Stereo- and Regioselective Alkyne Hydrometallation with Gold(III) Hydrides

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1. General considerations

When required, manipulations were performed using standard Schlenk techniques under dry nitrogen or a MBraun glove box. Nitrogen was purified by passing through columns of supported P2O5 with moisture indicator, and of activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. IR spectra were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer with a diamond ATR attachment. Elemental analyses were carried out at London Metropolitan University. 4-tert-Butylphenylboronic acid, [Pd(PPh3)4]2, K[AuCl4], (LH)AuCl, and (C^Npz^C)AuCl were prepared using literature methods. 4-tert-Butylpyridine (Aldrich), 2,6-dichloropyridine (Alfa Aesar), LiHBEt3 (1M solution in THF, Aldrich), and LiAlH4 (1M solution in THF, Aldrich), were used as purchased. Diphenylacetylene, 4-ethynylbenzaldehyde, 4-pentynoic acid, propargyl 4-bromobenzamide, TEMPO (Aldrich) and AIBN (BDH Chemicals) were evacuated and stored under N2 in the glovebox before use. Phenylacetylene, 1-phenyl-1-propyne, trimethylsilylacetylene, (tert-butyl)dimethylsilylacetylene, 1-hexyne, 3-hexyne, propargyl alcohol, and 1-phenyl-1-pentyn-3-ol (Aldrich) were freeze-pump-thaw degassed and stored on activated 4 Å molecular sieves before use. CDCl3, DMSO-d6, toluene-d8 and CD2Cl2 (Apollo Scientific) were degassed by three freeze-pump-thaw cycles and stored on activated 4 Å molecular sieves prior to use when required. 1H, 13C{1H} NMR spectra (75.47 MHz) were referenced to the D-coupled 13C resonances of the NMR solvent. The numbering scheme for the assignments is given in Scheme S3. For the photoisomerization experiments, a Blak-Ray B-100 Series high powered UV lamp from UVP was employed.

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2. Synthesis and characterization of precursors

2.1 Synthesis of ligand precursors

2,6-Dichloro-4-tert-butylpyridine (IV) was prepared starting from 4-tert-butylpyridine following a modification of published procedures. 5-8

![Scheme S1. Route to 2,6-dichloro-4-tert-butylpyridine (IV).]

4-tert-butylpyridine-N-oxide (I)

4-tert-Butylpyridine (27.0 mL, 25.0 g, 185.0 mmol) was mixed with glacial acetic acid (200 mL) and hydrogen peroxide (140 mL, 30% in water). The mixture was stirred at 80°C for 4h. Further H₂O₂ (140 mL) was added and the solution stirred at the same temperature overnight. The volume of the mixture was reduced to 150 mL, and the concentrate was neutralized with solid Na₂CO₃. The organic phase was extracted with dichloromethane. The combined organic layers were washed with water, dried over MgSO₄, and evaporated to dryness. A thick orange oil was obtained, which was used for the following step without further purification, yield 20.0 g (132.0 mmol, 71%). ¹H-NMR (300.13 MHz, CDCl₃): δ 8.44 (d, 2H, ³J = 7.2 Hz, o-H), 7.47 (d, 2H, ³J = 7.2 Hz, m-H), 1.42 ppm (s, 9H, tBu).

2-chloro-4-tert-butylpyridine (II)

2-chloro-4-tert-butylpyridine-N-oxide (20.0 g, 132.0 mmol) was dissolved in 60 mL of POCl₃, and the mixture was refluxed overnight under N₂. After removing the excess POCl₃ under reduced pressure, the remaining thick brownish solution was poured into ice water. The mixture was extracted with diethyl ether. The organic phase was dried over MgSO₄ and evaporated to dryness, leaving a brown oil which was used without further purification, yield 5.0 g (30.0 mmol, 23%). ¹H-NMR (300.13 MHz, CDCl₃): δ 8.29 (d, 1H, ³J = 5.3 Hz, o-H), 7.30 (d, 1H, ³J = 1.7 Hz, m-H), 7.21 (dd, 1H, ³J = 5.3 Hz, ⁴J = 1.7 Hz, m-H), 1.31 ppm (s, 9H, tBu).

2-Chloro-4-tert-butylpyridine-N-oxide (III)

A mixture of 2-chloro-4-tert-butylpyridine (12.0 g, 71.0 mmol), glacial acetic acid (100 mL) and hydrogen peroxide (80 mL, 30% in water) was stirred at 80°C for 4h. Further hydrogen peroxide (80 mL) was added, and stirring was continued at the same temperature overnight. The volume was reduced to 50 mL and the concentrate neutralized with solid Na₂CO₃. The organic phase was extracted with dichloromethane. The combined organic layers were washed with water, dried over MgSO₄, and evaporated to dryness. A yellow solid was
obtained, yield 10.0 g (54.0 mmol, 76%). $^1$H-NMR (300.13 MHz, CDCl$_3$): $\delta$ 8.31 (d, 1H, $^3J$ = 6.9 Hz, $\alpha$-H), 7.45 (d, 1H, $^4J$ = 2.7 Hz, $m$-H), 7.20 (dd, 1H, $^3J$ = 6.9 Hz, $^4J$ = 2.7 Hz, $m$-H), 1.31 ppm (s, 9H, tBu).

2,6-Dichloro-4-tert-butylpyridine (IV)

2-Chloro-4-tert-butylpyridine-N-oxide (4.8 g, 26.0 mmol) was slowly dissolved in 12 mL of POCl$_3$ at 0°C, and the mixture was refluxed overnight under N$_2$. After removing the excess POCl$_3$ under reduced pressure, the remaining thick brownish suspension was poured into ice water. The mixture was extracted with light petroleum. The organic phase was dried over MgSO$_4$ and evaporated to dryness, to yield a brown oil mixed with white crystals. The crude product was purified by column chromatography over silica (eluent: dichloromethane), affording white crystals, yield: 2.7 g (13.0 mmol, 50%). $^1$H-NMR (300.13 MHz, CDCl$_3$): $\delta$ 7.23 (s, 2H, $m$-H), 1.30 ppm (s, 9H, tBu).

2,6-Dichloro-4-methoxypyridine (VII) and 2,6-dichloro-4-dimethylaminopyridine (VIII)

2,4,6-Trichloropyridine was prepared from 2,6-dichloropyridine, by conversion into 2,6-dichloropyridine-N-oxide$^{11-13}$ followed by chlorination.$^{7,14}$ 2,6-Dichloro-4-methoxypyridine (VII) and 2,6-dichloro-4-dimethylaminopyridine (VIII) were synthesized from 2,4,6-trichloropyridine following published procedures, through the reaction with sodium methoxide$^9$ and dimethylamine,$^{10}$ respectively.

Scheme S2. Route to 2,6-dichloro-4-methoxypyridine (VII) and 2,6-dichloro-4-dimethylaminopyridine (VIII).

2,6-Dichloropyridine-N-oxide (V)

A mixture of 2,6-dichloropyridine (30.0 g, 203.0 mmol), trifluoroacetic acid (200 mL) and hydrogen peroxide (35 mL, 30% in water) was stirred at 100 °C for 5 h. The resulting solution was cooled to r.t. and poured into 750 mL of water, resulting in the precipitation of the unreacted 2,6-dichloropyridine, which was filtered off. The volume of the filtrate was reduced to 150 mL and the concentrate was neutralized with solid Na$_2$CO$_3$. The organic phase was extracted with dichloromethane. The combined organic layers were dried over MgSO$_4$, and evaporated to dryness. A white solid was obtained, yield 22.0 g (134.0 mmol,
he combined organic layer, whose content was 11.0 mmol, 50\% of the total content, was dried over MgSO\textsubscript{4}. The excess POCl\textsubscript{3} was removed by distillation under reduced pressure. The remaining thick brownish solution was poured into ice water. The mixture was extracted with light petroleum. The organic phase was dried over MgSO\textsubscript{4} and evaporated to dryness, to yield a low-melting white solid, yield 12.0 g (66.0 mmol, 73\%). \textsuperscript{1}H-NMR (300.13 MHz, CDCl\textsubscript{3}): \(\delta\) 7.31 ppm (s, 2H, \(m\)-H).

### 2,4,6-Trichloropyridine (VI)

2,6-Dichloropyridine-\(N\)-oxide (15.0 g, 91.0 mmol) was dissolved in 50 mL of POCl\textsubscript{3}, and the mixture was refluxed under N\(_2\) for 5 h. After removing the excess POCl\textsubscript{3} under reduced pressure, the remaining thick brownish solution was poured into ice water. The mixture was extracted with light petroleum. The organic phase was dried over MgSO\textsubscript{4} and evaporated to dryness, to yield a low-melting white solid, yield 12.0 g (66.0 mmol, 73\%). \textsuperscript{1}H-NMR (300.13 MHz, CDCl\textsubscript{3}): \(\delta\) 7.31 ppm (s, 2H, \(m\)-H).

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2.2 Synthesis of ligands H$_2$L$^R$ (R = ^1$Bu, OMe, NMe$_2$)

2,6-bis(4'-tert-butylphenyl)-4-tert-butylpyridine (H$_2$L$^{{^1}$Bu}), 2,6-bis(4'-tert-butylphenyl)-4-methoxypyridine (H$_2$L$^{OMe}$), and 2,6-bis(4'-tert-butylphenyl)-4-dimethylaminopyridine (H$_2$L$^{NMe_2}$) ligands were synthesized by Suzuki-Miyaura cross-coupling between the p-substituted-2,6-dichloropyridine precursors (IV, VI, and VII, respectively) and 4-tert-butylphenylboronic acid.

Scheme S3. General route to ligands and numbering scheme for $^1$H and $^{13}$C peak assignment.

General procedure for the synthesis of ligands

Under a N$_2$ atmosphere, the desired p-substituted-2,6-dichloropyridine precursor (1 equiv), 4-tert-butylphenylboronic acid (2.5 equiv), K$_3$PO$_4$ trihydrate (0.6 equiv), and [Pd(PPh$_3$)$_4$] (5mol%) were suspended in degassed isopropanol, and the resulting mixture was refluxed for 48 h. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography using dichloromethane as an eluent.

2,6-bis(4'-tert-butylphenyl)-4-tert-butylpyridine (H$_2$L$^{{^1}$Bu}). This compound was synthesized from 2,6-dichloro-4-tert-butylpyridine (2.0 g, 9.8 mmol), 4-tert-butylphenylboronic acid (4.3 g, 24.0 mmol), K$_3$PO$_4$ trihydrate (3.4 g, 15.0 mmol), and [Pd(PPh$_3$)$_4$] (0.11 g, 0.095 mmol) in 100 mL of isopropanol. A pale yellow solid was isolated, yield 2.4 g (6.0 mmol, 61%). $^1$H-NMR (300.13 MHz, CDCl$_3$): $\delta$ 8.00 (d, 4H, $^3$J = 8.5 Hz, H5), 7.59 (s, 2H, H2), 7.47 (d, 4H, $^3$J = 8.5 Hz, H6), 1.36 (s, 18H, tBu on py), 1.33 ppm (s, 18H, H11). $^{13}$C($^1$H)NMR (75.47 MHz, CDCl$_3$): $\delta$ 161.3 (s, C1), 157.1 (s, C7), 151.9 (s, C3), 137.5 (s, C4), 127.0 (s, C5), 125.7 (s, C6), 115.9 (s, C2), 35.1 (s, -CCH3 on py), 34.8 (s, C10), 31.5 (s C11), 30.8 ppm (s, -CCH3 on py). Anal. Calcd. (found) for C$_{29}$H$_{37}$N: C, 87.16 (86.89); H, 9.33 (9.93); N, 3.51 (3.25).

2,6-bis(4'-tert-butylphenyl)-4-methoxypyridine (H$_2$L$^{OMe}$) was made from 2,6-dichloro-4-methoxypyridine (2.0 g, 11.0 mmol), 4-tert-butylphenylboronic acid (4.9 g, 27.0 mmol), K$_3$PO$_4$ trihydrate (3.9 g, 17.0 mmol), and [Pd(PPh$_3$)$_4$] (0.12 g, 0.10 mmol) as a white solid, yield 2.2 g (5.9 mmol, 54%). $^1$H-NMR (300.13 MHz, CDCl$_3$): $\delta$ 8.04 (d, 4H, $^3$J = 8.2 Hz, H5), 7.50 (d, 4H, $^3$J = 8.2 Hz, H6), 7.18 (s, 2H, H2), 3.96 (s, 3H, OMe), 1.37 ppm (s, 18H, H11). $^{13}$C($^1$H)NMR (75.47 MHz, CDCl$_3$): $\delta$ 167.2 (s, C1), 158.6 (s, C7), 152.3 (s, C3), 136.9 (s, C4), 127.0 (s, C5), 125.7 (s, C6), 104.6 (s, C2), 55.3 (s, OMe), 34.8 (s, C10), 31.5 ppm (s, C11). Anal. Calcd. (found) for C$_{28}$H$_{35}$NO: C, 83.60 (83.49); H, 8.37 (8.50); N, 3.75 (3.72).

2,6-bis(4'-tert-butylphenyl)-4-dimethylaminopyridine (H$_2$L$^{NMe_2}$) was made from 2,6-dichloro-4-dimethylaminopyridine (1.4 g, 7.3 mmol), 4-tert-butylphenylboronic acid (3.3 g, 18.0 mmol), K$_3$PO$_4$ trihydrate (2.8 g, 12.0 mmol), and [Pd(PPh$_3$)$_4$] (0.09 g, 0.078 mmol) as a yellow solid, yield: 1.7 g (4.4 mmol, 60%). $^1$H-NMR (300.13 MHz, CDCl$_3$): $\delta$ 7.99 (d, 4H, $^3$J
2.3 Organomercury(II) compounds

\[ \text{Scheme S4. Route and numbering for mercury compounds.} \]

General procedure for the synthesis of mercury complexes.

A stoichiometric mixture of the desired ligand and mercury(II) acetate in ethanol was refluxed for 3-5 days, then poured into a solution of lithium chloride (2 equiv) in MeOH, resulting in the precipitation of the product as a white solid. The suspension was stirred at 60 °C for 30 min, and for further 30 min at r.t after the addition of distilled water. The solid was recovered by filtration, and washed with water and petrol.

