Dicordinate Au(I)–Ethylene Complexes as Hydroamination Catalysts

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1. NMR spectroscopic experiments

Figure S1. $^1$H NMR of complex 7.

Figure S2. DEPT $^{13}$C{1H} NMR of complex 7.
$^{31}$P-$^1$H NMR
(C$_2$D$_6$, 202 MHz, 25°C)

![NMR spectrum of complex 7](image)

Figure S3. $^{31}$P-$^1$H NMR of complex 7.

$^1$H NMR
(CD$_2$Cl$_2$, 300 MHz, 25°C)

![NMR spectrum of complex 8](image)

Figure S4. $^1$H NMR of complex 8.
Figure S5. $^{13}$C{${}^1$H} NMR of complex 8.

Figure S6. $^{31}$P{${}^1$H} NMR of complex 8.
Figure S7. $^1$H NMR of complex 2·C$_2$H$_4$ in excess of ethylene.

Figure S8. $^1$H NMR of complex 2·C$_2$H$_4$ in excess of ethylene at –30 °C.
Figure S9. $^1$H NMR of complex 2·C$_2$H$_4$ in excess of ethylene at –70 °C.

Figure S10. $^{13}$C($^1$H) NMR of complex 2·C$_2$H$_4$ in excess of ethylene at 25 °C.
Figure S11. $^{13}\text{C}({^1\text{H}}) \text{ NMR of complex } 2\cdot\text{C}_2\text{H}_4 \text{ in excess of ethylene at } -30 \degree \text{C.}$

Figure S12. $^{13}\text{C}({^1\text{H}}) \text{ NMR of complex } 2\cdot\text{C}_2\text{H}_4 \text{ with inset of the coordinated ethylene region at } 25 \degree \text{C.}$
Figure S13. $^{31}$P($^1$H) NMR of complex $2\cdot C_2H_4$.

Figure S14. $^1$H NMR of complex $3\cdot C_2H_4$. 
Figure S15. $^{13}$C($^1$H) NMR of complex 3·C$_2$H$_4$.

Figure S16. $^{31}$P($^1$H) NMR of complex 3·C$_2$H$_4$. 
Figure S17. $^1$H NMR of complex 4·C$_2$H$_4$ in excess of ethylene at 25 °C.

Figure S18. $^1$H NMR of complex 4·C$_2$H$_4$ with inset of the coordinated ethylene region at 25 °C.
Figure S19. $^{13}$C($^1$H) NMR of complex 4·C$_2$H$_4$ in excess of ethylene at 25 ºC.

Figure S20. $^{13}$C($^1$H) NMR of complex 4·C$_2$H$_4$ with inset of the coordinated ethylene region at 25 ºC.
Figure S21. $^{31}$P($^1$H) NMR of complex 4·C$_2$H$_4$.

Figure S22. $^1$H NMR of complex 5·C$_2$H$_4$ in excess of ethylene at 25 ºC.
**Figure S23.** $^1$H NMR of complex $5\cdot C_2H_4$ with inset of the coordinated ethylene region at 25 °C.

**Figure S24.** $^1$H NMR of complex $5\cdot C_2H_4$ in excess of ethylene at −30 °C.
**Figure S25.** $^{13}$C($^1$H) NMR of complex 5·C$_2$H$_4$ in excess of ethylene at 25 ºC.

**Figure S26.** $^{13}$C($^1$H) NMR of complex 5·C$_2$H$_4$ with inset of the coordinated ethylene region at 25 ºC.
Figure S27. $^{13}$C($^1$H) NMR of complex 5·C$_2$H$_4$ in excess of ethylene at –30 ºC.

Figure S28. $^{31}$P($^1$H) NMR of complex 5·C$_2$H$_4$. 
Figure S29. $^1$H NMR of complex $6\cdot C_2H_4$ in excess of ethylene at 25 °C.

Figure S30. $^1$H NMR of complex $6\cdot C_2H_4$ with inset of the coordinated ethylene region at 25 °C.
Figure S31. $^1$H NMR of complex 6·C$_2$H$_4$ in excess of ethylene at –30 °C.

Figure S32. $^{13}$C($^1$H) NMR of complex 6·C$_2$H$_4$ in excess of ethylene at 25 °C.
Figure S33. $^{13}$C($^1$H) NMR of complex 6·C$_2$H$_4$ with inset of the coordinated ethylene region at 25 ºC.

