 9 | -5.464721 | -1.498918 | -4.727280 |
| 143 | 9 | -5.837959 | -3.620986 | -4.607845 |
| 144 | 9 | -3.816290 | -2.872822 | -4.650486 |
| 145 | 9 | -6.946286 | -5.262664 | -0.231004 |
| 146 | 9 | -5.284013 | -5.013578 | 1.119608 |
| 147 | 9 | -7.017766 | -3.761659 | 1.317497 |
| 148 | 9 | 0.318315  | -2.837345 | 3.375112 |
| 149 | 9 | -1.293084 | -3.948074 | 2.471697 |
| 150 | 9 | -1.377665 | -3.412972 | 4.560835 |
| 151 | 9 | -1.327007 | 1.500609 | 5.622374 |
| 152 | 9 | -1.662402 | 2.834488 | 3.958483 |
| 153 | 9 | -3.335313 | 2.040484 | 5.049565 |
| 154 | 9 | -1.122202 | 4.583832 | -2.315306 |
| 155 | 9 | 0.822176  | 4.174173 | -1.487148 |
| 156 | 9 | -0.873829 | 4.442459 | -0.183048 |
| 157 | 9 | 0.076851  | -1.843585 | -3.275060 |
| 158 | 9 | 0.892543  | -0.098360 | -4.251907 |
| 159 | 9 | 1.783494  | -0.826227 | -2.439653 |
Table S6. tBuXPhosAu(η²-phenylacetylene)BF₄ complex 8c.

![Chemical Structure](image)

| Center Number | Atomic Number | Cartesian Coordinates (Angstroms) |
|---------------|---------------|----------------------------------|
|               |               | X      | Y      | Z      |
| 1             | 15            | 0.297605 | 2.070894 | 0.125488 |
| 2             | 6             | 0.853979 | 2.670720 | 1.835029 |
| 3             | 6             | 1.266091 | 2.935933 | -1.274485 |
| 4             | 79            | 0.612061 | -0.252583 | -0.048170 |
| 5             | 6             | 3.493681 | -1.483878 | -2.613470 |
| 6             | 6             | 4.728711 | -1.006541 | -3.029487 |
| 7             | 6             | 5.720635 | -0.729273 | -2.089589 |
| 8             | 6             | 5.485089 | -0.935205 | -0.730636 |
| 9             | 6             | 4.256105 | -1.414639 | -0.299131 |
| 10            | 6             | 3.255849 | -1.686020 | -1.246031 |
| 11            | 1             | 2.703118 | -1.694202 | -3.32861 |
| 12            | 1             | 4.919279 | -0.845973 | -4.088539 |
| 13            | 1             | 6.686123 | -0.350859 | -2.420434 |
| 14            | 1             | 6.265233 | -0.720415 | -0.003258 |
| 15            | 1             | 4.035062 | -1.576178 | 0.755003 |
| 16            | 6             | 1.970935 | -2.116730 | -0.797532 |
| 17            | 6             | 0.858839 | -2.456490 | -0.391649 |
| 18            | 1             | 0.007146 | -3.031930 | -0.70778 |
| 19            | 6             | -1.477548 | 2.514134 | -0.096578 |
| 20            | 6             | -1.799524 | 3.881285 | -0.131296 |
| 21            | 6             | -2.513056 | 1.570198 | -0.299033 |
| 22            | 6             | -3.089747 | 4.334925 | -0.362088 |
| 23            | 1             | -1.018605 | 4.620891 | 0.023414 |
| 24            | 6             | -3.808927 | 2.054937 | -0.536258 |
| 25            | 6             | -4.104965 | 3.409904 | -0.570307 |
| 26            | 1             | -3.294764 | 5.403087 | -0.382066 |
| 27            | 1             | -4.604351 | 1.327121 | -0.699160 |
| 28            | 1             | -5.124850 | 3.738791 | -0.759736 |
| 29            | 6             | 1.585628 | 4.412577 | -1.032297 |
| 30            | 1             | 2.129164 | 4.786167 | -1.911459 |
| 31            | 1             | 0.689986 | 5.036232 | -0.927487 |