\((\text{HL}^\text{Bu})\text{HgCl}\). The compound was made as described from \(\text{H}_2\text{L}^\text{Bu}\) (2.0 g, 5.0 mmol), mercury(II) acetate (1.6 g, 5.0 mmol) in ethanol (50 mL) followed by LiCl (0.4 g, 9.4 mmol) in methanol (40 mL). White solid, yield 2.1 g (3.3 mmol, 66%). \(^1\)H-NMR (300.13 MHz, DMSO-\(d_6\)): \(\delta 8.11 (d, 2H, J = 8.3 Hz, H5), 7.97 (d, 1H, J = 8.2 Hz, H5\'), 7.88 (d, 1H, J = 1.1 Hz, H2 or H2\'), 7.84 (d, 1H, J = 1.1 Hz, H2 or H2\'), 7.80 (d, 1H, J = 2.0 Hz, H8\'), 7.53 (d, 2H, J = 8.3 Hz, H6), 7.47 (dd, 1H, J = 8.2 Hz, \(J = 2.0 Hz, H6\)'), 1.45 (s, 9H, tBu on py), 1.37 ppm (s, 18H, H11+H11\'). \(^{13}\)C\{\(^1\)H\}NMR (75.47 MHz, CDCl\(_3\)): \(\delta 162.5 (s), 158.1 (s), 157.5 (s), 157.5 (s), 152.5 (s), 152.3 (s), 149.1 (s), 141.1 (s), 136.3 (s), 134.8 (s), 127.7 (s), 126.0 (s), 125.8 (s), 118.0 (s), 116.7 (s), 35.4 (s), 35.0 (s), 34.8 (s), 31.4 (s), 31.4 (s), 30.8 ppm (s). Anal. Calc. (found) for \(\text{C}_{29}\text{H}_{36}\text{ClHgN}\): C, 54.88 (54.97); H, 5.72 (5.79); N, 2.21 (2.29).

\((\text{HL}^\text{OMe})\text{HgCl}\). The compound was made as described from \(\text{H}_2\text{L}^\text{OMe}\) (2.0 g, 5.3 mmol) and mercury(II) acetate (1.7 g, 5.3 mmol) in ethanol (50 mL) followed by LiCl (0.4 g, 9.4 mmol) in methanol (40 mL). White solid, yield 2.7 g (4.4 mmol, 83%). \(^1\)H-NMR (300.13 MHz, DMSO-\(d_6\)): \(\delta 8.09 (d, 2H, J = 8.5 Hz, H5), 7.96 (d, 1H, J = 8.2 Hz, H5\'), 7.78 (d, 1H, J = 2.1 Hz, H8\'), 7.51 (d, 2H, J = 8.5 Hz, H6), 7.45 (m, 3H, H2+H2\'+H6\'), 4.03 (s, 3H, OMe), 1.37 ppm (s, 18H, H11+H11\'). \(^{13}\)C\{\(^1\)H\}NMR (75.47 MHz, CDCl\(_3\)): \(\delta 167.6 (s), 160.0 (s), 159.1 (s), 152.9 (s), 152.6 (s), 149.0 (s), 140.6 (s), 135.9 (s), 134.8 (s), 127.6 (s), 126.1 (s), 125.8 (s), 106.4 (s), 105.7 (s), 55.6 (s), 55.0 (s), 34.9 (s), 31.4 (s), 31.4 (s), 30.8 ppm (s). Anal. Calc. (found) for \(\text{C}_{26}\text{H}_{30}\text{ClHgNO}\): C, 51.31 (51.38); H, 4.97 (5.06); N, 2.30 (2.27).
(HL\textsuperscript{NMe2})HgCl. The compound was made as described from H\textsubscript{2}L\textsuperscript{NMe2} (1.0 g, 2.6 mmol) and mercury(II) acetate (0.8 g, 2.6 mmol) in ethanol (25 mL) followed by LiCl (0.2 g, 4.7 mmol) in methanol (20 mL). White solid, yield 1.4 g (2.2 mmol, 85%). \textsuperscript{1}H-NMR (300.13 MHz, DMSO-d\textsubscript{6}): \(\delta\) 8.02 (d, 2H, \(^3J = 8.4\) Hz, H5), 7.96 (d, 1H, \(^3J = 8.4\) Hz, H5'), 7.72 (d, 1H, \(^4J = 2.1\) Hz, H6'), 7.48 (d, 2H, \(^3J = 8.4\) Hz, H6), 7.44 (dd, 1H, \(^2J = 8.4\) Hz, \(^4J = 2.1\) Hz, H6'), 7.06 (s, 2H, H2+H2'), 3.17 (s, 6H, NMe\textsubscript{2}), 1.36 ppm (s, 18H, H11+H11'). \textsuperscript{13}C{\textsuperscript{1}H}NMR (75.47 MHz, CDCl\textsubscript{3}): \(\delta\) 158.2 (s), 157.4 (s), 156.0 (s), 152.3 (s), 152.0 (s), 149.3 (s), 135.5 (s), 134.5 (s), 127.6 (s), 127.3 (s), 125.7 (s), 125.5 (s), 103.7 (s), 102.4 (s), 39.6 (s), 34.9 (s), 34.7 (s), 31.3 (s), 31.3 ppm (s). The elemental analysis indicated that the product was a mixture of (HL\textsuperscript{NMe2})HgCl and its HCl adduct.

2.4 Gold(III) chloro complexes

The gold(III) chlorides were prepared according to Scheme S5.

![Scheme S5. Route to \(^{[L]}\)AuCl and numbering scheme for \(^1\)H and \(^{13}C\) peak assignment.](image)

General procedure for the synthesis of gold(III) chloro complexes

A stoichiometric mixture of (HL\textsuperscript{R})HgCl and K[AuCl\textsubscript{4}] in water/acetonitrile (v/v 3:2) was stirred at r.t. for 1h, then refluxed for 3 days. The mixture was cooled to 0°C, resulting in the precipitation of the product, which was then recovered by filtration and dissolved in dichloromethane. The resulting suspension was filtered. The filtrate was dried over MgSO\textsubscript{4} and evaporated to dryness to afford the desired products.

(L\textsuperscript{tBu})AuCl

This compound was made from (HL\textsuperscript{tBu})HgCl (1.5 g, 2.4 mmol) and K[AuCl\textsubscript{4}] (0.9 g, 2.4 mmol) in 100 mL of 3:2 water/acetonitrile as a pale yellow solid, yield 1.2 g (1.9 mmol, 79%). \textsuperscript{1}H-NMR (300.13 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 7.91 (d, 2H, \(^4J = 2.0\) Hz, H8), 7.55 (d, 2H, \(^3J = 8.3\) Hz, H5), 7.44 (s, 2H, H2), 7.31 (dd, 2H, \(^3J = 8.3\) Hz, \(^4J = 2.0\) Hz, H6), 1.43 (s, 9H, tBu of py), 1.37 ppm (s, 18H, H11'). \textsuperscript{13}C{\textsuperscript{1}H}NMR (75.47 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 170.6 (s, C9), 168.6 (s, C1), 164.5 (s, C3), 155.5 (s, C7), 145.8 (s, C4), 130.8 (s, C8), 125.0 (s, C5), 124.5 (s, C6), 114.2 (s, C2), 36.4 (s, -CCH\textsubscript{3} on py), 35.8 (s, C10), 31.3 (s, C11), 30.5 ppm (s, -CCH\textsubscript{3} on py). Anal. Calc. (found) for C\textsubscript{29}H\textsubscript{35}AuClN: C, 55.29 (55.11); H, 5.60 (5.75); N, 2.22 (2.27).
**L^{OMe}AuCl**

This compound was synthesized from (HL^{OMe})HgCl (1.5 g, 2.5 mmol) and K[AuCl₄] (0.9 g, 2.5 mmol) as a pale yellow solid, yield 0.9 g (1.5 mmol, 60%). Crystals suitable for X-ray diffraction were grown from a concentrated CH₂Cl₂ solution in the dark. ¹H-NMR (300.13 MHz, CD₂Cl₂): δ 7.89 (d, 2H, ³J = 2.0 Hz, H8), 7.37 (d, 2H, ³J = 8.2 Hz, H5), 7.25 (dd, 2H, ³J = 8.2 Hz, ⁴J = 2.0 Hz, H6), 6.83 (s, 2H, H2), 4.04 (s, 3H, OMe), 1.37 ppm (s, 18H, H11). ¹³C{¹H}NMR (75.47 MHz, CD₂Cl₂): δ 171.2 (s, C1), 170.3 (s, C9), 166.1 (s, C3), 155.4 (s, C7), 145.4 (s, C4), 130.4 (s, C8), 124.9 (s, C5), 124.3 (s, C6), 102.7 (s, C2), 56.9 (s, OMe), 35.8 (s, C10), 31.4 ppm (s, C11). Anal. Calc. (found) for C_{26}H_{29}AuClNO: C, 51.71 (51.63); H, 4.84 (4.72); N, 2.32 (2.42).

**L^{NMe₂}AuCl**

This compound was made from (HL^{NMe₂})HgCl (1.0 g, 1.6 mmol) and K[AuCl₄] (0.6 g, 1.6 mmol), in 65 mL of 3:2 water/acetonitrile as an off-white solid, yield 0.45 g (0.73 mmol, 46%). Crystals suitable for X-ray diffraction were grown from a concentrated CH₂Cl₂ solution in the dark. ¹H-NMR (300.13 MHz, CD₂Cl₂): δ 7.88 (d, 2H, ³J = 1.9 Hz, H8), 7.26 (d, 2H, ³J = 8.3 Hz, H5), 7.20 (dd, 2H, ³J = 8.3 Hz, ⁴J = 1.9 Hz, H6), 6.37 (s, 2H, H2), 3.16 (s, 6H, NMe₂), 1.37 ppm (s, 18H, H11). ¹³C{¹H}NMR (75.47 MHz, CDCl₃): δ 169.95 (s, C9), 163.25 (s, C3), 157.52 (s, C1), 154.43 (s, C7), 146.27 (s, C6), 146.27 (s, C4), 130.37 (s, C8), 124.09 (s, C5), 123.97 (s, C6), 98.25 (s, C2), 40.43 (s, NMe₂), 35.67 (s, C10), 31.4 ppm (s, C11). Anal. Calc. (found) for C_{27}H_{32}AuClN₂: C, 52.56 (52.65); H, 5.23 (5.35); N, 4.54 (4.55).

2.5 Gold(III) hydroxides (L^R)AuOH

The complexes were synthesized according to Scheme S6.

![Scheme S6. Synthesis and numbering scheme for (L^R)AuOH complexes.](image)

**General procedure for the synthesis of (L^R)AuOH**

The chloro complexes (L^R)AuCl were stirred with CsOH-H₂O (5 equiv) in a mixture of water, THF and toluene (v/v/v = 1:1:1) at 60°C for 48h. In the case of (L^Bu)AuOH the product was recovered from the organic layer, which was washed with water, dried over MgSO₄, and evaporated to dryness to yield the desired compound. Complexes (L^{OMe})AuOH and (L^{NMe₂})AuOH were instead collected as precipitates by filtration and redissolved in...
dichloromethane; the resulting suspension was filtered, and the volatiles were removed from the filtrate to afford the product.

(LBu)AuOH

This compound was synthesized from (LBu)AuCl (0.5 g, 0.8 mmol) and CsOH·H2O (0.67 g, 4.0 mmol), in 125 mL of 1:1:1 water/THF/toluene as a yellow solid, yield 0.33 g (0.54 mmol, 67%). 1H-NMR (300.13 MHz, CD2Cl2): δ 7.91 (d, 2H, 4J = 2.0 Hz, H8), 7.55 (d, 2H, 3J = 8.1 Hz, H5), 7.44 (s, 2H, H2), 7.31 (dd, 2H, 3J = 8.1 Hz, 4J = 2.0 Hz, H6), 1.43 (s, 9H, tBu on py), 1.37 ppm (s, 18H, H11). 13C{1H}NMR (75.47 MHz, CD2Cl2): δ 169.3 (s, C1), 167.6 (s, C9), 164.0 (s, C3), 154.9 (s, C7), 145.9 (s, C4), 128.7 (s, C8), 124.9 (s, C5), 124.3 (s, C6), 113.9 (s, C2), 36.3 (s –CCH3 on py), 35.7 (s, C10), 31.4 (s, C11), 30.5 ppm (s, -CCH3 on py). Anal. Calc. (found) for C29H36AuNO: C, 56.95 (55.94); H, 5.93 (6.34); N, 2.29 (2.40).

(LOMe)AuOH

This compound was made from (LOMe)AuCl (0.5 g, 0.83 mmol) and CsOH·H2O (0.95 g, 5.7 mmol), in 125 mL of 1:1:1 water/THF/toluene as a whitish solid, yield 0.22 g (0.38 mmol, 46%). 1H-NMR (300.13 MHz, CD2Cl2): δ 7.61 ppm (d, 2H, 4J = 2.0 Hz, H8), 7.46 (d, 2H, 3J = 8.3 Hz, H5), 7.28 (dd, 2H, 3J = 8.3 Hz, 4J = 2.0 Hz, H6), 6.88 (s, 2H, H2), 4.02 (s, 3H, OMe), 1.37 ppm (s, 18H, H11). 13C{1H}NMR (75.47 MHz, CD2Cl2): δ 170.9 (s, C1), 169.2 (s, C9), 154.9 (s, C7), 145.9 (s, C4), 128.6 (s, C8), 124.8 (s, C5), 124.4 (s, C6), 102.4 (s, C2), 56.8 (s, OMe), 35.7 (s, C10), 31.4 ppm (s, C11). Anal. Calc. (found) for C26H30AuNO2: C, 53.34 (53.19); H, 5.16 (4.98); N, 2.39 (2.50).

(LNMe2)AuOH

This compound was made from (LNMe2)AuCl (0.3 g, 0.49 mmol) and CsOH·H2O (0.41 g, 2.4 mmol), in 50 mL of 1:1:1 water/THF/toluene as a whitish solid, yield 0.24 g (0.40 mmol, 82%). 1H-NMR (300.13 MHz, CD2Cl2): δ 7.61 (d, 2H, 4J = 2.0 Hz, H8), 7.46 (d, 2H, 3J = 8.2 Hz, H5), 7.26 (dd, 2H, 3J = 8.2 Hz, 4J = 2.0 Hz, H6), 6.56 (s, 2H, H2), 3.20 (s, 6H, NMe2), 1.37 ppm (s, 18H, H11). 13C{1H}NMR (75.47 MHz, CD2Cl2): δ 168.8 (s, C9), 162.9 (s, C3), 157.4 (s, C1), 153.7 (s, C7), 146.4 (s, C4), 128.4 (s, C8), 124.1 (s, C5 or C6), 123.8 (s, C6 or C5), 98.2 (s, C2), 40.3 (NMe2), 35.6 (s, C10), 31.5 ppm (s, C11). Anal. Calc. (found) for C27H33AuN2O: C, 54.18 (54.08); H, 5.56 (5.50); N, 4.68 (4.75).
3. Synthesis and characterization of Gold(III) hydrides (L^R)AuH (1b-1e).