Figure S34. $^{13}$C($^1$H) NMR of complex 6·C$_2$H$_4$ in excess of ethylene at –30 ºC.
13C[1H] NMR of complex 6·C2H4.

1H NMR of complex 7·C2H4 in excess of ethylene at 25 ºC.

Figure S35. 31P[1H] NMR of complex 6·C2H4.

Figure S36. 1H NMR of complex 7·C2H4 in excess of ethylene at 25 ºC.
Figure S37. $^1$H NMR of complex 7·C$_2$H$_4$ with coordinated ethylene selected 25 °C.

Figure S38. $^1$H NMR of complex 7·C$_2$H$_4$ in excess of ethylene at –30 °C.
Figure S39. $^{13}$C($^1$H) NMR of complex 7·C$_2$H$_4$ in excess of ethylene at 25 °C.

Figure S40. $^{13}$C($^1$H) NMR of complex 7·C$_2$H$_4$ with coordinated ethylene selected at 25 °C.
Figure S41. $^{13}$C{$^1$H} NMR of complex 7·C$_2$H$_4$ in excess of ethylene at –30 ºC.

Figure S42. $^{31}$P{$^1$H} NMR of complex 7·C$_2$H$_4$. 
**Figure S43.** $^1$H NMR of complex 8·C$_2$H$_4$ in excess of ethylene at 25 ºC.

**Figure S44.** $^1$H NMR of complex 8·C$_2$H$_4$ in excess of ethylene at −30 ºC.
Figure S45. $^{13}$C{$^1$H} NMR of complex 8·C$_2$H$_4$ in excess of ethylene at 25 ºC.

Figure S46. $^{13}$C{$^1$H} NMR of complex 8·C$_2$H$_4$ in excess of ethylene at –30 ºC.
Figure S47. $^{31}$P($^1$H) NMR of complex 8·C$_2$H$_4$.

Figure S48. $^1$H NMR of complex 12.
**Figure S49.** $^{13}\text{C}\{^1\text{H}\}$ NMR of complex 12.

**Figure S50.** $^{31}\text{P}\{^1\text{H}\}$ NMR of complex 12.
2. Formation of Au(I)-Ag(I) multimetallic species

Reaction of the gold(I) chloride complexes 3–8 with AgSbF₆ in the absence of ethylene atmosphere did not lead to instant precipitation of AgCl, arguing in favor of the presence of silver within the resulting structure. Complexes 3–8 bearing bulky biphenyl and terphenylyl phosphine ligands formed species characterized by broad NMR resonances that we tentatively attribute to gold(I)–silver(I) multimetallic complexes by analogy with our prior studies on compound 1.¹

The ¹H and ³¹P{¹H} NMR spectra recorded at 25 °C of the resulting gold(I)–silver(I) multimetallic species derived from the reaction of complex 6 and AgSbF₆ is presented as an example:

Figure S51. ¹H NMR of the Au(I)-Ag(I) multimetallic species derived from complex 6.
Diffusion-Ordered Spectroscopy (DOSY) was performed to further support the notion of the formation of gold(I)-silver(I) multimetallic species. For instance, $^1$H DOSY experimental data revealed a diffusion coefficient for the in situ equimolar reaction between complex 6 and AgSbF$_6$ ($D = 9.13 \cdot 10^{-10}$ m/s$^2$) that accounts for only half of that for pure $6\cdot C_2H_4$ ($D = 1.75 \cdot 10^{-9}$ m$^2$/s), indicating a larger structure attributable to a multimetallic species in the former case.
Figure S53. $^1$H DOSY experiment for complex 6·C$_2$H$_4$ in CD$_2$Cl$_2$.

Figure S54. $^1$H DOSY experiment for the gold(I)-silver(I) multimetallic species derived from complex 6 in CD$_2$Cl$_2$. 
3. Formation of Au(I)-amine adducts

Different bulky amines were tested as substrates in the hydroamination of ethylene using gold(I) complexes 1 and 2, but no conversion was observed. In these cases, new signals were detected in the $^{31}$P{$^1$H} NMR spectra of the final mixtures that differ from the corresponding gold(I) chloride and gold(I) $\pi$-ethylene complexes. To confirm the ethylene displacement by the amines, stoichiometric reactions of complex $1\cdot C_2H_4$ and the corresponding amines in CD$_2$Cl$_2$ were monitored by $^{31}$P{$^1$H} NMR spectroscopy showing full displacement in all cases, except for tetramethylpiperidine, which coordinates to gold substituting ethylene but without full conversion under otherwise identical conditions (2 h, 25 °C).