| 32            | 1             | 2.232577 | 4.578194 | -0.163281 |
| 33            | 6             | 2.582849 | 2.177015 | -1.483906 |
| 34            | 1             | 3.211055 | 2.148173 | -0.585981 |
| 35            | 1             | 2.409193 | 1.140576 | -1.807853 |
| 36            | 1             | 3.155220 | 2.682752 | -2.275789 |
| 37            | 6             | 0.449967 | 2.819334 | -2.561195 |
|    |   |          |          |          |
|----|---|----------|----------|----------|
| 38 | 1 | 1.054074 | 3.209837 | -3.393197 |
| 39 | 1 | 0.205833 | 1.775663 | -2.795180 |
| 40 | 1 | -0.482925 | 3.396405 | -2.526963 |
| 41 | 6 | 0.427422 | 4.094528 | 2.185138 |
| 42 | 1 | 0.823621 | 4.330665 | 3.183518 |
| 43 | 1 | 0.819903 | 4.849409 | 3.193600 |
| 44 | 1 | -0.663841 | 2.795180 | 2.326352 |
| 45 | 6 | 2.375208 | 2.542887 | 1.932558 |
| 46 | 1 | 2.663236 | 2.705885 | 2.981782 |
| 47 | 1 | 2.724284 | 1.540173 | 1.656804 |
| 48 | 1 | 2.903936 | 3.293902 | 1.333024 |
| 49 | 6 | 0.218622 | 1.714701 | 2.844422 |
| 50 | 1 | 2.816391 | 0.681128 | 2.712676 |
| 51 | 1 | 0.501643 | 2.036582 | 3.857993 |
| 52 | 1 | -0.877662 | 1.738006 | 2.788040 |
| 53 | 6 | -2.412925 | 0.071017 | -0.890202 |
| 54 | 6 | -2.272682 | -0.634910 | -1.504103 |
| 55 | 6 | -2.690626 | -0.648332 | 0.909900 |
| 56 | 6 | -2.393595 | -2.026590 | -1.504663 |
| 57 | 6 | -2.770651 | -2.033125 | 0.850161 |
| 58 | 6 | -2.635103 | -2.748324 | -0.334158 |
| 59 | 1 | -2.294445 | -2.559116 | -2.451664 |
| 60 | 1 | -2.982030 | -2.586965 | 1.767616 |
| 61 | 6 | -3.015586 | 0.063724 | 2.203110 |
| 62 | 1 | -2.673269 | 1.106233 | 2.120013 |
| 63 | 6 | -2.835628 | -4.248729 | -0.334158 |
| 64 | 1 | -2.436603 | -4.624836 | 0.623308 |
| 65 | 6 | -2.122869 | -4.980744 | -1.464334 |
| 66 | 1 | -1.052113 | -4.739551 | -1.513075 |
| 67 | 1 | -2.216381 | -6.065586 | -1.328187 |
| 68 | 1 | -2.565339 | -4.739537 | -2.441387 |
| 69 | 6 | -4.332846 | -4.562766 | -0.372049 |
| 70 | 1 | -4.508523 | -5.645838 | -0.324513 |
| 71 | 1 | -4.866611 | -4.921122 | 0.463225 |
| 72 | 1 | -4.772735 | -4.187293 | -1.308012 |
| 73 | 6 | -2.338606 | -0.561105 | 3.420752 |
| 74 | 1 | -1.265819 | -0.728248 | 3.261510 |
| 75 | 1 | -2.463993 | 0.094983 | 4.293221 |
| 76 | 1 | -2.794678 | -1.526954 | 3.680238 |
| 77 | 6 | -4.531399 | 0.106381 | 2.410091 |
| 78 | 1 | -4.941353 | -0.911553 | 2.481503 |
| 79 | 1 | -4.777905 | 0.633992 | 3.341631 |
| 80 | 1 | -5.042967 | 0.617956 | 1.584115 |
| 81 | 6 | -2.050059 | 0.069316 | -2.827597 |
| 82 | 1 | -1.861130 | 1.133211 | -2.621254 |
| 83 | 6 | -0.838562 | -0.480896 | -3.579446 |
| 84 | 1 | -0.993443 | -1.523122 | -3.891718 |
| 85 | 1 | -0.649057 | 0.108670 | -4.487368 |
| 86 | 1 | 0.068573 | -0.454264 | -2.955267 |
| 87 | 6 | -3.301715 | -0.007466 | -3.701619 |
|   |   |       |       |       |
|---|---|-------|-------|-------|
| 88| 1 | -3.147874 | 0.532025 | -4.645987 |
| 89| 1 | -3.547276 | -1.050248 | -3.947802 |
| 90| 1 | -4.172599 | 0.430706  | -3.196619 |
| 91| 5 | 2.089686  | -1.750394 | 2.933176  |
| 92| 9 | 2.189244  | -1.958502 | 4.299429  |
| 93| 9 | 0.723024  | -1.681238 | 2.567884  |
| 94| 9 | 2.705076  | -0.538250 | 2.584078  |
| 95| 9 | 2.704682  | -2.789610 | 2.232308  |