The hydride complexes were prepared by two methods: Method A: Following the procedure previously reported for (C^N^C)AuH (1a) (D.-A. Roşca et al., Angew. Chem. Int. Ed. 2012, 51, 10643), the hydroxides (L^R)AuOH were reacted with LiHBEt₃ in toluene at -78°C. Method B: By treating the chloro complexes (L^R)AuCl with LiAlH₄ in toluene/THF at -78°C (Scheme S7).

Scheme S7. Synthetic routes to Au(III) hydrides and numbering scheme.

General procedure A

Under a N₂ atmosphere, the hydroxides (L^R)AuOH were charged in a dry Schlenk flask with dry toluene. To this was added dropwise LiHBEt₃ in THF (1.2 equiv) with a syringe at -78 °C and the mixture was stirred at -78 °C in the dark for 15 min before being allowed to warm to r.t. The resulting suspension was filtered under N₂, and the filtrate evaporated to dryness, to afford the desired product as a powder.

(L^tBu)AuH (1b)

This compound was synthesized from (L^tBu)AuOH (0.15 g, 0.24 mmol), and LiHBEt₃ (1M solution in THF, 0.29 mL, 0.29 mmol) in 15 mL of toluene as a pale yellow solid, yield 0.10 g (0.17 mmol, 71%). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ 7.93 (d, 2H, J = 2.0 Hz, H8), 7.59 (d, 2H, J = 8.2 Hz, H5), 7.46 (s, 2H, H2), 7.25 (dd, 2H, J = 8.2 Hz, J = 2.0 Hz, H6), 1.42 (s, 9H, tBu of py), 1.35 (s, 18H, H11), -6.42 ppm (s, 1H, Au-H). ¹³C{¹H}NMR (75.47 MHz, CD₂Cl₂): δ 167.2 (s, C1), 166.1 (s, C3), 163.1 (s, C9), 155.0 (s, C7), 148.5 (s, C4), 138.1 (s, C8), 124.9 (s, C5), 123.1 (s, C6), 113.7 (s, C2), 36.3 (s, -CCH₃ on py), 35.2 (s, C10), 31.4 (s,
(L^{OMe})AuH (1c)

This compound was synthesized from (L^{OMe})AuOH (0.15 g, 0.26 mmol) and LiHBEt3 (1M solution in THF, 0.31 mL, 0.31 mmol) in 15 mL of toluene as a white solid, yield 0.10 g (0.18 mmol, 69%). $^1$H-NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta$ 7.94 (s, 2H, H8), 7.53 (d, 2H, $^3$J = 8.4 Hz, H5), 7.25 (dd, 2H, $^3$J = 8.4 Hz, $^4$J = 2.0 Hz, H6), 6.94 (s, 2H, H2), 4.01 (s, 3H, OMe), 1.34 (s, 18H, H11), −6.48 ppm (s, 1H, Au-H). $^{13}$C{$^1$H}NMR (75.47 MHz, CD$_2$Cl$_2$): $\delta$ 170.8 (s, C1), 166.1 (s, C3), 165.1 (s, C9), 155.1 (s, C7), 148.2 (s, C4), 138.0 (s, C8), 124.9 (s, C5), 123.1 (s, C6), 102.4 (s, C2), 56.5 (s, OMe), 35.3 (s, C10), 31.4 ppm (s, C11). IR: $\nu_{Au-H}$ = 2199 cm$^{-1}$. Anal. Calc. (found) for C$_{26}$H$_{30}$AuNO: C, 54.84 (54.59); H, 5.31 (5.45); N, 2.46 (2.37).

(L^{NMe2})AuH (1d)

This compound was synthesized from (L^{NMe2})AuOH (0.14 g, 0.23 mmol), and LiHBEt3 (1M solution in THF, 0.28 mL, 0.28 mmol) in 15 mL of toluene as a white solid, yield 0.09 g (0.15 mmol, 65%). Crystals suitable for X-ray diffraction were grown from a concentrated CH$_2$Cl$_2$ solution in the dark. $^1$H-NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta$ 7.93 (s, 2H, H8), 7.53 (d, 2H, $^3$J = 8.1 Hz, H5), 7.23 (dd, 2H, $^3$J = 8.1 Hz, $^4$J = 2.0 Hz, H6), 6.63 (s, 2H, H2), 3.20 (s, 6H, NMe$_2$), 1.34 (s, 18H, H11), −6.26 ppm (s, 1H, Au-H). $^{13}$C{$^1$H}NMR (75.47 MHz, CD$_2$Cl$_2$): $\delta$ 165.9 (s, C3), 162.6 (s, C9), 157.9 (s, C1), 154.1 (s, C7), 149.0 (s, C4), 137.9 (s, C8), 124.2 (s, C5), 122.6 (s, C6), 98.2 (s, C2), 40.3 (s, NMe$_2$), 35.2 (s, C10), 31.4 ppm (s, C11). IR: $\nu_{Au-H}$ = 2171 cm$^{-1}$. Anal. Calc. (found) for C$_{27}$H$_{33}$AuN$_2$: C, 55.67 (55.48); H, 5.71 (5.61); N, 4.81 (4.93).

**General procedure B**

Under a N$_2$ atmosphere, the chloro complexes (L$^R$)AuCl were charged in a dry Schlenk flask with dry toluene. To this was added dropwise a 0.05 M solution of LiAlH$_4$ (1 equiv) in dry THF at -78°C. The mixture was stirred at -78 °C in the dark for 30 min. The resulting suspension was filtered under N$_2$, and the filtrate evaporated to dryness, to afford the products as powders.

(L$^H$)AuH (1a)

From (L$^H$)AuCl (0.08 g, 0.14 mmol) in 10 mL of dry toluene and LiAlH$_4$ (1M solution in THF, 0.14 mL, 0.14 mmol) in 2.5 mL of dry THF. Yield 0.05 g (0.10 mmol, 71%).

(L$^{tBu}$)AuH (1b)

From (L$^{tBu}$)AuCl (0.08 g, 0.13 mmol) in 10 mL of dry toluene and LiAlH$_4$ (1 M solution in THF, 0.13 mL, 0.13 mmol) in 2.5 mL of dry THF. Yield 0.06 g (0.10 mmol, 77%).

(L$^{OMe}$)AuH (1c)
From (L^{OMe})AuCl (0.08 g, 0.13 mmol) in 10 mL of dry toluene and LiAlH₄ (1 M solution in THF, 0.13 mL, 0.13 mmol) in 2.5 mL of dry THF. Yield 0.06 g (0.11 mmol, 84%).

(L^{NMe2})AuH (1d)

From (L^{NMe2})AuCl (0.08 g, 0.13 mmol) in 10 mL of dry toluene and LiAlH₄ (1 M solution in THF, 0.13 mL, 0.13 mmol) in 2.5 mL of dry THF. Yield 0.06 g (0.10 mmol, 77%).

(C^{Npz}^C)AuH (1e)

From (C^{Npz}^C)AuCl (0.10 g, 0.17 mmol) in 5 mL of dry toluene and LiAlH₄ (1 M solution in THF, 0.17 mL, 0.17 mmol) in 5 mL of dry THF. Deep-yellow solid. Yield 0.08 g (0.15 mmol, 88%). ¹H-NMR (300.13 MHz, CD₂Cl₂): δ 8.80 (s, 2H, H₂), 7.94 (br, H₈), 7.62 (d, 2H, ³J = 8.2 Hz, H₅) 7.28 (dd, 2H, ³J = 8.2 Hz, ⁴J = 1.9 Hz, H₆), 1.35 (s, 18H, H₁₁), -6.50 ppm (s, 1H, Au-H). ¹³C{¹H}NMR (75.47 MHz, CD₂Cl₂): δ 166.4 (s, C₉), 156.1 (s, C₃ or C₇), 156.1 (s, C₇ or C₃), 145.5 (s, C₄), 138.0 (s, C₂ or C₈), 138.0 (s, C₈ or C₂), 125.3 (s, C₅), 123.2 (s, C₆), 35.1 (s, C₁₀), 30.9 ppm (s, C₁₁). IR: νAu-H = 2200 cm⁻¹. Anal. Calc. (found) for C₆₄H₂₇AuN₂: C, 53.34 (53.15); H, 5.04 (5.25); N, 5.18 (5.10).
4. $^1$H-NMR spectra of Gold(III) hydrides ($L^R$)AuH (1b-1e)

**Figure S1.** $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{tBu}$)AuH (1b). Peaks marked with an asterisk correspond to solvent (*) and grease (x) signals.

**Figure S2.** Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{tBu}$)AuH (1b).
Figure S3. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{OMe}$)AuH (1c). Peaks marked with an asterisk correspond to solvent (*), water (#) and grease (x) signals.

Figure S4. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{OMe}$)AuH (1c).
Figure S5. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{NMe2}$)AuH (1d). Peaks marked with an asterisk correspond to solvent (*), water (#) and grease (x) signals.

Figure S6. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (L$^{NMe2}$)AuH (1d).
Figure S7. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (C$^\text{N}$p$^2$C)AuH (1e). Peaks marked with an asterisk correspond to solvent (*), and grease (x) signals.

Figure S8. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of (C$^\text{N}$p$^2$C)AuH (1e).
5. Synthesis of insertion products 2-13

As a general procedure, a solution of (L^{OMe})AuH (1c) (0.005–0.009 mmol) in toluene-d$_8$ (0.7 mL) was prepared inside the glovebox in a J-Young NMR tube. 9–36 equivalents of the desired acetylene were added to the tube by a micrometric syringe, followed by 2-4 equivalents of AIBN. The tube was shaken and heated in the dark to 50 °C, and the reactions were monitored by $^1$H NMR spectroscopy. The volatile components were removed in vacuo at the end of the reaction, the excess alkynes were removed by adding dry n-hexane to the crude product, which was then redissolved in CD$_2$Cl$_2$ for the NMR characterization. Yields were calculated from the NMR integration.

$\text{(L}^{\text{OMe}}\text{)}\text{Au(C(H)=CHPh)}$ (2)

This compound was synthesized from 1c (3.0 mg, 0.005 mmol), phenylacetylene (20 μL, 19 mg, 0.18 mmol), and 3 mg of AIBN (0.018 mmol) and the reaction resulted complete after 85 min at 50°C. Yield: >95%. $^1$H-NMR (300.13 MHz, CD$_2$Cl$_2$): δ 7.80 (d, 1H, $^2$J = 10.8 Hz, H13), 7.74 (d, 2H, $^2$J = 7.3 Hz, H15), 7.54 (d, 1H, $^3$J = 10.8 Hz, H12), 7.52 (d, 2H, $^3$J = 8.2 Hz, H5), 7.50 (d, 2H, $^4$J = 2.0 Hz, H8), 7.20 (dd, 2H, $^4$J = 8.2, $^4$J = 2.0 Hz, H6), 7.11 (m, 2H, H16), 7.03 (m, 1H, H17), 6.98 (s, 2H, H2), 4.02 (s, 3H, OMe), 1.19 ppm (s, 18H, H11). $^{13}$C($^1$H)NMR (75.47 MHz, CD$_2$Cl$_2$): δ 170.8 (s, C1), 166.2 (s, C9), 165.0 (s, C3), 154.3 (s, C7), 147.7 (s, C4), 141.8 (s, C14), 137.0 (s, C12), 133.1 (s, C8), 130.7 (s, C13), 128.0 (s, C16), 127.8 (s, C15), 126.2 (s, C17), 124.9 (s, C5), 123.3 (s, C6), 102.3 (s, C2), 56.6 (s, OMe), 35.3 (s, C10), 31.2 ppm (s, C11).

$\text{(L}^{\text{OMe}}\text{)}\text{Au(C(Me)=CHPh)}$ (3)
This compound was synthesized from 1c (3.5 mg, 0.006 mmol), 1-phenyl-1-propyne (23 µL, 21 mg, 0.18 mmol), and 3 mg of AIBN (0.018 mmol), and the reaction resulted complete after 5 min at 50°C. Yield: >95%. $^{1}$H-NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta$ 7.68 (d, 2H, $^3J$ = 7.4 Hz, H15), 7.58 (d, 2H, $^4J$ = 1.9 Hz, H8), 7.53 (d, 2H, $^3J$ = 8.2 Hz, H5), 7.36 (s, 1H, H13), 7.21 (dd, 2H, $^3J$ = 8.3, $^4J$ = 1.9 Hz, H6), 7.06 (ps, 2H, $^3J$ = 7.4 Hz, H16), 6.98 (s, 2H, H2), 6.95 (t, 1H, $^3J$ = 7.4 Hz, H17), 4.02 (s, 3H, OMe), 2.55 (d, 3H, $^4J$ = 1.2 Hz, Me substituent at the vinyl), 1.24 ppm (s, 18H, H11). $^{13}$C-$^{1}$H-NMR (75.47 MHz, CD$_2$Cl$_2$): $\delta$ 170.9 (s, C1), 166.9 (s, C9), 165.0 (s, C3), 154.7 (s, C7), 151.4 (s, C12), 147.8 (s, C4), 141.6 (s, C14), 133.1 (s, C8), 127.9 (s, C16), 127.7 (s, C15), 125.5 (s, C13), 125.2 (s, C17), 124.8 (s, C5), 123.2 (s, C6), 102.4 (s, C2), 56.6 (s, OMe), 35.4 (s, C10), 31.3 (s, C11), 30.0 ppm (s, Me substituent at the vinyl).