![Diagram of Au(I)-amine adducts](image)

**Figure S55.** Comparison of the $^{31}$P{$^1$H} NMR spectra of the Au(I)-amine adducts formed by the displacement of ethylene in complex $1\cdot C_2H_4$ by different amines.
4. Kinetic experiments.

Complex 1·MeCN (6 mg, 0.003 mmol) and 1-methyl-imdazolidin-2-one (6 mg, 0.06 mmol) were dissolved in CDCl$_3$ (0.5 mL) in a high-pressure NMR tube. The tube was freeze-pumped to remove the nitrogen gas, filled with 4 bar of ethylene pressure and heated at 100 °C. The reaction was monitored by $^1$H NMR spectroscopy at different times. As stated in the main text, the reaction follows a second order dependence on the amide as evinced by the representation of the corresponding integrated rate law (Figure 4 in the main text). For comparison, zero and first order representations are depicted in Figures S58 and S59, respectively.

![Figure S56. $^1$H NMR monitoring of the catalytic hydroamination of ethylene by 1-methyl-imdazolidin-2-one. The proton signals of 1-methyl-imdazolidin-2-one are marked in a blue rectangle and the proton signals of the into 1-methyl-2-ethylimidazolidin-2-one product are marked in red rectangles.](image-url)
Figure S57. $^1$H NMR monitoring of the catalytic hydroamination of ethylene by 1-methyl-imidazolidin-2-one. Selected region in which the proton signals of the coordinated ethylene in gold(I)-ethylene complex $1\cdot\text{C}_2\text{H}_4$ (marked in a black rectangle) are detected.

![Amide Conversion](image)

**Figure S58.** Conversion plot of 1-methyl-imidazolidin-2-one (concentration vs time).
Figure S59. First-order kinetic representation of the consumption of 1-methyl-imdazolidin-2-one at 100 °C in CDCl₃ under 4 bar of ethylene pressure.

The activation energy ($\Delta G$) of the process was calculated at 373.15 K ($T$) from the Arrhenius equation:

$$k = \frac{k_B \cdot T}{h} e^{-\Delta G / RT}$$

where $k$ is the kinetic constant obtained from the second-order kinetic representation ($k = 6.07 \times 10^{-5} \text{ s}^{-1}$), $k_B$ is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$), $h$ is the Planck constant ($6.63 \times 10^{-34} \text{ J} \cdot \text{s}$) and $R$ is the gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) giving $\Delta G_{373 K} = 29.2 \text{ kcal/mol}$ as the free energy of activation.
5. Crystal structure determinations

Crystallographic details. Low-temperature diffraction data were collected on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IμS 3.0 microfocus X-ray source (7, 8, 3-C₃H₄, 8-C₃H₄, [6]ₜₐₜ and 12) at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-III software. Structures 7 and 8 were solved with SHELXT. Using Olex2,² the structures of (3-C₃H₄, 8-C₃H₄, [6]ₜₐₜ and 12) were solved with olex2.solve 1.3.³ All structures were refined against F² on all data by full-matrix least squares with SHELXL.⁴ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). In three of the six reported structures we used the program SQUEEZE to compensate for the contribution of disordered solvent molecules, which account for 2 pentane ([6]ₜₐₜ), 12 benzene (7), and 2 dichloromethane molecules (12), in the unit cell.

A summary of the fundamental crystal and refinement data are given in Table S1 and Table S2. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files, which have been deposited in the Cambridge Crystallographic Data Centre with no. 2129167–2129172. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

![ORTEP diagram of complex 7](image)

Figure S60. ORTEP diagram of complex 7. Hydrogen atoms are excluded for clarity. Thermal ellipsoids are set at 50% probability.
Figure S61. ORTEP diagram of complex 8. Hydrogen atoms are excluded for clarity while the cyclohexyl groups are represented in wireframe format. Thermal ellipsoids are set at 50% probability.