(L$^{\text{OMe}}$)Au(C(Ph)=CHPh) (4)

This compound was synthesized from 1c (3.0 mg, 0.005 mmol), diphenylacetylene (20 mg, 0.11 mmol), and 3 mg of AIBN (0.018 mmol), and the reaction resulted complete after 5 min at 50°C. Yield: >95%. $^{1}$H-NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta$ 7.81 ppm (d, 2H, $^3J$ = 7.4 Hz, H15), 7.70 (s, 1H, H13), 7.66 (d, 2H, $^3J$ = 7.4 Hz, H19), 7.54 (d, 2H, $^4J$ = 2.0 Hz, H8), 7.52 (d, 2H, $^3J$ = 8.3 Hz, H5), 7.26 (dd, 2H, $^3J$ = 7.4 Hz, H20), 7.18 (dd, 2H, $^3J$ = 8.3, $^4J$ = 2.0 Hz, H6), 7.16 (1H, overlapped with H6 and H16, H21), 7.12 (m, 2H, H16), 7.03 (m, 1H, H17), 6.98 (s, 2H, H2), 4.02 (s, 3H, OMe), 1.17 ppm (s, 18H, H11). $^{13}$C-$^{1}$H-NMR (75.47 MHz, CD$_2$Cl$_2$): $\delta$ 170.9 (s, C1), 166.2 (s, C9), 165.1 (s, C3), 154.5 (s, C7), 153.3 (s, C12), 148.7 (s, C18), 147.6 (s, C4), 142.1 (s, C14), 133.6 (s, C8), 128.9 (s, C19), 128.7 (s, C13), 128.2 (s, C15+C20), 128.0 (s, C16), 126.5 (s, C21), 126.0 (s, C17), 124.8 (s, C5), 123.2 (s, C6), 102.4 (s, C2), 56.5 (s, OMe), 35.2 (s, C10), 31.1 ppm (s, C11).
This compound was synthesized from 1c (3.0 mg, 0.005 mmol), (tert-butyldimethylsilyl)acetylene (20 μL, 15 mg, 0.11 mmol), and 3 mg of AIBN (0.018 mmol), and the reaction resulted complete after 110 min at 50°C. Yield: 90%. ¹H-NMR (300.13 MHz, CD₂Cl₂): δ 8.59 (d, 1H, ²J = 13.5 Hz, H12), 7.72 (d, 2H, ⁴J = 1.7 Hz, H8), 7.53 (d, 2H, ³J = 8.2 Hz, H5), 7.26 (dd, 2H, ⁴J = 1.7 Hz, H6), 7.09 (d, 1H, ³J = 13.5 Hz, H13), 6.96 (s, 2H, H2), 4.01 (s, 3H, OMe), 1.32 (s, 18H, H11), 0.89 (s, 9H, Si′Bu), −0.02 ppm (s, 6H, SiMe₂). ¹³C{¹H}NMR (75.47 MHz, CD₂Cl₂): δ 170.7 (s, C1), 167.8 (s, C9), 164.7 (s, C7), 153.7 (s, C12), 147.5 (s, C4), 133.5 (s, C8), 130.1 (s, C13), 124.7 (s, C5), 123.2 (s, C6), 102.3 (s, C2), 56.5 (s, OMe), 35.2 (s, C10), 31.4 (s, C11), −0.4 ppm (s, SiMe₃).
This compound was synthesized from 1c (5.0 mg, 0.009 mmol) and 1-hexyne (15 µL, 11 mg, 0.13 mmol), and 3 mg of AIBN (0.018 mmol), and the reaction resulted complete after 35 min heating at 50°C. Yield: >95%. \(^1\)H-NMR (300.13 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.73 (d, 2H, \(^4J = 1.5\) Hz, H8), 7.54 (d, 2H, \(^3J = 8.1\) Hz, H5), 7.25 (dd, 2H, \(^3J = 8.1, ^4J = 1.5\) Hz, H6), 7.00 (d, 1H, \(^3J = 9.0\) Hz, H12), 6.96 (s, 2H, H2), 6.61 (dt, 1H, \(^3J = 9.0, ^4J = 7.2\) Hz, H13), 4.01 (s, 3H, OMe), 2.11 (q, 2H, \(^3J = 7.2\) Hz, H14), 1.39 (m, 2H, H15), 1.33 (s, 18H, H11), 1.26 (m, 2H, H16), 0.78 ppm (t, 3H, \(^3J = 7.1\) Hz, H17). \(^{13}\)C\(^{\{1\}H}\)NMR (75.47 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 170.7 (s, C1), 167.1 (s, C9), 164.7 (s, C3), 154.0 (s, C7), 147.9 (s, C4), 134.2 (s, C12), 133.1 (s, C8), 130.8 (s, C13), 124.8 (s, C5), 123.2 (s, C6), 102.2 (s, C2), 56.5 (s, OMe), 37.5 (s, C14), 35.4 (s, C10), 32.2 (s, C15), 31.4 (s, C11), 22.7 (s, C16), 14.2 ppm (s, C17).

This compound was synthesized from 1c (3.0 mg, 0.005 mmol) and 3-hexyne (20 µL, 14 mg, 0.18 mmol), and 3 mg of AIBN (0.018 mmol), and the reaction resulted complete after 60 min heating at 50°C. Yield: 90%. \(^1\)H-NMR (300.13 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.74 ppm (d, 2H, \(^4J = 1.9\) Hz, H8), 7.54 (d, 2H, \(^3J = 8.2\) Hz, H5), 7.24 (dd, 2H, \(^3J = 8.2, ^4J = 2.1\) Hz, H6), 6.97 (s, 2H, H2), 6.17 (t, 1H, \(^3J = 6.9\) Hz, H13), 4.01 (s, 3H, OMe), 2.60 (q, 2H, \(^3J = 7.3\) Hz, H14), 2.05 (dq, 2H, \(^3J = 7.3\) Hz, H14), 1.33 (s, 18H, H11), 1.14 (t, 3H, \(^3J = 7.5\) Hz, H17), 0.93 ppm (t, 3H, \(^3J = 7.5\) Hz, H15). \(^{13}\)C\(^{\{1\}H}\)NMR (75.47 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 170.7 (s, C1), 167.6 (s, C9), 164.5 (s, C3), 154.5 (s, C12), 154.3 (s, C7), 147.9 (s, C4), 133.8 (s, C8), 124.8 (s, C5), 123.9 (s, C13), 123.1 (s, C6), 102.3 (s, C2), 68.6 (s, OMe), 35.7 (s, C16), 35.4 (s, C10), 31.4 (s, C11), 29.4 (s, C14), 16.8 (s, C17), 14.4 ppm (s, C15).
(L^{O Me})Au(C(H)=CHCH_{2}OH) \ (9)

This compound was synthesized from 1c (4.5 mg, 0.008 mmol) and propargyl alcohol (10 μL, 9.6 mg, 0.17 mmol) in the presence of AIBN (3 mg, 0.018 mmol), and the reaction resulted complete after 60 min heating at 50°C. Yield: >95%. ^{1}H-NMR (300.13 MHz, CD_{2}Cl_{2}): δ 7.66 (d, 2H, \( ^{3}J = 2.0 \) Hz, H8), 7.54 (d, 2H, \( ^{3}J = 8.2 \) Hz, H5), 7.26 (dd, 2H, \( ^{3}J = 8.2, ^{4}J = 2.0 \) Hz, H6), 7.24 (d, 1H, \( ^{3}J = 9.4 \) Hz, H12), 6.96 (s, 2H, H2), 6.86 (dt, 1H, \( ^{3}J = 9.4, ^{4}J = 6.2 \) Hz, H13), 4.12 (m, 2H, H14), 4.01 (s, 3H, OMe), 1.33 ppm (s, 18H, H11).

^{13}C\{}^{1}H\}NMR (75.47 MHz, CD_{2}Cl_{2}): δ 170.8 (s, C1), 166.6 (s, C9), 164.7 (s, C3), 154.5 (s, C7), 147.8 (s, C4), 137.4 (s, C12), 132.7 (s, C8), 130.4 (s, C13), 125.0 (s, C5), 123.5 (s, C6), 102.4 (s, C2), 67.8 (s, C14), 56.5 (s, OMe), 35.4 (s, C10), 31.3 ppm (s, C11).

(L^{O Me})Au(C(Et)=CHC_{6}H_{5}CHO) \ (10)

This compound was synthesized from 1c (5.0 mg, 0.009 mmol) and 4-ethynylbenzaldehyde (15 mg, 0.12 mmol) in the presence of AIBN (3 mg, 0.018 mmol), and the reaction resulted complete after 20 min heating at 50°C. The presence of both the Z and the E isomers in a 82/18 ratio was revealed by NMR. The signal corresponding to the tBu substituent at the pyridine was used to determine the E/Z ratio. Total yield for the mixture of the two isomers: >95%. ^{1}H-NMR (300.13 MHz, CD_{2}Cl_{2}): δ 9.81 (s, 1H, H18), 7.93 (d, 2H, \( ^{3}J = 8.3 \) Hz, H15), 7.86 (m, 2H, H12+H13), 7.61 (d, 2H, \( ^{3}J = 8.3 \) Hz, H16), 7.53 (d, 2H, \( ^{3}J = 8.1 \) Hz, H5), 7.46 (d, 2H, \( ^{3}J = 2.0 \) Hz, H8), 7.20 (dd, 2H, \( ^{3}J = 8.1, ^{4}J = 2.0 \) Hz, H6), 6.98 (s, 2H, H2), 4.03 (s, 3H, OMe), 1.18 ppm (s, 18H, H11). ^{13}C\{}^{1}H\}NMR (75.47 MHz, CD_{2}Cl_{2}): δ 192.1 (s, C18), 170.9 (s, C1), 165.8 (s, C9), 165.0 (s, C3), 154.5 (s, C7), 147.8 (s, C14), 147.7 (s, C4), 142.4 (s, C12), 134.6 (s, C17), 133.0 (s, C8), 130.1 (s, C13), 129.8 (s, C16), 128.2 (s, C15), 125.0 (s, C5), 23.5 (s, C6), 102.5 (s, C2), 56.6 (s, OMe), 35.3 (s, C10), 31.2 ppm (s, C11).
(L^{OMe})Au(C(H)=CHCH_{2}CH_{2}COOH) (11)

This compound was synthesized from 1c (5.0 mg, 0.009 mmol) and 4-pentynoic acid (17 mg, 0.17 mmol) in the presence of AIBN (3 mg, 0.018 mmol), and the reaction resulted complete after 25 min heating at 50°C. Yield: 75% (25% of unidentified byproduct present). \(^1\)H-NMR (300.13 MHz, CD\(_2\)Cl\(_2\)): \(\delta 7.68 \text{ (d, 2H, } J = 2.0 \text{ Hz, H8), 7.52 (d, 2H, } J = 8.1 \text{ Hz, H5), 7.24 (dd, 2H, } J = 8.1, J = 2.0 \text{ Hz, H6), 7.11 (d, 1H, } J = 9.1 \text{ Hz, H12), 6.94 (s, 2H, H2), 6.64 (dt, 1H, } J = 9.1, J = 7.0 \text{ Hz, H13), 4.00 (s, 3H, OMe), 2.40 (m, 4H, H14+H15), 1.32 ppm (s, 18H, H11).} \(^1\)C\(^{1}\)H-NMR (75.47 MHz, CD\(_2\)Cl\(_2\)): \(\delta 176.8 \text{ (s, C16), 170.8 \text{ (s, C1), 166.8 \text{ (s, C9), 164.7 \text{ (s, C3), 154.4 \text{ (s, C7), 147.9 \text{ (s, C4), 136.6 \text{ (s, C12), 133.0 \text{ (s, C8), 128.4 \text{ (s, C13), 124.9 \text{ (s, C5), 123.4 \text{ (s, C6), 102.3 \text{ (s, C2), 56.5 \text{ (s, OMe), 35.4 \text{ (s, C10), 33.8 \text{ (s, C14 or C15), 32.6 \text{ (s, C15 or C14), 31.3 ppm (s, C11).}}}

(L^{OMe})Au(C(EtOH)=CHPh) (12)

This compound was synthesized from 1c (5.0 mg, 0.009 mmol) and 1-phenyl-1-pentyn-3-ol (20 \(\mu\)L, 27 mg, 0.17 mmol) in the presence of AIBN (3 mg, 0.018 mmol), and the reaction resulted complete after 40 min heating at 50°C. Yield: >95%. \(^1\)H-NMR (300.13 MHz, CD\(_2\)Cl\(_2\)): \(\delta 7.71 \text{ ppm d, 2H, } J = 7.7 \text{ Hz, H15), 7.66 (d, 1H, } J = 1.9 \text{ Hz, H8), 7.62 (m, 2H, H8+H13), 7.53 (m, 2H, H5+H5'), 7.22 (m, 2H, H6+H6'), 7.10 (t, 2H, } J = 7.8 \text{ Hz, H16), 7.00 (m, 1H, H17), 6.98 (s, 2H, H2+H2'), 4.46 (m, 1H, H18), 4.02 (s, 3H, OMe), 2.03 (d, 1H, } J = 4.8 \text{ Hz, OH), 1.91 (m, 2H, H19), 1.24 (s, 9H, H11), 1.23 (s, 9H, H11'), 1.03 ppm (t, 3H, } J = 7.4 \text{ Hz, H20).} \(^1\)C\(^{1}\)H-NMR (75.47 MHz, CD\(_2\)Cl\(_2\)): \(\delta 170.9 \text{ (s, C1), 166.4 \text{ (s, C9'), 165.7 \text{ (s, C9), 164.9 \text{ (s, C3+C3'), 159.6 \text{ (s, C12), 154.8 \text{ (s, C7 or C7'), 154.6 \text{ (s, C7' or C7), 147.9 \text{ (s, C4 or C4'), 147.7 \text{ (s, C4' or C4), 142.2 (s, C14), 134.0 \text{ (s, C8 or C8'), 133.9 (s, C8' or C8),}}})}}

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128.2 (s, C16), 128.0 (s, C15), 125.9 (s, C17), 125.1 (s, C5 or C5’), 124.9 (s, C5’ or C5), 124.6 (s, C13), 124.4 (s, C6 or C6’), 123.3 (s, C6’ or C6), 102.5 (s, C2 or C2’), 102.4 (s, C2’ or C2), 82.06 (s, C18), 56.62 (s, OMe), 35.37 (s, C10 or C10’), 35.35 (s, C10’ or C10), 33.09 (s, C19), 31.39 (s, C11 or C11’), 31.27 (s, C11’ or C11), 10.96 ppm (s, C20).

\((\text{L}^{\text{OMe}})\text{Au(C(H)=CH}_2\text{NHCOC}_6\text{H}_4\text{Br})\) (13)

This compound was synthesized from \(1c\) (4.8 mg, 0.008 mmol) and propargyl 4-bromobenzamide (15 mg, 0.07 mmol) in the presence of AIBN (3 mg, 0.018 mmol), and the reaction resulted complete after 17h heating at 50°C. The presence of both the Z and the E isomers in a 80/20 ratio was revealed by NMR. The H12 signal was used to determine the E/Z ratio. Total yield for the mixture of the two isomers: >95%. \(^1\text{H-NMR}\) (300.13 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta 7.66\) (d, 2H, \(^4J = 2.1\) Hz, H8), \(7.52\) (d, \(^3J = 8.1\) Hz, overlapped with H15(E), H15), \(7.43\) (d, 1H, \(^3J = 9.5\) Hz, H12), \(7.27\) (dd, \(^3J = 8.1\), \(^4J = 2.1\) Hz, overlapped with H6(E), H6), \(7.24\) (d, \(^3J = 8.5\) Hz, overlapped with H18(E), H18), \(7.13\) (d, 2H, \(^3J = 8.5\) Hz, H17), 6.98-6.86 (m, 1H, H13), 6.91 (s, overlapped with H12(E), H2), 6.42 (br, 1H, NH), 4.01 (s, overlapped with OMe(E), OMe), 3.98 (m, 2H, H14), 1.30 ppm (s, overlapped with H11(E), H11). \(^{13}\text{C\{^1\text{H}\}}\)NMR (75.47 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta 170.9\) (s, C1), 166.3 (s, C9), 165.8 (s, C15), 164.6 (s, C3), 154.8 (s, C7), 147.9 (s, C4), 138.8 (s, C12), 136.2 (s, C16), 132.8 (s, C8), 131.3 (s, C18), 128.6 (s, C17), 125.5 (s, C19+C13), 125.2 (s, C5), 123.7 (s, C6), 102.5 (s, C2), 56.6 (s, OMe), 44.2 (s, C14), 35.5 (s, C10), 31.4 ppm (s, C11).
6. Photoisomerisation of (L^{OMe})Au(C(H)=CHPh) (2)

![Scheme S8. Photoisomerization of complex 2.](image)

A solution of 2 (6 mg, 0.09 mmol) in of CD$_2$Cl$_2$ (0.6 mL) inside a J-Young NMR tube was exposed to UV light (365 nm) for 1h. The resulting mixture was characterized by NMR, revealing the presence of the E and Z isomer in a roughly 50/50% ratio (determined by integrating the signals of the tBu substituent at the pyridine), along with a 10% of a side product which was identified as (L^{OMe})AuCl. $^1$H-NMR for the E isomer (300.13 MHz, CD$_2$Cl$_2$): $\delta$ 7.82 (d, 2H, $^3J = 2.0$ Hz, H8), 7.72 (d, 1H, $^3J = 16.5$ Hz, H13), 7.56 (d, 2H, $^3J = 8.2$, H5), 7.54 (d, 2H, $^3J = 6.7$, H15), 7.37 (m, 2H, H16), 7.29 (dd, 2H, $^3J = 8.2$, $^4J = 2.0$, H6), 7.24 (partially overlapped with H6 and H6(Z), H17), 7.06 (d, 1H, $^3J = 16.5$, H12), 6.97 (s, overlapped with H2(Z), H2), 4.02 (s, overlapped with –OMe(Z), –OMe), 1.35 ppm (s, 18H, H11). $^{13}$C{$^1$H}NMR (75.47 MHz, CD$_2$Cl$_2$): $\delta$ 170.8 (s, overlapped with C1(Z), C1), 167.5 (s, C9), 164.9 (s, C3), 154.4 (s, C7), 147.9 (s, C4), 141.5 (s, C14), 136.6 (s, C13), 135.6 (s, C12), 131.5 (s, C8), 128.9 (s, C16), 126.6 (s, C17), 125.9 (s, C15), 125.0 (s, C5), 123.7 (s, C6), 102.4 (s, C2), 56.6 (s, overlapped with –OMe(Z), –OMe), 35.6 (s, C10), 31.4 ppm (s, C11).

![Figure S9. A section of the $^1$H COSY NMR spectrum of the mixture obtained after the irradiation of complex 2 with UV light (CD$_2$Cl$_2$; asterisk denote gold chloride).](image)
7. $^1$H NMR spectra of insertion products 2-13

**Figure S10.** $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 2. Peaks marked with an asterisk correspond to solvent (*), and grease (x) signals.

**Figure S11.** Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 2.
Figure S12. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 3. Peaks marked with an asterisk correspond to solvent (*), water (#), and grease (x) signals.

Figure S13. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 3.
Figure S14. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 4. Peak marked with an asterisk corresponds to solvent (*) and water (#) signals.

Figure S15. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 4. Peak marked with an asterisk corresponds to residual unreacted diphenylacetylene.
**Figure S16.** $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 5. Peaks marked with an asterisk correspond to solvent (*) and grease (x) signals.

**Figure S17.** Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 5.
Figure S18. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 6. Peaks marked with an asterisk correspond to solvent (*), water (#), and grease (x) signals.

Figure S19. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 6. Unassigned peaks correspond to unidentified sideproduct.
Figure S20. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 7. Peaks marked with an asterisk correspond to solvent (*), grease (x), and residual AIBN ($) signals.

Figure S21. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 7.
Figure S22. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 8. Peaks marked with an asterisk correspond to solvent (*), grease (x), and residual AIBN (§) signals.

Figure S23. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 8. Unassigned peaks correspond to unidentified sideproduct.
Figure S24. \(^1\text{H}-\text{NMR (CD}_2\text{Cl}_2, 300.13 \text{ MHz)}\) spectrum of 9. Peaks marked with an asterisk correspond to solvent (*), grease (x), and residual AIBN (§) signals.

Figure S25. Aromatic region of the \(^1\text{H}-\text{NMR (CD}_2\text{Cl}_2, 300.13 \text{ MHz)}\) spectrum of 9.
Figure S26. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 10. Peaks marked with an asterisk correspond to solvent (*), grease (x), and residual AIBN ($) signals. Unassigned peaks correspond to residual unreacted substrate.

Figure S27. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 10. Unassigned peaks correspond to residual unreacted substrate.
Figure S28. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 11. Peaks marked with an asterisk correspond to solvent (*), grease (x), and residual AIBN ($) signals.

Figure S29. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 11.
Figure S30. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 12. Peaks marked with an asterisk correspond to solvent (*), grease (x), water (#), and residual AIBN (§) signals.

Figure S31. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 12.
Figure S32. $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 13. Peaks marked with an asterisk correspond to solvent (*), grease (x), water (#), and residual AIBN (§) signals.

Figure S33. Aromatic region of the $^1$H-NMR (CD$_2$Cl$_2$, 300.13 MHz) spectrum of 13.
8. Relevant 2D NMR spectra for insertion products 2-13

Figure S34. A section of the $^1$H NOESY (left) and $^1$H-$^{13}$C HMQC (right) NMR spectra of complex 2 (CD$_2$Cl$_2$).

Figure S35. Three sections of the $^1$H NOESY (left) and two sections of the $^1$H-$^{13}$C HMBC NMR spectra of complex 3 (CD$_2$Cl$_2$).
Figure S36. A section of the $^1$H NOESY NMR spectrum of complex 4 (CD$_2$Cl$_2$; asterisk denotes residual acetylene).

Figure S37. Two sections of the $^1$H NOESY NMR spectrum of complex 8 (CD$_2$Cl$_2$; asterisk denotes residual AIBN).
Figure S38. Four sections of the $^1$H NOESY NMR spectrum of complex 12 (CD$_2$Cl$_2$).

Figure S39. Two sections of the $^1$H NOESY NMR spectrum of complex 13 (CD$_2$Cl$_2$).
9. Reactions of complex 3 with I₂

Experiment a. A sample of complex 3 was generated in a J–Young NMR tube by hydroauration of MeC≡CPh in dry toluene–d₈ without the addition of AIBN. The sample was then dried under vacuum to remove the excess of acetylene and redissolved in dry benzene–d₆. In the glovebox, a crystal of I₂ was added to the mixture, the tube was shaken and kept at room temperature for 30 min. The ¹H NMR spectrum of the resulting mixture revealed that the starting complex was consumed completely to give a new set of signals, featuring a vinylic CH and a methyl group resonating at δ_H = 6.29 (δ_C = 134.5) and 2.33 (δ_C = 35.2) ppm, respectively, in agreement with the formation of (Z)-ICMe=CHPh. A ¹³C NMR signal at δ_C = 100.0 ppm was assigned to the IC(Me) moiety. No appreciable amount of the (E) isomer was observed. A ¹H PGSE NMR experiment revealed that residual pincer resonances and vinyl ones diffused with two different diffusion coefficients, showing hydrodynamic volume values of 700 and 143 Å³, respectively.

![Figure S40](image1)

Figure S40. Evolution of the ¹H NMR spectrum of complex 3 before and after the addition of a crystal of I₂ in benzene–d₆ at 297 K.

![Figure S41](image2)

Figure S41. ln(I/I₀) versus G² plot derived by ¹H PGSE NMR of the mixture obtained upon reacting complex 3 with I₂ in benzene–d₆. Hydrodynamic volumes have been derived from the Stokes-Einstein relationship imposing a spherical shape.¹⁶
**Experiment b.** A sample of 3 was prepared as described above, dried and redissolved in dry CD$_2$Cl$_2$. In the glovebox, a crystal of I$_2$ was added to the mixture, the tube was shaken and kept at room temperature for 30 min. $^1$H NMR spectroscopy revealed that the starting material was consumed to give the same products reported before. Successively, the mixture was diluted in hexane and the solution was columned over SiO$_2$ by using a pipette. Elution with hexane allowed to separate (Z)-ICMe=CHPh from the residual gold complex, which was recovered from silica by using ethyl acetate. Z/E ratio in the isolated fraction was 95/5.

![Figure S42](image)

**Figure S42.** $^1$H NMR spectrum of the fraction obtained upon eluting the products of the reaction between 3 and I$_2$ with hexane (CD$_2$Cl$_2$, 300.13 MHz, 297K; # denotes residual hexane; x denotes silicone grease).

**References**

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(16) (a) A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, *Chem. Soc. Rev.* **2008**, *37*, 479–489; (b) L. Rocchigiani, G. Bellachioma, G. Ciancaleoni, S. Crocchianti, A. Laganà, C. Zuccaccia, D. Zuccaccia, A. Macchioni, *ChemPhysChem* **2010**, *11*, 3243.
10. X-ray crystallography

Crystals of each sample were mounted on a MiTeGen MicroMesh and fixed in the cold nitrogen stream on a diffractometer. Diffraction intensities were recorded at low temperature on a Rigaku HG Saturn724+ (2×2 bin mode) by the UK national crystallography service. Data were processed using the CrysAlisPro 1.171.38.41. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.\(^\text{17}\)

The structures of all samples were determined by the direct methods routines with SHELXT programs and refined by full-matrix least-squares methods on \(F^2\) in SHELXL using the WinGX suit of programs.\(^\text{18}\)

In the refinement, non-hydrogen atoms were generally refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions. For 1d, the hydride hydrogen was located in the Fourier map and refined anisotropically. No missed symmetry was reported by PLATON.\(^\text{19}\)

Refinement results are included in Table S1. Scattering factors for neutral atoms were taken from reference.\(^\text{20}\)

References

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(20) ‘International Tables for X-ray Crystallography’, Kluwer Academic Publishers, Dordrecht. Vol. C. 1992, pp. 500, 219 and 193.
Table S1. Selected crystal data and structure refinement details for \( (L^{\text{OMe}})\text{AuCl}, (L^{\text{NMe}_2})\text{AuCl}, \) and \( 1\text{d}. \)

|                        | \( (L^{\text{OMe}})\text{AuCl} \) | \( (L^{\text{NMe}_2})\text{AuCl} \) | \( (L^{\text{NMe}_2})\text{AuH (1d)} \) |
|------------------------|-----------------------------------|-------------------------------------|----------------------------------------|
| **Empirical formula**  | \( \text{C}_{26}\text{H}_{29}\text{AuClNO} \) | \( \text{C}_{27}\text{H}_{32}\text{AuClN} \) | \( \text{C}_{27}\text{H}_{33}\text{AuN}_2 \) |
| **Crystal dimensions (mm), colour** | 0.02×0.05×0.1, bronze | 0.20×0.02×0.01, colourless | 0.29×0.025×0.01, colourless |
| **\( F_w \)**          | 603.92                           | 616.96                              | 582.52                                 |
| **\( T (K) \)**        | 100(2)                           | 100(2)                              | 100(2)                                 |
| **Crystal system, space group** | triclinic; \( \text{P-1} \) | monoclinic; \( \text{P 2}_1/c \) | orthorhombic; \( \text{C m c a} \) |
| **\( a(\text{Å}) \)**   | 7.0892(3)                        | 14.1194(3)                          | 7.0326(2)                              |
| **\( b(\text{Å}) \)**   | 11.1465(6)                       | 24.6945(6)                          | 27.9177(7)                            |
| **\( c(\text{Å}) \)**   | 15.1957(6)                       | 6.9663(2)                           | 23.498(2)                             |
| **\( \alpha(\text{deg}) \)** | 73.212(4)                      | 90                                  | 90                                    |
| **\( \beta(\text{deg}) \)**  | 88.102(3)                        | 101.500(2)                          | 90                                    |
| **\( \gamma(\text{deg}) \)** | 88.040(4)                      | 90                                  | 90                                    |
| **Volume (\( \text{Å}^3 \))** | 1148.57(9)                     | 2380.19(10)                        | 4613.4(4)                             |
| **\( Z \)**            | 2                                | 4                                   | 8                                      |
| **\( D_{\text{calc}} (\text{Mg/m}^3) \)** | 1.746                           | 1.722                               | 1.677                                  |
| **Absorption coefficient (mm\(^{-1}\))** | 6.538                          | 6.31                                 | 6.394                                  |
| **F(000)**             | 592                              | 1216                                | 2304                                   |
| **\( \theta \) range for data collection (º)\)** | 2.673 to 27.484                 | 2.251 to 27.572                     | 2.919 to 27.481                       |
| **Data // restraints // params** | 5207 // 0 // 278                  | 4506 // 0 // 264                    | 2863 // 0 // 183                      |
| **Goodness-of-fit on \( F^2 \)[a]** | 1.054                           | 1.076                               | 1.024                                  |
| **Final R indexes [I>2\( \sigma(I) \)][a]** | R1 = 0.0314, wR2 = 0.0683         | R1 = 0.0457, wR2 = 0.1468            | R1 = 0.0201, wR2 = 0.0446             |
| **R indexes (all data)[a]** | R1 = 0.037, wR2 = 0.0701          | R1 = 0.0548, wR2 = 0.1579            | R1 = 0.0234, wR2 = 0.0457            |
| **Largest diff peak and hole (e.Å\(^{-3}\))** | 2.093 and -2.528                 | 2.864 and -3.48                      | 0.904 and -0.749                      |

[a] \( R1 = \Sigma( | F_o | - | F_c |) / \Sigma | F_o |; wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}; \) goodness of fit = [\( \Sigma \) \( w(F_o^2 - F_c^2)^2 / \Sigma wF_o^2 \) \( / (N_{\text{obs}} - N_{\text{param}}) \) \( )^{1/2} \); \( w = [\sigma(F_o)^2 + (g_1 P)^2 + g_2 P]^2 \); \( P = \max(F_o^2,0) + 2F_c^2 / 3 \).
**Figure S43.** Selected bond distances (Å) and angles (°) for (L\textsuperscript{DMe})AuCl: Au1-Cl1 2.273(1), Au1-N1 1.972(2), Au1-C8 2.071(5), Au1-C18 2.065(5), N1-Au1-C8 81.3(2), N1-Au1-C18 81.0(2), C8-Au1-Cl1 98.5(1), C18-Au1-Cl1 99.1(1), N1-Au1-Cl1 179.5(1), C8-Au1-C18 162.3(2).