Figure S62. ORTEP diagram of complex 12. Counteranion and hydrogen atoms are excluded for clarity, while tert-butyl groups and one biaryl fragment are represented in wireframe format. Thermal ellipsoids are set at 50% probability.
**Table S1.** Crystal data and structure refinement for compounds 7, 8 and 3·C₂H₄.

|                      | 7                                               | 8                                               | 3·C₂H₄                          |
|----------------------|-------------------------------------------------|-------------------------------------------------|--------------------------------|
| **formula**          | C₁₂₀H₁₆₅Au₃Cl₃P₃                               | C₄₈₇H₆₇AuClIP                                  | C₃₁H₄₉AuFe₃PSb                  |
| **Fw**               | 2397.67                                         | 883.38                                         | 885.39                         |
| **cryst. size, mm**  | 0.12 × 0.11 × 0.04                              | 0.20 × 0.17 × 0.10                            | 0.21 × 0.13 × 0.11             |
| **crystal system**   | Monoclinic                                      | Orthorhombic                                   | Triclinic                       |
| **space group**      | C₂/c                                           | P₂₁₂₁₂₁                                        | P-1                            |
| **a, Å**             | 54.233 (8)                                      | 12.6694 (2)                                    | 8.7636 (7)                     |
| **b, Å**             | 14.371 (2)                                      | 18.1472 (4)                                    | 13.6876 (12)                   |
| **c, Å**             | 32.268 (5)                                      | 18.8940 (4)                                    | 28.412 (2)                     |
| **α, deg**           | 90                                              | 90                                             | 86.489 (3)                     |
| **β, deg**           | 102.216 (9)                                     | 90                                             | 89.678 (3)                     |
| **γ, deg**           | 90                                              | 90                                             | 77.831 (3)                     |
| **V, Å³**            | 24579 (6)                                       | 4344 (15)                                      | 3325.1 (5)                     |
| **T, K**             | 193                                             | 193                                             | 100                            |
| **Z**                | 8                                               | 4                                               | 4                              |
| **ρ calc, g cm⁻³**   | 1.296                                           | 1.351                                           | 1.769                          |
| **μ, mm⁻¹ (MoKα)**   | 3.718                                           | 3.514                                           | 5.320                          |
| **F(000)**           | 9744                                            | 1816                                            | 1736                           |
| **absorption**       | multi-scan, 0.60–0.74                           | multi-scan, 0.60–0.75                          | multi-scan, 0.44–0.75          |
| **corrections**      |                                                 |                                                 |                                |
| **θ range, deg**     | 1.291–2525.999                                  | 2.156–30.543                                   | 2.030–26.000                   |
| **no. of rflns measd** | 194519                                         | 48475                                          | 95123                          |
| **Rint**             | 0.1138                                          | 0.0297                                         | 0.1226                         |
| **no. of rflns unique** | 24156                                         | 13243                                          | 13023                          |
| **no. of params / restraints** | 1201 / 18                                    | 454 / 0                                        | 745 / 10                       |
| **R₁ (I > 2σ(I))**   | 0.0604                                          | 0.0217                                         | 0.0576                         |
| **R₁ (all data)**    | 0.1113                                          | 0.0267                                         | 0.0832                         |
| **wR₂ (I > 2σ(I))**  | 0.1473                                          | 0.0393                                         | 0.1175                         |
| **wR₂ (all data)**   | 0.1790                                          | 0.0404                                         | 0.1311                         |
| **Diff.Fourier,peaks** | min/max, eÅ⁻³                                  |                                                 |                                |
|                      | -2.13 / 2.11                                    | -0.47 / 0.85                                   | -2.644 / 3.576                 |
| **CCDC number**      | 2129167                                         | 2129168                                        | 2129172                        |


Table S2. Crystal data and structure refinement for compounds 8·C₂H₄, [6]ᵣᵣ and 12.