**Figure S44.** Selected bond distances (Å) and angles (°) for (L\textsuperscript{NMe2})AuCl: Au1-Cl1 2.272(2), Au1-N1 1.972(7), Au1-C9 2.060(8), Au1-C19 2.063(9), N1-Au1-C9 81.2(3), N1-Au1-C19 81.7(3), C9-Au1-Cl1 98.2(2), C19-Au1-Cl1 98.9(3), N1-Au1-Cl1 179.3(2), C9-Au1-C19 162.7(3).
Figure S45. Selected bond distances (Å) and angles (°) for \((L^{\text{NMe}_2})\text{AuH} \text{(1d)}\): Au1-H1 1.64(5), Au1-N1 2.019(3), Au1-C9 2.060(3), Au1-C18 2.058 (4), N1-Au1-C9 81.06(13), N1-Au1-C18 80.79(13), C9-Au1-H1 98.2(19), C18-Au1-H1 100.0(19), N1-Au1-H1 179.2(19), C9-Au1-C18 161.85(14).

Figure S46. Selected views for the supramolecular aggregation in \((L^{\text{NMe}_2})\text{AuH} \text{(1d)}\).
11. Computational modelling

11.1 Modelling for BDE and charge distribution

Theoretical calculations were performed at the Density Functional Theory (DFT) level\textsuperscript{(21)} by using the Gaussian 09 package of programs.\textsuperscript{(22)} Geometry optimizations were carried out by using the PBE0 (PBE1PBE) hybrid functional,\textsuperscript{(23)} along with the Schäfer, Horn, and Schäfer, Horn, and Ahlrichs double-\(\zeta\) plus polarization all-electron basis sets\textsuperscript{(24)} for C, H, N, and O, whereas CRENBL BS\textsuperscript{(25)} with relativistic effective core potentials (RECPs)\textsuperscript{(26)} was chosen for the heavier Au species. The nature of the minima of each optimized structure was verified by harmonic frequency calculations. Bond dissociation energies were calculated from the difference in energy of complete molecules and the sum of the energy of the appropriate optimised fragments obtained by homolytic bond cleavage. Natural\textsuperscript{(27)} and Mulliken\textsuperscript{(28)} charge distributions and Wiberg bond indices\textsuperscript{(29)} were calculated at the optimized geometries.

References

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Table S2. Optimized bond lengths (Å), Wiberg bond indeces, and bond dissociation energies (BDE, kcal/mol) for the Au-H bond, and Mulliken and NBO charges (e) calculated on the Au atom and H ligand of 1a-1e.

|     | Au-H distance | Wiberg bond index | BDE  | Charge on Au | Charge on H |     |
|-----|---------------|-------------------|------|--------------|-------------|-----|
|     |               |                   |      | Mulliken     | NBO         |     |
| 1a  | 1.555         | 0.754             | 79.90| 0.483        | 0.434       | –0.057 0.005 |
| 1b  | 1.556         | 0.755             | 80.04| 0.480        | 0.432       | –0.058 0.001 |
| 1c  | 1.556         | 0.755             | 80.12| 0.483        | 0.431       | –0.057 0.001 |
| 1d  | 1.557         | 0.755             | 80.24| 0.480        | 0.427       | –0.059 –0.005 |
| 1e  | 1.554         | 0.755             | 79.85| 0.490        | 0.436       | –0.051 0.009 |
11.2 Modelling of Alkyne Reactions

Methods

All geometries were fully optimized at the b3-lyp$^{30-32}$/def-SV(P)$^{24}$ level (Stuttgart effective core potential at Au)$^{33}$ using Turbomole V6.3$^{34}$ coupled to an external optimizer.$^{35,36}$ The nature of all stationary points (minima zero, transition states precisely one imaginary frequency) was verified through vibrational analyses (analytical frequencies) at this level. Improved total energies were calculated with the tpssh functional$^{37}$ and def-TZVP basis set$^{38,39}$ (Stuttgart effective core potential at Au)$^{36}$. Dispersion corrections were calculated with Grimme DFTD3 program$^{40}$ (options: "-func tpssh -zero"). Final free energies were obtained by combining the tpssh/def-TZVP total energies with these dispersion corrections and with thermal (enthalpy and entropy) corrections based on the b3-lyp/def-SV(P) vibrational analyses (298 K, gas phase, 1 bar).

Mechanistic alternatives for Au-H addition of 1a to acetylenes HC≡CH, HC≡CPh and MeC≡CPh were probed by DFT calculations. Relative free energies for all relevant species derived from MeC≡CPh addition are collected in Table S3.

Table S3. Calculated free energies (kcal/mol) for mononuclear and dinuclear paths for addition of LAuH to MeC≡CPh.

|                     | radical recombination | 1+1 addition TS |
|---------------------|-----------------------|-----------------|
|                     |                       |                 |
| LAuAuL              | -59.52                |                 |
| to C(Me), cis       | 51.00                 |                 |
| to C(Me), trans     | 42.38                 |                 |
| to C(Ph), cis       | 53.49                 |                 |
| to C(Ph), trans     | 45.33                 |                 |
| cationic path       |                       |                 |
| LAu⁺(MeC≡CPh)       | -42.54                |                 |
Despite extensive searches, no reasonable pathways were found for 1,2-addition of LAuH to acetylenes in either *cis* or *trans* fashion. The gold center is coordinatively saturated and is unable to participate in a standard migratory insertion type of step. In contrast, we did locate several transition states for 1,1-addition of the Au-H bond to a single acetylene carbon atom, resulting in formation of a carbene carbon center at the second acetylene carbon (Scheme S9).

In some cases, this aurated carbene was a local minimum that easily rearranged through a 1,2-shift of the Au atom, in others optimization past the 1,1-addition TS led directly to a 1,2-insertion product, without passing through a locatable carbene-like local minimum. All 1,1-addition transition states are high in energy ($\Delta G^+ > 35$ kcal/mol), incompatible with a reaction proceeding at or around room temperature, so these are not relevant to experimentally observed addition chemistry. Figure S47 shows the lowest-energy variation for addition of 1a to MeC≡CPh.
In view of these negative results, more complicated binuclear mechanisms were considered, involving either radical (LAu•) or cationic (LAu+) catalytic species (Scheme S10).

In the cationic cycle (energy profile in Figure S48, geometries in Figure S49), initial acetylene coordination is barrierless and very strong (30-45 kcal/mol). The subsequent transfer of a hydride has a small or vanishing barrier (0-6 kcal/mol) and is highly exergonic (~30 kcal/mol); the preferred regiochemistry involves LAuH transferring a hydride to the acetylene carbon bearing a phenyl group (if present). The immediate product from the addition has the LAu+ product still strongly coordinated to the C=C bond of the newly formed gold-bound vinyl group; dissociation into the separated products is endergonic by 50 kcal/mol and can be considered prohibitive, ruling out this cationic variation. This leaves as the only viable path the radical mechanism discussed in the main text; geometries along this path are shown in Figure S50.

Figure S47. Lowest-energy transition state (42.4 kcal/mol above reactants) for 1,1-addition of 1a to MeC≡CPh. tBu groups and most hydrogens omitted for clarity. Bond lengths in Å.
Figure S48. Free energy profile (kcal/mol) for LAu⁺ cation catalyzed *trans* addition to MeC≡CPh.
Figure S49. Geometries (Å) along the path for cation-mediated addition of LAuH to MeC≡CPh. tBu substituents and most hydrogens omitted for clarity.
Figure S50. Geometries (Å) along the path for radical-mediated addition of LAuH to MeC≡CPh. tBu substituents and most hydrogens omitted for clarity.
Table S4. Calculated energies, thermal corrections and dispersion corrections for addition of LAuH to acetylenes.\(^a\)

| Name                      | \(E_{\text{elec}}\) | \(H_{\text{corr}}\) | \(TS_{\text{corr}}\) | \(E_{\text{disp}}\) | \(E_{\text{elec}}\) | \(G_{\text{final}}\) | \(G_{\text{on scale}}\) | \(G_{\text{rel}}\) |
|---------------------------|----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|-----------------------|-----------------------|
|                           | b3-lyp/SV(P) 298 K   | 298 K                | tpssh/TZVP            |                      |                      |                       |                       |                       |
|                           | h                    | h                    | h                     | h                    | h                    | h                     | h                     | kcal/mol              |
| C2H2                      | -77.21543            | 0.03077              | 0.02333               | -0.00025             | -77.36102            | -77.35383             |                       |                       |
| C2HPh                     | -307.96216           | 0.11693              | 0.03703               | -0.00581             | -308.51367           | -308.43957            |                       |                       |
| C2MePh                    | -347.22622           | 0.14689              | 0.04439               | -0.00676             | -347.85421           | -347.75847            |                       |                       |
| LAuH                      | -844.49889           | 0.25245              | 0.05643               | -0.02542             | -845.74021           | -845.56961            |                       |                       |
| LAu                        | -843.87660           | 0.24327              | 0.05672               | -0.02421             | -845.10742           | -844.94508            |                       |                       |
| LAu+                       | -843.61528           | 0.24358              | 0.05656               | -0.02411             | -844.84865           | -844.68574            |                       |                       |
| **radical recombination** |                      |                      |                       |                      |                       |                       |                       |                       |
| LAu_AuL                   | -1687.83223          | 0.48925              | 0.09393               | -0.06527             | -1690.30504          | -1689.97499           | -0.08484              | -53.24                |
| LAu_C2H2_AuL              | -1765.08700          | 0.52349              | 0.09997               | -0.06410             | -1767.70267          | -1767.34325           | -0.09927              | -62.29                |
| LAu_C2HPh_AuL             | -1995.81958          | 0.60915              | 0.11095               | -0.08262             | -1998.84446          | -1998.42887           | -0.09915              | -62.22                |
| LAu_C2MePh_AuL            | -2035.06829          | 0.63844              | 0.11292               | -0.09084             | -2038.17218          | -2037.73751           | -0.08889              | -55.78                |
| **1+1 addition**          |                      |                      |                       |                      |                       |                       |                       |                       |
| LAuH_C2H2_cisTS           | -921.64546           | 0.28264              | 0.06357               | -0.03057             | -923.03694           | -922.84845           | 0.07499               | 47.06                 |
| LAuH_C2H2_transTS         | -921.64953           | 0.28330              | 0.06418               | -0.03110             | -923.04182           | -922.85381           | 0.06963               | 43.69                 |
| LAuH_C2HPh_cisTS          | -1152.39703          | 0.36944              | 0.07712               | -0.03792             | -1154.19432          | -1153.93991          | 0.06927               | 43.47                 |
| LAuH_C2HPh.transTS        | -1152.40285          | 0.37014              | 0.07750               | -0.04185             | -1154.20096          | -1153.95017          | 0.05901               | 37.03                 |
| Name                          | \(E_{\text{elec}}\)  | \(H_{\text{corr}}\) | \(T_{\text{corr}}\) | \(E_{\text{dip}}\) | \(E_{\text{elec}}\) | \(G_{\text{final}}\) | \(G_{\text{on scale}}\) | \(G_{\text{rel}}\) | \(\text{kcal/mol}\) |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
|                              | \(b3-lyp/\text{SV(P)}\)   | \(298\ K\) | \(298\ K\) | \(\text{tpssh/TZVP}\) |
|                              | \(h\) | \(h\) | \(h\) | \(h\) | \(h\) | \(h\) | \(h\) | \(h\) | \(kcal/mol\) |
| LAuH\_C2PhH\_cisTS          | -1152.37804 | 0.36908 | 0.07518 | -0.04320 | -1154.17672 | -1153.92602 | 0.08316 | 52.18 |
| LAuH\_C2PhH\_transTS        | -1152.38397 | 0.36955 | 0.07522 | -0.04368 | -1154.18359 | -1153.93293 | 0.07624 | 47.84 |
| LAuH\_C2MePh\_cisTS         | -1191.64556 | 0.39959 | 0.08082 | -0.04255 | -1193.51997 | -1193.24375 | 0.08433 | 52.92 |
| LAuH\_C2MePh\_transTS       | -1191.65537 | 0.39991 | 0.08062 | -0.04616 | -1193.53039 | -1193.25725 | 0.07083 | 44.45 |
| LAuH\_C2PhMe\_cisTS         | -1191.63761 | 0.39870 | 0.07952 | -0.04597 | -1193.51280 | -1193.23960 | 0.08848 | 55.52 |
| LAuH\_C2PhMe\_transTS       | -1191.64920 | 0.39894 | 0.08073 | -0.04615 | -1193.52490 | -1193.25285 | 0.07523 | 47.21 |
| **cationic**                 |             |         |         |         |             |             |         |         |
| LAu\_\_C2H2                 | -920.89228  | 0.27694 | 0.06265 | -0.03043 | -922.27546  | -922.09160  | -0.05203 | -32.65 |
| LAu\_\_C2H2\_H\_AuL\_TS    | -1765.39872 | 0.52982 | 0.10447 | -0.06491 | -1768.02431 | -1767.66386 | -0.05469 | -34.32 |
| LAu\_\_C2H3\_AuL            | -1765.47455 | 0.53650 | 0.10011 | -0.07164 | -1768.09895 | -1767.73420 | -0.12502 | -78.45 |
| LAuC2H3                      | -921.77462  | 0.28894 | 0.06335 | -0.03074 | -923.16118  | -922.96634  | -0.04290 | -26.92 |
| LAu\_\_C2PhH                | -1151.65767 | 0.36335 | 0.07676 | -0.03780 | -1153.44460 | -1153.19582 | -0.07051 | -44.25 |
| LAu\_\_C2PhH\_H\_AuL\_TS   | -1996.16044 | 0.61602 | 0.11462 | -0.07715 | -1999.18981 | -1998.76556 | -0.07065 | -44.33 |
| LAu\_\_C2PhH\_AuL           | -1996.20771 | 0.62269 | 0.11074 | -0.08885 | -1999.24120 | -1998.81810 | -0.12319 | -77.30 |
| LAuC2H2Ph\_trans             | -1152.51285 | 0.37510 | 0.07566 | -0.04141 | -1154.30698 | -1154.04894 | -0.03976 | -24.95 |
| LAuC2H2Ph\_cis               | -1152.51481 | 0.37525 | 0.07613 | -0.03882 | -1154.30824 | -1154.04794 | -0.03876 | -24.32 |
| LAu\_\_C2PhH                | -1151.65767 | 0.36335 | 0.07676 | -0.03780 | -1153.44460 | -1153.19582 | -0.07051 | -44.25 |
| LAu\_\_C2PhH\_H\_AuL\_TS\_b| -1996.14521 | 0.61580 | 0.11622 | -0.07755 | -1999.17753 | -1998.75551 | -0.06059 | -38.02 |
| LAu\_\_C2PhH\_H\_AuL\_TS\_a| -1996.14537 | 0.61593 | 0.11643 | -0.07701 | -1999.17786 | -1998.75538 | -0.06046 | -37.94 |
| Name                                      | $E_{\text{e}}$ | $H_{\text{corr}}$ | $T_{\text{corr}}$ | $E_{\text{dip}}$ | $G_{\text{final}}$ | $G_{\text{on scale}}$ | $G_{\text{rel}}$ |
|-------------------------------------------|----------------|------------------|------------------|-----------------|-------------------|-----------------------|--------------|
|                                           | h3-lyp/SV(P)   | 298 K            | 298 K            | tpsh/TZVP       |                   |                       |              |
|                                           | h              | h                | h                | h               | h                 | h                     | kcal/mol     |
| LAu+\_C2PhH2\_AuL\_a                     | -1996.21900    | 0.62258          | 0.11079          | -0.08978        | -1999.25024       | -1998.82823          | -0.13331     |-83.66         |
| LAu+\_C2PhH2\_AuL\_b                     | -1996.20864    | 0.62208          | 0.11094          | -0.08575        | -1999.24006       | -1998.81466          | -0.11975     |-75.14         |
| LAuC2H2Ph\_ips                           | -1152.51063    | 0.37473          | 0.07541          | -0.04261        | -1154.30545       | -1154.04875          | -0.03957     |-24.83         |
| LAu+\_C2PhMe                             | -1190.91860    | 0.39344          | 0.08057          | -0.04318        | -1192.78434       | -1192.51466          | -0.07045     |-44.21         |
| LAu+\_C2MePh\_H\_AuL\_TS                | -2035.41889    | 0.64576          | 0.11675          | -0.08515        | -2038.52683       | -2038.08298          | -0.06916     |-43.40         |
| LAu+\_C2MePhH\_AuL                       | -2035.45113    | 0.65066          | 0.11430          | -0.09155        | -2038.56086       | -2038.11605          | -0.10224     |-64.15         |
| LAuC2MeHPh\_trans                        | -1191.76736    | 0.40430          | 0.07917          | -0.04557        | -1193.63954       | -1193.35999          | -0.03191     |-20.02         |
| LAuC2MeHPh\_cis                           | -1191.76419    | 0.40437          | 0.07930          | -0.04363        | -1193.63616       | -1193.35472          | -0.02665     |-16.72         |
| LAu+\_C2PhMe                             | -1190.91860    | 0.39344          | 0.08057          | -0.04318        | -1192.78434       | -1192.51466          | -0.07045     |-44.21         |
| LAu+\_C2PhMe\_H\_AuL\_TS                | -2035.41120    | 0.64578          | 0.11887          | -0.08523        | -2038.51973       | -2038.07806          | -0.06424     |-40.31         |
| LAu+\_C2PhMe\_AuL                        | -2035.45466    | 0.65106          | 0.11413          | -0.09226        | -2038.56478       | -2038.12011          | -0.10630     |-66.70         |
| LAuC2PhMe\_trans                          | -1191.76653    | 0.40411          | 0.07922          | -0.04614        | -1193.63908       | -1193.36033          | -0.03225     |-20.24         |
| LAuC2PhMe\_cis                            | -1191.76337    | 0.40433          | 0.07890          | -0.04615        | -1193.63555       | -1193.35627          | -0.02820     |-17.69         |
| **radical**                               |                |                  |                  |                 |                   |                       |              |
| LAu\_C2H2\_bindTS                         | -921.09226     | 0.27391          | 0.06722          | -0.02944        | -922.47013        | -922.29288           | 0.00603      | 3.78          |
| LAu\_C2H2\_trans                          | -921.10546     | 0.27513          | 0.06402          | -0.02997        | -922.48766        | -922.30652           | -0.00762     |-4.78          |
| LAu\_C2H2\_cis                            | -921.10133     | 0.27460          | 0.06415          | -0.02962        | -922.48319        | -922.30236           | -0.00346     |-2.17          |
| LAuC2H2\_HAuL\_TS                         | -1765.60502    | 0.52832          | 0.10490          | -0.05939        | -1768.22828       | -1767.86426          | 0.00426      | 2.67          |
| LAuC2H2\_HAuL\_TS\_a                      | -1765.60496    | 0.52841          | 0.10526          | -0.05915        | -1768.22815       | -1767.86416          | 0.00436      | 2.74          |
| Name                                | $E_{\text{elec}}$ | $H_{\text{corr}}$ | $TS_{\text{corr}}$ | $E_{\text{disp}}$ | $E_{\text{elec}}$ | $G_{\text{final}}$ | $G_{\text{on scale}}$ | $G_{\text{rel}}$ |
|-------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|----------------|
|                                    | h3-lyp/SV(P) 298 K | 298 K             | tpssh/TZVP        | h                | h                | h                | h                | kcal/mol |
| LAuC2H2_HAuL_TS_b                  | -1765.60493      | 0.52841          | 0.10537          | -0.05901         | -1768.22813      | -1767.86409      | 0.00443          | 2.78     |
| LAuC2H3                             | -921.77462       | 0.28894          | 0.06335          | -0.03074         | -923.16118       | -922.96634       | -0.04290         | -26.92    |
| LAu_C2HPh_bindTS                   | -1151.84049      | 0.36086          | 0.08032          | -0.03783         | -1153.62328      | -1153.38057      | 0.00408          | 2.56     |
| LAu_C2HPh_lin                      | -1151.86118      | 0.36134          | 0.07730          | -0.03734         | -1153.64939      | -1153.40268      | -0.01803         | -11.32    |
| LAu_C2HPh_trans                    | -1151.86100      | 0.36139          | 0.07685          | -0.03792         | -1153.64883      | -1153.40220      | -0.01756         | -11.02    |
| LAu_C2HPh_cis                      | -1151.86066      | 0.36150          | 0.07655          | -0.03823         | -1153.64829      | -1153.40158      | -0.01693         | -10.62    |
| LAuC2HPh_HAuL_TS                   | -1996.35538      | 0.61406          | 0.11635          | -0.07497         | -1999.38572      | -1998.96298      | -0.00872         | -5.47     |
| LAuC2H2Ph_trans                    | -1152.51285      | 0.37510          | 0.07566          | -0.04141         | -1154.30698      | -1154.04894      | -0.03976         | -24.95    |
| LAuC2H2Ph_cis                      | -1152.51481      | 0.37525          | 0.07613          | -0.03882         | -1154.30824      | -1154.04794      | -0.03876         | -24.32    |
| LAu_C2PhH_bindTS                   | -1151.83222      | 0.35988          | 0.07869          | -0.04038         | -1153.61931      | -1153.37849      | 0.00615          | 3.86      |
| LAu_C2PhH_trans                    | -1151.84084      | 0.36134          | 0.07629          | -0.04111         | -1153.63139      | -1153.38745      | -0.00280         | -1.76     |
| LAu_C2PhH_cis                      | -1151.83607      | 0.36104          | 0.07645          | -0.04096         | -1153.62609      | -1153.38246      | 0.00219          | 1.37      |
| LAuC2PhH_HAuL_TS                   | -1996.34005      | 0.61462          | 0.11700          | -0.07319         | -1999.37204      | -1998.94761      | 0.00665          | 4.17      |
| LAuC2H2Ph_ips                      | -1152.51063      | 0.37473          | 0.07541          | -0.04261         | -1154.30545      | -1154.04875      | -0.03957         | -24.83    |
| LAu_C2MePh_bindTS                  | -1191.10379      | 0.39060          | 0.08336          | -0.04156         | -1192.96517      | -1192.69949      | 0.00406          | 2.55      |
| LAu_C2MePh_trans                   | -1191.11572      | 0.39115          | 0.08079          | -0.04163         | -1192.98188      | -1192.71314      | -0.00960         | -6.02     |
| LAu_C2MePh_cis b                   | -1191.09886      | 0.39091          | 0.08196          | -0.04333         | -1192.96548      | -1192.69987      | 0.00368          | 2.31      |
| LAuC2MePh_HAuL_TS                  | -2035.60951      | 0.64362          | 0.11915          | -0.08193         | -2038.71805      | -2038.27551      | -0.00235         | -1.47     |
| LAuC2MeHPh_trans                   | -1191.76736      | 0.40430          | 0.07917          | -0.04557         | -1193.63954      | -1193.35999      | -0.03191         | -20.02    |
| Name | E\text{elec} | H\text{corr} | TS\text{corr} | E\text{dip} | E\text{elec} | G\text{final} | G\text{on scale} | G_{\text{rel}} |
|------|--------------|--------------|--------------|-------------|-------------|---------------|-----------------|-------------|
|      | h3-lyp/SV(P) | 298 K        | 298 K        | tpsh/TZVP   | h3-lyp/SV(P)| 298 K        | 298 K          | kcal/mol     |
|      | h            | h            | h            | h            | h            | h             | h               | kcal/mol     |
| LAuC2MeHPh\_cis b | -1191.76419 | 0.40437 | 0.07930 | -0.04363 | -1193.63616 | -1193.35472 | -0.02665 | -16.72 |
| LAu\_C2PhMe\_bindTS | -1191.09874 | 0.38997 | 0.08339 | -0.04305 | -1192.96238 | -1192.69885 | 0.00469 | 2.94 |
| LAu\_C2PhMe\_trans | -1191.10425 | 0.39101 | 0.08150 | -0.04376 | -1192.97157 | -1192.70582 | -0.00227 | -1.43 |
| LAu\_C2PhMe\_cis b | -1191.10426 | 0.39103 | 0.08145 | -0.04375 | -1192.97159 | -1192.70576 | -0.00221 | -1.39 |
| LAuC2PhMe\_HAuL\_TS\_b | -2035.60190 | 0.64408 | 0.11956 | -0.08204 | -2038.71072 | -2038.26825 | 0.00491 | 3.08 |
| LAuC2PhHMe\_trans | -1191.76653 | 0.40411 | 0.07922 | -0.04614 | -1193.63908 | -1193.36033 | -0.03225 | -20.24 |
| LAuC2PhHMe\_cis b | -1191.76337 | 0.40433 | 0.07890 | -0.04615 | -1193.63555 | -1193.35627 | -0.02820 | -17.69 |
| **radical recombination** | | | | | | | | |
| LbAu\_AuLb | -2315.84905 | 0.95790 | 0.14213 | -0.12819 | -2319.56858 | -2318.88100 | -0.09485 | -59.52 |
| LbAu\_C2H2\_AuLb | -2393.10477 | 0.99199 | 0.14882 | -0.11933 | -2396.96744 | -2396.24360 | -0.10362 | -65.02 |
| LbAu\_C2HPh\_AuLb | -2623.83473 | 1.07793 | 0.15834 | -0.14550 | -2628.10643 | -2627.33233 | -0.10661 | -66.90 |
| LbAu\_C2MePh\_AuLb | -2663.08597 | 1.10710 | 0.15888 | -0.15609 | -2667.43565 | -2666.64351 | -0.09888 | -62.05 |
| **1+1 addition** | | | | | | | | |
| LbAu\_H\_C2H2\_cisTS | -1235.65601 | 0.51689 | 0.08793 | -0.05710 | -1237.67099 | -1237.29912 | 0.07259 | 45.55 |
| LbAu\_H\_C2H2\_transTS | -1235.65913 | 0.51752 | 0.08873 | -0.05757 | -1237.67497 | -1237.30374 | 0.06797 | 42.65 |
| LbAu\_H\_C2HPh\_cisTS | -1466.40679 | 0.60365 | 0.10095 | -0.06556 | -1468.82764 | -1468.39049 | 0.06696 | 42.02 |
| LbAu\_H\_C2HPh\_transTS | -1466.41208 | 0.60441 | 0.10172 | -0.06947 | -1468.83381 | -1468.40058 | 0.05687 | 35.68 |
| LbAu\_H\_C2PhH\_cisTS | -1466.38833 | 0.60342 | 0.09874 | -0.07243 | -1468.80997 | -1468.37772 | 0.07973 | 50.03 |
| LbAu\_H\_C2PhH\_transTS | -1466.39389 | 0.60392 | 0.09922 | -0.07260 | -1468.81683 | -1468.38472 | 0.07273 | 45.64 |
| Name                              | $E_{\text{elec}}$ | $H_{\text{corr}}$ | $T_{\text{corr}}$ | $E_{\text{dip}}$ | $E_{\text{elec}}$ | $G_{\text{final}}$ | $G$ on scale | $G_{\text{rel}}$ |
|----------------------------------|------------------|------------------|-------------------|------------------|-------------------|-------------------|--------------|--------------|
|                                  | b3-lyp/SV(P)     | 298 K            | 298 K             | tpsh/TZVP        |                   |                   |              |              |
| LbAuH$_2$C$_2$MePh$_2$TS cis     | -1505.65514      | 0.63378          | 0.10498           | -0.07074         | -1508.15314       | -1507.69507     | 0.08128      | 51.00        |
| LbAuH$_2$C$_2$MePh$_2$TS trans   | -1505.66499      | 0.63411          | 0.10564           | -0.07351         | -1508.16377       | -1507.70882     | 0.06753      | 42.38        |
| LbAuH$_2$C$_2$PhMe$_2$TS cis     | -1505.64711      | 0.63301          | 0.10313           | -0.07570         | -1508.14529       | -1507.69111     | 0.08524      | 53.49        |
| LbAuH$_2$C$_2$PhMe$_2$TS trans   | -1505.65882      | 0.63322          | 0.10497           | -0.07431         | -1508.15805       | -1507.70411     | 0.07224      | 45.33        |
| **Cationic**                     |                  |                  |                   |                  |                   |                   |              |              |
| LbAu$_2$C$_2$H$_2$                | -1234.90649      | 0.51114          | 0.08716           | -0.05671         | -1236.91364       | -1236.54638     | -0.05041     | -31.63       |
| LbAu$_2$C$_2$H$_2$ H$_2$ AuLb TS  | -2393.42148      | 0.99823          | 0.15140           | -0.12446         | -2397.29382       | -2396.57144     | -0.05759     | -36.14       |
| LbAu$_2$C$_2$H$_3$ AuLb          | -2393.49730      | 1.00490          | 0.14859           | -0.13243         | -2397.36882       | -2396.64944     | -0.13109     | -82.26       |
| LbAu$_2$C$_2$H$_3$               | -1235.78402      | 0.52325          | 0.08763           | -0.05703         | -1237.79411       | -1237.41552     | -0.04381     | -27.49       |
| LbAu$_2$C$_2$PhH                 | -1465.66984      | 0.59748          | 0.10095           | -0.06525         | -1468.08027       | -1467.64899     | -0.06728     | -42.22       |
| LbAu$_2$C$_2$PhH H$_2$ AuLb TS   | -2624.18023      | 1.08461          | 0.16118           | -0.13878         | -2628.45617       | -2627.67152     | -0.07193     | -45.13       |
| LbAu$_2$C$_2$PhH$_2$ AuLb        | -2624.22903      | 1.09130          | 0.15879           | -0.15489         | -2628.50948       | -2627.73186     | -0.13227     | -83.00       |
| LbAu$_2$C$_2$PhH$_2$ trans        | -1466.52257      | 0.60943          | 0.09998           | -0.06832         | -1468.94034       | -1468.49921     | -0.04176     | -26.20       |
| LbAu$_2$C$_2$PhH$_2$ cis         | -1466.52432      | 0.60949          | 0.10064           | -0.06575         | -1468.94132       | -1468.49822     | -0.04077     | -25.58       |
| LbAu$_2$C$_2$PhH$_2$ cis a       | -1465.66984      | 0.59748          | 0.10095           | -0.06525         | -1468.08027       | -1467.64899     | -0.06728     | -42.22       |
| LbAu$_2$C$_2$PhH$_2$ cis a TS a  | -2624.16830      | 1.08348          | 0.16002           | -0.13658         | -2628.44836       | -2627.66147     | -0.06188     | -38.83       |
| LbAu$_2$C$_2$PhH$_2$ cis a TS b  | -2624.16538      | 1.08437          | 0.16090           | -0.14099         | -2628.44403       | -2627.66155     | -0.06195     | -38.88       |
| LbAu$_2$C$_2$PhH$_2$ AuLb a      | -2624.23932      | 1.09097          | 0.15782           | -0.15675         | -2628.51750       | -2627.74110     | -0.14151     | -88.80       |
| LbAu$_2$C$_2$PhH$_2$ AuLb b      | -2624.23004      | 1.09082          | 0.15798           | -0.15144         | -2628.50842       | -2627.72702     | -0.12743     | -79.96       |
| Name                  | $E_{\text{elec}}$ | $H_{\text{corr}}$ | $T{S \text{corr}}$ | $E_{\text{dip}}$ | $E_{\text{elec}}$ | $G_{\text{final}}$ | $G_{\text{on scale}}$ | $G_{\text{rel}}$ |
|----------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-------------------|-------------------|---------------|
|                      | $b3$-lyp/SV(P)     | 298 K             | 298 K             |                 |                 |                   |                   |               |
|                      | $h$               | $h$               | $h$               | $h$             | $h$             | $h$               | $h$               | $h$           |
|                      | kcal/mol          |                   |                   |                 |                 |                   |                   |               |
| LbAuC2H2Ph_ips       | -1466.52034       | 0.60901           | 0.09985           | -0.07020        | -1468.93868     | -1468.49972       | -0.04227         | -26.53        |
| LbAu+_C2PhMe         | -1504.93102       | 0.62766           | 0.10455           | -0.07114        | -1507.42039     | -1506.96841       | -0.06780         | -42.54        |
| LbAu+_C2MePh_H_AuLb_TS | -2663.43874     | 1.11433           | 0.16421           | -0.14841        | -2667.79302     | -2666.99130       | -0.07281         | -45.69        |
| LbAu+_C2MePhH_AuLb   | -2663.47398       | 1.11954           | 0.16123           | -0.16003        | -2667.83030     | -2667.03202       | -0.11353         | -71.24        |
| LbAuC2MeHPh_trans    | -1505.77701       | 0.63862           | 0.10320           | -0.07283        | -1508.27274     | -1507.81016       | -0.03381         | -21.22        |
| LbAuC2MeHPh_cis     | -1505.77366       | 0.63860           | 0.10406           | -0.07076        | -1508.26920     | -1507.80541       | -0.02906         | -18.24        |
| LbAu+_C2PhMe         | -1504.93102       | 0.62766           | 0.10455           | -0.07114        | -1507.42039     | -1506.96841       | -0.06780         | -42.54        |
| LbAu+_C2PhMe_H_AuLb_TS | -2663.43150     | 1.11442           | 0.16362           | -0.14875        | -2667.78624     | -2666.98420       | -0.06571         | -41.23        |
| LbAu+_C2PhMe_AuLb    | -2663.47409       | 1.11968           | 0.16106           | -0.15888        | -2667.83087     | -2667.03113       | -0.11264         | -70.68        |
| LbAuC2PhHMe_trans    | -1505.77620       | 0.63836           | 0.10357           | -0.07375        | -1508.27223     | -1507.81120       | -0.03485         | -21.87        |
| LbAuC2PhHMe_cis     | -1505.77289       | 0.63858           | 0.10339           | -0.07410        | -1508.26851     | -1507.80742       | -0.03107         | -19.50        |