|                      | 8·C₂H₄                      | [6]ᵣᵣ                      | 12                          |
|----------------------|-----------------------------|----------------------------|------------------------------|
| **formula**          | C₄₈H₇₁AuPF₆Sb + 2(CH₂Cl₂) + C₄H₇ | C₃₂H₃₉AuF₆PSb              | C₆₀H₉₀AuF₆NPSb              |
| **Fw**               | 1324.67                     | 887.32                     | 1361.07                     |
| **cryst.size, mm**   | 0.18 × 0.15 × 0.12           | 0.17 × 0.13 × 0.10         | 0.20 × 0.16 × 0.13          |
| **crystal system**   | Monoclinic                  | Monoclinic                 | Triclinic                   |
| **space group**      | C2/c                        | P2₁/n                      | P-1                         |
| **a, Å**             | 33.253(3)                   | 11.3949(8)                 | 15.3509(9)                  |
| **b, Å**             | 13.3849(11)                 | 16.7262(9)                 | 15.4730(9)                  |
| **c, Å**             | 26.020(2)                   | 18.5670(12)                | 19.0096(10)                 |
| **α, deg**           | 90                          | 90                         | 95.2651(17)                 |
| **β, deg**           | 93.079(3)                   | 104.780(3)                 | 103.1408(17)                |
| **γ, deg**           | 90                          | 90                         | 117.9130(18)                |
| **V, Å³**            | 11564.5(17)                 | 3421.7(4)                  | 3781.0(4)                   |
| **T, K**             | 100                         | 193                        | 193                         |
| **Z**                | 8                           | 4                          | 2                           |
| **ρcalc, g cm⁻³**    | 1.522                       | 1.722                      | 1.196                       |
| **μ, mm⁻¹ (MoKα)**   | 3.266                       | 5.171                      | 2.363                       |
| **F(000)**           | 5336                        | 1720                       | 1384                        |
| **absorption corrections** | multi-scan, 0.44 – 0.75 | multi-scan, 0.57 – 0.75 | multi-scan, 0.59 – 0.75 |
| **θ range, deg**     | 1.938–25.999                | 2.213–26.000               | 1.993–26.745                |
| **no. of rflns measd** | 100015                     | 65592                      | 124627                      |
| **Rint**             | 0.0988                      | 0.1169                     | 0.0946                      |
| **no. of rflns unique** | 11354                     | 6718                       | 16058                       |
| **no. of params / restraints** | 647/67                   | 374/7                      | 739/0                       |
| **R₁ (I > 2σ(I))**   | 0.0503                      | 0.0385                     | 0.0366                      |
| **R₁ (all data)**    | 0.0686                      | 0.0662                     | 0.0574                      |
| **wR₂ (I > 2σ(I))**  | 0.1252                      | 0.0782                     | 0.0815                      |
| **wR₂ (all data)**   | 0.1425                      | 0.0921                     | 0.0922                      |
| **Diff.Fourier.peaks min/max, eÅ⁻³** | -2.479/2.185 | -1.807/1.242 | -2.140/1.471 |
| **CCDC number**      | 2129171                     | 2129170                    | 2129169                     |
6. Buried volume analysis

The steric description of percent buried volume (\(\%\text{Vbur}\)) has been shown to be a valid measure of the steric properties of monodentate ligands such as phosphines. Comparison of all phosphines used in this study is shown in Figure S63.\(^5\)
Figure S63. Schematic (a) and 3D representation (b) of the ligands, together with the corresponding steric maps (c) and calculated %Vbur for all the gold(I) chloride complexes in the study. The %Vbur of each quadrant are also indicated in red.
7. Computational details

Calculations were performed at the DFT level with the Gaussian 09 (Revision D.01) program. The hybrid functional PBE0 was used throughout the computational study, and dispersion effects were accounted for by using Grimme’s D3 parameter set with Becke–Johnson (BJ) damping at the optimization stage. Geometry optimizations were carried out without geometry constraints, using the 6-31G(d,p) basis set to represent the C, H, N, O and P atoms and the Stuttgart/Dresden Effective Core Potential and its associated basis set (SDD) to describe the Au atoms. Bulk solvent effects (dichloromethane) were included at the optimization stage with the SMD continuum model. The stationary points and their nature as minima or saddle points (TS) were characterized by vibrational analysis, which also produced enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum. Free energies were corrected (ΔG_{qh}) to account for errors associated with the harmonic oscillator approximation, temperature (373.15 K) and concentration of all gold(I) species (c = 0.01 M) and imidazolidine-2-one (c = 0.2 M) with the Goodvibes code. Thus, according to Truhlar’s quasi-harmonic approximation for vibrational entropy, all vibrational frequencies below 100 cm⁻¹ were set to this value.
7.1 Hydroamination of ethylene: alternative mechanistic pathways

**Figure S64.** Free energy profile for the Au(I)-catalyzed hydroamination of ethylene with imidazolidine-2-one (path A).

**Figure S65.** Free energy profile for the Au(I)-catalyzed hydroamination of ethylene with imidazolidine-2-one (path B).
Figure S66. Free energy profile for the Au(I)-catalyzed hydroamination of ethylene with imidazolidine-2-one assisted by a second molecule of imidazolidine-2-one acting as a proton shuttle (path C).
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