**radical**

| Name                  | $E_{\text{elec}}$ | $H_{\text{corr}}$ | $T{S \text{corr}}$ | $E_{\text{dip}}$ | $E_{\text{elec}}$ | $G_{\text{final}}$ | $G_{\text{on scale}}$ | $G_{\text{rel}}$ |
|----------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-------------------|-------------------|---------------|
|                      | $b3$-lyp/SV(P)     | 298 K             | 298 K             |                 |                 |                   |                   |               |
|                      | $h$               | $h$               | $h$               | $h$             | $h$             | $h$               | $h$               | $h$           |
|                      | kcal/mol          |                   |                   |                 |                 |                   |                   |               |
| LbAu_C2H2_bindTS     | -1235.10101       | 0.50812           | 0.09173           | -0.05562        | -1237.10237     | -1236.74160       | 0.00531          | 3.33          |
| LbAu_C2H2_trans      | -1235.11484       | 0.50947           | 0.08822           | -0.05622        | -1237.12056     | -1236.75553       | -0.00863         | -5.41         |
| LbAu_C2H2 cis       | -1235.11078       | 0.50894           | 0.08830           | -0.05587        | -1237.11614     | -1236.75135       | -0.00445         | -2.79         |
| LbAuC2H2_HAuLb_TS    | -2393.62373       | 0.99697           | 0.15212           | -0.11428        | -2397.49399     | -2396.76342       | 0.00137          | 0.86          |
| LbAuC2H3             | -1235.78402       | 0.52325           | 0.08763           | -0.05703        | -1237.79411     | -1237.41552       | -0.04381         | -27.49        |
| LbAu_C2HPh_bindTS    | -1465.84947       | 0.59517           | 0.10459           | -0.06501        | -1468.25554     | -1467.82997       | 0.00267          | 1.68          |
| LbAu_C2HPh_lin       | -1465.87058       | 0.59561           | 0.10123           | -0.06460        | -1468.28208     | -1467.85230       | -0.01965         | -12.33        |
| Name                      | $E_{\text{elec}}$ | $H_{\text{corr}}$ | $TS_{\text{corr}}$ | $E_{\text{dip}}$ | $E_{\text{elec}}$ | $G_{\text{final}}$ | $G_{\text{on scale}}$ | $G_{\text{rel}}$ |
|--------------------------|------------------|------------------|-------------------|-----------------|-----------------|--------------------|----------------------|------|
|                          | b3-lyp/SV(P) 298 K | tpssh/TZVP       |                   |                 |                 |                    |                      |      |
|                          | $h$              | $h$              | $h$               | $h$             | $h$             | $h$                | $h$                  | $h$  |
| LbAu_C2HPh_trans         | -1465.87021      | 0.59566          | 0.10075           | -0.06568        | -1468.28127      | -1467.85204         | -0.01939             | -12.17 |
| LbAuC2HPh_HAuLb_TS       | -2624.37374      | 1.08270          | 0.16300           | -0.13556        | -2628.65053      | -2627.86639         | -0.01586             | -9.95  |
| LbAuC2H2Ph_trans         | -1466.52257      | 0.60943          | 0.09998           | -0.06832        | -1468.94034      | -1468.49921         | -0.04176             | -26.20 |
| LbAuC2H2Ph_cis           | -1466.52432      | 0.60949          | 0.10064           | -0.06575        | -1468.94132      | -1468.49822         | -0.04077             | -25.58 |
| LbAu_C2PhH_bindTS        | -1465.84116      | 0.59411          | 0.10293           | -0.06750        | -1468.25164      | -1467.82797         | 0.00468              | 2.93   |
| LbAu_C2PhH_trans         | -1465.85054      | 0.59565          | 0.10108           | -0.06836        | -1468.26469      | -1467.83849         | -0.00584             | -3.66  |
| LbAu_C2PhH_cis           | -1465.84570      | 0.59534          | 0.10079           | -0.06836        | -1468.25926      | -1467.83307         | -0.00042             | -0.26  |
| LbAuC2PhH_HAuLb_TS       | -2624.35927      | 1.08296          | 0.16289           | -0.13350        | -2628.63820      | -2627.85164         | -0.00111             | -0.70  |
| LbAuC2H2Ph_ips           | -1466.52034      | 0.60901          | 0.10079           | -0.06836        | -1468.25926      | -1467.83307         | -0.00042             | -0.26  |
| LbAu_C2MePh_bindTS       | -1505.11254      | 0.62479          | 0.10796           | -0.06885        | -1507.59718      | -1507.14920         | 0.00235              | 1.47   |
| LbAu_C2MePh_lin          | -1505.12504      | 0.62540          | 0.10475           | -0.06922        | -1507.61444      | -1507.16300         | -0.01145             | -7.19  |
| LbAu_C2MePh_cis          | -1505.10830      | 0.62522          | 0.10586           | -0.07111        | -1507.59844      | -1507.15018         | 0.00137              | 0.86   |
| LbAuC2MePh_HAuLb_TS      | -2663.62650      | 1.11237          | 0.16441           | -0.14507        | -2667.98114      | -2667.17826         | -0.00883             | -5.54  |
| LbAuC2MeHP_h_trans       | -1505.77701      | 0.63862          | 0.10320           | -0.07283        | -1508.27274      | -1507.81016         | -0.03381             | -21.22 |
| LbAuC2MeHP_cis           | -1505.77366      | 0.63860          | 0.10406           | -0.07076        | -1508.26920      | -1507.80541         | -0.02906             | -18.24 |
| LbAu_C2PhMe_bindTS       | -1505.10754      | 0.62420          | 0.10826           | -0.07015        | -1507.59464      | -1507.14886         | 0.00268              | 1.68   |
| LbAu_C2PhMe_trans        | -1505.11377      | 0.62532          | 0.10597           | -0.07135        | -1507.60470      | -1507.15669         | -0.00515             | -3.23  |
| LbAu_C2PhMe_cis          | -1505.11378      | 0.62534          | 0.10570           | -0.07130        | -1507.60471      | -1507.15637         | -0.00483             | -3.03  |
| LbAuC2PhMe_HAuLb_TS      | -2663.62043      | 1.11258          | 0.16532           | -0.14283        | -2667.97572      | -2667.17128         | -0.00186             | -1.16  |
| Name                     | \(E_{\text{elec}}\)  | \(H_{\text{corr}}\) | \(TS_{\text{corr}}\) | \(E_{\text{disp}}\) | \(E_{\text{elec}}\)  | \(G_{\text{final}}\) | \(G_{\text{on scale}}\) | \(G_{\text{rel}}\) |
|-------------------------|------------------------|----------------------|----------------------|----------------------|------------------------|-------------------------|-------------------------|------------------------|
| \(\text{LbAuC2PhMe_trans}\) | -1505.77620            | 0.63836              | 0.10357              | -0.07375             | -1508.27223            | -1507.81120            | -0.03485                | -21.87                 |
| \(\text{LbAuC2PhMe_cis}\) | -1505.77289            | 0.63858              | 0.10339              | -0.07410             | -1508.26851            | -1507.80742            | -0.03107                | -19.50                 |

\(^a\) Lb represents the full C\(\text{C}^N\text{C}\) ligand, L is the model ligand lacking 'Bu substituents. \(^b\) Greyed-out rows are for species not on the main reaction paths, such as isomers or slightly higher-energy local minima. \(^c\) DFTD3 options: "-func tpssh -zero". \(^d\) \(G_{\text{final}} = E_{\text{elec}}(\text{TPSSh/TZVP}) + E_{\text{disp}} + H_{\text{corr}} - TS_{\text{corr}}\)